Gas Phase Infrared Spectra of some PAHs and Diols: Experiment and Theory

A Thesis

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In the Faculty of Science

by

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Dedicated to

My Parents

STATEMENT

I hereby declare that the research work described in this thesis is the result of investigation carried out by me in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India, under the supervision of **Prof. Puspendu K. Das and Prof. E. Arunan**.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described in this thesis is based on the findings of other investigators. Any omission that might have occurred due to oversight or error is regretted.

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<u>*CERTIFICATE*</u>

This is to certify that the work presented in the thesis titled "**Gas Phase Infrared Spectra of some PAHs and Diols: Experiment and Theory**" has been carried out by Mr. Prasanta Das under our supervision and the same has not been submitted elsewhere for a degree.

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Thesis Synopsis

In this thesis, I report the gas phase infrared spectra of some polycyclic aromatic hydrocarbons (PAHs) namely 1, 5-, 1, 6-, and 2, 6-dimethyl naphthalenes (DMNs); 2, 4-, 2, 6-, 2, 7-, and 2,8-dimethyl quinolines (DMQs); and 1, 9-, 2, 4-, and 3, 9-dimethyl phenanthrenes (DMPs) and diols such as 1, 2-ethylene glycol (1,2-EG) and 1, 4-butanediol (1,4-BD). Assignment of the IR spectra has been done with the help of DFT calculations followed by scaled quantum mechanical force field calculations.

Chapter 1 gives a brief introduction to PAHs and diols. A brief survey of literature pertinent to their sources, their importance, experimental techniques for identification of PAHs and different conformers of diols and intramolecular interactions between the two hydroxyl groups in the diols are presented. The scope and motivation of the present investigation have been described at the end of the chapter.

In Chapter 2, I have discussed all the methods used in carrying out this work. The details of the experimental FT IR set-up and quantum-chemical calculations employed in this work have been elaborated in this chapter.

The subsequent chapters 3 - 5 deal with the experimental and theoretical results obtained for DMNs, DMQs, and DMPs. *In chapter 3,* infrared spectra of 1,5-, 1,6-, and 2,6-DMN have been described. The spectra have been recorded using a multi-pass gas cell coupled with Nexus-870 spectrometer (Thermonicolet, US). Qualitatively, spectral assignments have been made with the help of calculated doubly scaled (one scaling factor for the C-H stretching and another factor for the non C-H stretching frequencies) harmonic frequencies at the B3LYP/6-31G* level of theory. The spectral features to distinguish three different isomers of DMN have

been identified. ***In chapter 4,*** IR spectra of 2,4-, 2,6-, 2,7-, and 2,8-DMQ in the gas phase have been recorded using a high resolution Vertex-70 (Bruker Optics, Germany) FT-IR spectrometer. DFT calculations have been carried out in order to get harmonic and anharmonic frequencies and their intensities at the B3LYP/6-31G* level of theory. Unambiguous assignments of IR bands could not be made with the help of anharmonic or selectively scaled harmonic frequencies. Therefore, scaled quantum mechanical (SQM) force field calculations were performed where force fields in local coordinates were scaled for getting frequencies in close agreement with experiment. Potential energy distributions (PEDs) of the normal modes in terms of the local coordinates of the molecule using a modified UMAT program in the QCPE package were also obtained in order to identify the nature of the fundamental vibration modes. ***In chapter 5,*** I have presented the gas phase IR spectra of 1,9-, 2,4-, and 3,9-DMP. The harmonic and anharmonic frequencies and their intensities were obtained at the B3LYP/6-31G* and B3LYP/6-311G** levels of theory. I have carried out SQM calculations for the assignment of the experimental frequencies in a similar fashion as was done for the DMQs.

In chapter 6, IR spectra of two diols namely 1,2-ethylene glycol and 1,4-butane diol are reported and discussed. DFT calculations have been carried out for the harmonic fundamental frequencies and intensities at the experimental temperatures with 10 unique chosen conformers of the diols at the B3LYP/6-311++G** level of theory. Gas phase equilibrium population analysis has been done in order to generate the theoretical spectrum with the weighted average contributions from the 10 conformers to match the experimental spectrum. The hydrogen bond enthalpy, strength and nature have been investigated in details. From this experimental and theoretical studies, it has been concluded that the intramolecular hydrogen bond is absent in 1,2-EG at ordinary temperatures whereas it is present in 1,4-BD.

Chapter 7 is the concluding chapter where the main work done in this thesis is summarized and future direction is presented.

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List of Abbreviations

BCP	**:**	**B**ond **C**ritical **P**oint
BD	**:**	**B**utanediol
BO	**:**	**B**orn **O**ppenheimer
BS	**:**	**B**eamsplitter
D	**:**	**D**etector
DFT	**:**	**D**ensity **F**unctional **T**heory
DMN	**:**	**D**imethyl **n**aphthalene
DMP	**:**	**D**imethyl **p**henanthrene
DMQ	**:**	**D**imethyl **q**uinoline
DTGS	**:**	**D**euterated **T**riglycine **S**ulfate
EG	**:**	**E**thylene **g**lycol
ESI-MS	**:**	**E**lectrospray **I**onization **M**ass **S**pectrometry
FT-IR	**:**	**F**ourier **T**ransform **I**nfrared **S**pectroscopy
GC-FID	**:**	**G**as **c**hromatography with **f**lame **i**onization **d**etection
GC-MS	**:**	**G**as **C**hromatography **M**ass **S**pectrometry
HB	**:**	**H**ydrogen **b**ond
HPLC	**:**	**H**igh **p**erformance **l**iquid **c**hromatography
IHB	**:**	**I**ntramolecular **h**ydrogen **b**onding
InSb	**:**	**I**ndium **A**ntimonide
IDP	**:**	**I**nterplanetary **d**ust **p**articles
LD	**:**	**L**aser **D**etector

LN - MCT : **L**iquid **N**$_2$ cooled **M**ercury **C**admium **T**elluride

MCT : **M**ercury **C**admium **T**elluride

MMP : **M**ono-**m**ethyl **p**henanthrene

MN : **M**ethyl **n**aphthalene

MQ : **M**ethyl **q**uinoline

NBO : **N**atural **B**ond **O**rbital

NMR : **N**uclear **M**agnetic **R**esonance

OPL : **O**ptical **p**ath **l**engths

PAH: : **P**olycyclic **A**romatic **H**ydrocarbon

PD : **P**ropanediol

PED : **P**otential **e**nergy **d**istribution

QCPE : **Q**uantum **C**hemistry **P**rogram **E**xchange

QDMC : **Q**uantum **D**iffusion **M**onte Carlo

UHP : **U**ltra **H**igh **P**ure

UIR : **U**nidentified **I**nfrared

UV : **U**ltraviolet

SQM : **S**caled **Q**uantum **M**echanical

TMQ : **T**ri-**m**ethyl **q**uinoline

ZPVE : **Z**ero **p**oint **v**ibrational **e**nergy

Chapter-1

An Introduction to PAHs, Diols and Infrared Spectroscopy

1.1 Introduction

1.1.1 Definition of PAHs and diols
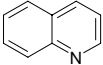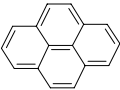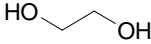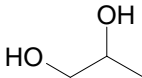
Polycyclic aromatic hydrocarbons (PAHs) are a family of aromatic compounds containing more than one benzene or heterocyclic (O, N, S) benzene rings whereas diols belongs to a class of compounds containing two hydroxyl groups separated by a $(-CH_2-)_n$ (where n=2, 3, 4,…) backbone. Methylated polycyclic aromatic compounds belong to the PAHs. A few representative structures and some physical properties of PAHs[1a,b] and diols[2] are listed in Table 1.1.

1.1.2 Sources and importance of PAHs

There are several sources which are responsible for the presence of PAHs in the gas phase and in particulates in the atmosphere. These hydrocarbons are mostly formed during incomplete combustion and pyrolysis of fossil fuels or wood, and petroleum products. Terrestrial sources of PAHs are from non-anthropogenic burning of forests, woodland and moorland due to lightning strikes, and volcanic eruptions.[3,4] Furthermore, some cosmic sources such as carbonaceous chondrites, which originate in the main asteroid belt, have also been proposed.[5a-c] Other sources of PAHs include petroleum spills, oil seepage, and organic matter in anoxic sediments. In general, there are five major emission sources of PAHs i.e., domestic,[6,7] mobile,[8a-d] industrial,[9a-d] agricultural,[10a-c] and natural. PAHs are the most stable hydrocarbons present in atmosphere in the gas phase (containing 2 - 3 rings) or as particulate matters (containing more than 4 rings). PAHs having two to three rings show higher vapor pressures at room temperature compared to their higher analogs (see Table 1.1).

Table 1.1: Structure and vapor pressure of a few representative PAHs and Diols

Name of PAHs and Diols	Structure	P(mmHg) @25 ^{o}C
1. Naphthalene		7.80×10^{-2}
2. Quinoline		9.12×10^{-2}
3. Acenaphthene		2.10×10^{-3}
4. Phenanthrene		1.20×10^{-4}
5. Pyrene		4.50×10^{-6}
6. Perylene		4.12×10^{-9}
7. Coronen		2.51×10^{-12}
8. Ethanediol		$*6.0 \times 10^{-2}$
9. Propan-1,2-diol		12.9×10^{-2}
10. Butane-2,3-diol		26.0×10^{-2}

Vapor pressure at 20 ^{o}C.

PAHs are known to be carriers of unidentified IR band (UIR) in the interstellar medium (ISM).[11] Many are carcinogenic,[12,13] mutagenic,[14,15] toxic,[13,16] and hence cause health hazard to human being and aquatic lives. Some of them are used in medicine or to make dyes, plastics

and pesticides.[17a-e] Therefore, it is necessary to identify/distinguish them and find out some way of removal from the lower and upper atmospheres.

1.1.3 Diols and intramolecular hydrogen bonding

Diols exist in a mixture of conformers with several possibilities of intramolecular and intermolecular interactions between the two hydroxyl groups depending on the temperature and the physical state. The extent of the latter kind of interaction is dependent on the concentration of the compound, while the former is concentration independent. Intramolecular hydrogen bonding is particularly sensitive to changes in the molecular geometry.

Ethanediol or 1,2-ethylene glycol (1,2-EG) is one of the simplest molecules with two vicinal hydroxyl groups which serves as a simple model for understanding the influence of hydrogen bonding on the conformation of biological molecules such as sugars. In EG, the intramolecular hydrogen bond (IHB) conformation will form a five-member quasi-ring. The hydrogen bond angle in such a five member ring is far from an optimal 180° and thus the hydrogen bond is expected to be weak. On the otherhand, butanediol isomers are compound with numerous applications in biochemical fields such as protein-stabilizing agents. Butane-1,4-diol or 1,4-butanediol (1,4-BD) represents an interesting diol with many possibilities of intramolecular interactions between the two hydroxyl groups.

1.2 Experimental techniques for identification of PAHs

Many experimental techniques have been employed for the separation and identification of PAHs in a complex mixture. The GC/MS spectrometry is one of the popular techniques

which has been used for the analysis of PAHs. Gas chromatography with flame ionization detection (GC-FID) and GC-MS has been used for the qualitative and quantitative analysis of PAHs in cigarette smoke,[18] diesel engine soot,[8c,19] synthetic fuel,[20] coke oven and wood combustion,[21] biodiesel,[22,23] coal derived liquid,[24] and in sugar cane soot.[25] Furthermore, high-performance liquid chromatographic (HPLC) and GC-MS have been employed for the separation and identification of PAHs.[26] Identification of PAHs has been done by the Programmed-Temperature Capillary-Column Gas Chromatography technique.[27,28] Bate et al. reported the analysis of particle bound PAHs with the help of a Thermal Desorption (TD) – GC/MS technique.[29] In 2004, Porter et al. used Electrospray Ionization Mass Spectrometry (ESI-MS) for the analysis of petroleum resins.[30] Recently, mars organic analyzer michrochip capillary electrophoresis system has been used by Stockton et al. for the analysis of PAHs.[31] In addition to mass spectrometric techniques, FT-IR spectroscopy has been used by Wornat et al. for the analysis of substituted PAHs present in bituminous coal.[32] GC/FT-IR & GC/FT-IR/MS techniques have also been employed for the isomeric identification of PAHs.[33a-c] IR spectroscopic identification and discrimination of PAHs will be presented separately below.

1.3 Experimental techniques for the conformational analysis and characterization of hydrogen bonding in diols

In section 1.1.3, I have discussed that diols exist in a mixture of conformers. Whether or not 1,2-EG form an IHB has large significance since this molecule has been used as a part of the training set for parametrizing molecular mechanics programs.[34] It is used in pharmacologically active materials[35] and in polymer synthesis.[36] In the past, structure of diols

including 1,2-EG and 1,4-BD in the gas, liquid and solid phases have been studied extensively by different experimental methods such as x-ray[37a,b] and electron diffractions[38a,b] and microwave,[39a-d] NMR[40a-c] and FT-IR[41a,b] spectroscopy. The electron and x-ray diffraction studies on 1,2-EG indicate that the *gauche* conformer is considerably more stable than the *trans* in the gas phase[38b] because of the presence of the H-bonding in the gauche conformer. The NMR investigation of 1,2-EG by Roberts and co-workers led the authors to conclude that "the bulk of the NMR evidence indicates that intramolecular hydrogen bonding between the hydroxyl groups is unlikely to be a significant factor in determining that preference, except possibly in fairly non-polar solvents. The '*gauche* effect' is clearly very important, especially in aqueous solution".[40c] Recent X-ray crystallographic studies on crystalline 1,2-EG suggests that the intramolecular hydrogen bond (IHB) does not exist in this molecule.[42] IR spectroscopy is one of the simple methods for the identification and characterization of hydrogen bonding. Generally, hydrogen bonding manifests in a red shift of the X-H-stretching frequency. For the hydroxyl group, increase in the IR band intensity and a red-shift of the O–H stretching frequency are spectroscopic signatures of hydrogen bond formation. The magnitude of both the intensity and frequency shift increase with increasing hydrogen bond strength.[43] Since IR spectroscopy has been widely used for studying the IHB in diols, it will be discussed separately below.

1.4 Infrared spectroscopy

Infrared spectroscopy is a branch of spectroscopy that deals with the interaction of molecules with infrared radiation. IR spectra result from the transitions between two quantized

vibrational energy states in a molecule. Molecular vibrations can range from the simple coupled motion of two atoms in a diatomic molecule to the much more complex motion of many atoms in a large polyatomic molecule. Molecules with N atoms have 3N degrees of freedom of which 3N−6 degrees of freedom give the number of ways that the atoms in a non-linear molecule can vibrate whereas for linear molecules the number of vibrational modes is 3N-5.

Each vibrational mode, i in a molecule involves displacements of the atoms from their equilibrium positions such that all the atoms vibrate at a certain characteristic frequency, ν_i. The potential energy, $V(r)$ of such an oscillator is shown by the green line in Figure 1.1 as a function of the distance between the atoms, r assuming harmonic motion. For any mode in which the atoms vibrate with simple harmonic motion (i. e., obeying Hook's law), the vibrational energy, $V_{i\upsilon}$ can be described by the equation

$$V_{i\upsilon} = h\nu_i(\upsilon_i + \frac{1}{2}) - - - - - - - -(1.1)$$

where h is the Plank's constant, ν_i , the fundamental frequency and υ_i is the vibrational quantum number of the i-th mode. The energy difference for transitions between the ground state ($\upsilon_i = 0$) and the first excited state ($\upsilon_i = 1$) for most molecular vibrations fall in the mid-infrared region (between 400 to 4000 cm^{-1}). The motion of the atoms during the vibration can also described in terms of the normal modes, Q_i of vibration. The molecule is promoted to the excited state only if its dipole moment, μ, changes during that normal mode vibration i.e., $(\partial\mu / \partial Q_i) \neq 0$.

The actual variation of the potential energy as a function of the displacement of the atoms from their equilibrium position is shown in Figure 1.1 as the blue line.
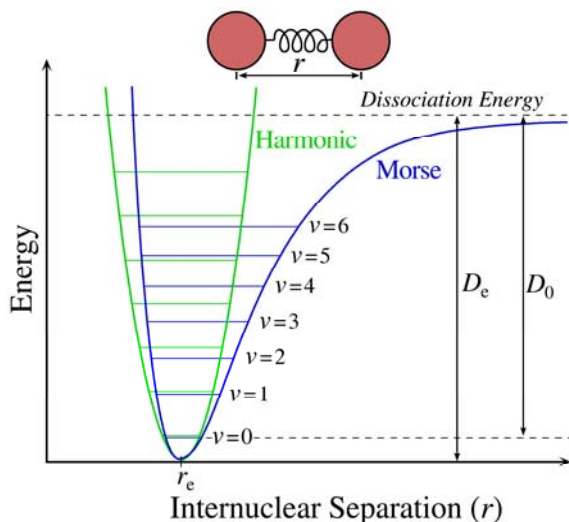
Figure 1.1. The harmonic (green line) and anharmonic (Morse type, blue line) potentials of a diatomic molecule as a function of the internuclear separation.

From the curve it can be seen that equation 1.1 is valid only for low vibrational quantum number. In practice, $V_{i\upsilon}$ must be described using an anharmonic (Morse-type) potential function.[44,45] This behavior is shown in Figure 1.1 as the blue line, and the potential energy is given to a first approximation by the expression

$$V_{i\upsilon} = h\nu_i(\upsilon_i + \frac{1}{2}) + h\nu_i x_i(\upsilon_i + \frac{1}{2})^2 \quad - - - - - - - -(1.2)$$

where x_i is the anharmonicity constant.

For polyatomic molecules, accurate representation of potential energy becomes more difficult, since more coordinates and potential parameters are required. Therefore, to describe

the potential energy either conceptually or mathematically, it is convenient to use internal coordinates such as bond stretches and angle bends. A nonlinear polyatomic molecule consisting of N atoms has 3N−6 (3N-5 for linear molecule) independent internal coordinates. Additional internal coordinates are called "redundant coordinates." The representation of a potential energy surface is often facilitated by including redundant internal coordinates. In general, no difficulty arises in including redundant internal coordinates in a potential energy function as long as the function correctly represents the molecular symmetry.

1.5 Infrared Spectroscopy of PAHs and Diols

IR spectroscopy is a classical experimental technique for the determination of fundamental vibrational frequencies in a molecule and for the identification of various positional isomers of a molecule in the gas phase. Due to their low vapor pressures at room temperature (see Table 1.1), vibrational spectroscopy of PAHs namely naphthalene, phenanthrene, anthracene, 1-methylanthracene, 9-methyanthracene, 9-cyanoanthracene, 2-aminoanthracene, acridine, 1,2-benzantracene, chrysene, pyrene, tetracene, pentacene, perylene, triphenylene, coronene, fluoranthene, benzo[a]fluoranthene, benzo[b]fluoranthene, benzo[z]fluoranthene, and benzo[k]fluoranthene and their cations have been carried out mostly in rare gas matrices.[46] There are a few literature reports on the gas-phase IR studies of PAHs with vibrational mode assignment. Jobline et al. recorded IR spectra of gas-phase pyrene, coronene and ovalene at a high temperature with the help of a 7.0 cm^3 oven made of nickel-chromium alloy and fitted with IR transparent diamond windows at a spectral resolution of 1 cm^{-1} or lower.[47,48] They compared the gas phase spectra with the solid and matrix phase

spectra and found that the matrix spectrum was much sharper. They identified the bands by comparing the gas phase spectra with previously assigned matrix spectra. In 1997, Cane et al. recorded the gas phase IR spectra of anthracene and phenanthrene, and their deuterated analogs with the help of a multi-pass gas cell of 4.8 and 5.6 meter, respectively, at a resolution of 0.2 cm^{-1} at 100 ^{0}C.[49a,b] They assigned the vibrational bands using DFT and scaled self-consistent force fields and found that both theoretical methods reproduce the sequence of the experimental frequencies well. The room temperature IR spectra of naphthalene in the gas phase have been reported by Pirali et al. recently using an 8 meter path-length gas cell at a resolution of 0.005 cm^{-1}.[50] At this high resolution they saw rotational structure in the spectra. The vibrational assignments were made using anharmonic DFT calculations.

Generally both harmonic and anharmonic DFT calculations have been carried out to assign the experimental IR spectra of polycyclic aromatic compounds.[51a-d] Calculated harmonic frequencies deviate by several hundreds of wavenumbers from the observed frequencies and thus one or more scaling factors have been used to multiply the calculated frequencies in order to get a close agreement with experiment. In 1996, Langhoff carried out the harmonic frequency and intensity calculation of 13 PAHs using the DFT method. He found that the harmonic frequencies, when uniformly scaled agree with the matrix isolation IR fundamentals with an average error of about 10 cm^{-1}.[51a] In the same year, Martin et al. did harmonic calculation for naphthalene, azulene, phenanthrene, and anthracene using B3LYP functional and basis sets of *spd* and *spdf* quality. They have used three scaling factors for the harmonic frequencies of C-H stretching, in-plane-bending and rest of the vibrations to find agreement with the observed bands within 10 - 20 cm^{-1}.[51b] In 1997, Bauschlicher et al. carried

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out DFT calculation to determine the harmonic frequencies and intensities of perdeuterated naphthalene, phenanthrene, pyrene, and chrysene.[51c] They performed the calculations with two different basis sets, 4-31G* and 6-31G* and found maximum mismatch of frequencies by about 12.4 and 36.6 cm^{-1}, respectively, when harmonic frequencies were scaled uniformly by a factor of 0.958. In 2007, Cane et al. did DFT calculations in order to get the cubic and the quartic semidiagonal anharmonic force fields of naphthalene and deuterated naphthalene.[51d] They found that the fundamental frequencies computed by second-order vibrational perturbation are in good agreement with the experimental frequencies with a mean deviation of 4 cm^{-1}. However, in the case of aromatic C–H stretching vibrations deviation is more ~10 cm^{-1} due to the possible presence of Fermi resonances. We have found earlier that for methyl C–H stretching vibrations the differences between scaled harmonic DFT and experimental frequencies are even more than 30 cm^{-1}.[52] McKean et al. have pointed out that even for methyl C-H symmetric and antisymmetric stretches, different scaling factors for calculated harmonic frequencies are necessary to match the experimental frequencies.[53]

IR spectroscopy has also been used for the identification of different conformers and characterization of hydrogen bonding in diols as discussed in section 1.3. Conformational isomers of ethylene glycol have been investigated by IR spectroscopy in the gas (up to 125 ^{o}C), liquid and solid phases in 1967 by Buckle et al.[41a] Normally two closely spaced IR absorption peaks are seen in these molecules. The peaks correspond to a free O–H and a H-bonded O–H stretching frequencies. The difference in frequency between these two peaks are known as the red shift between bound and free OHs. The gas phase result of Buckle et al. shows a 33 cm^{-1} red-shift. The red shift is believed to be an evidence for the presence of the

gauche conformer in the gas phase which is stabilized by IHB. IR spectroscopy of 1,2-, 1,3-, 2,3-, and 1,4-BD have been studied by Fishman et al. in the gas and liquid phases at $\pm$ 2 cm^{-1}.[41b] They found a large red-shift of 110 cm^{-1} in 1,4-BD. Their results also show that the enthalpies of IHB formation in these isomers depend strongly on their conformation. In 2003, Jesus et al. did conformational analysis of BD isomers by means of DFT calculations and matrix isolation IR spectroscopic studies.[54] They have also characterized the HB strength. The conformations of 1,4-BD have been investigated using a combination of MP2 calculation, natural bond orbital (NBO) and AIM analysis, and matrix-isolation infrared spectroscopy by the same group in 2008.[55] They found that the intramolecular hydrogen bonded conformers contributes 46% in the equilibrium conformation at room temperature. In 2009, Ma et al. carried out IR spectroscopic study and DFT calculation on 1,2-EG, 1,2-PD, 2,3-BD and 1,2-BD in solution.[56] In solution they found that the red shift was of the order of 40 cm^{-1} in the vicinal diols and that is due to IHB.

For the past 20 years, extensive quantum-chemical calculations have been carried out for the conformational analysis and characterization of the hydrogen bond between two vicinal hydroxyl groups in EG.[57-65] Electron density topological analysis has shown a bond critical point (BCP) and atomic bond path to be absent which implies that no IHB is present in 1,2 EG.[66,67] Furthermore, quantum diffusion Monte Carlo (QDMC) simulations corroborated the absence of IHB in 1,2-EG.[68]

1.6 Scope and motivation of this thesis work

From the above introduction it is clear that PAHs are important in atmospheric chemistry and astrophysics and, thus, it is important to identify and distinguish them in the gas phase at

low concentrations by using a suitable spectroscopic technique. Also suitable vibrational analysis method is required for the unambiguous assignment of the observed infrared bands which may eventually lead to the identification of UIR bands from the interstellar space and identification PAHs in the earth atmopsher. Therefore, my motivation of this work is twofold: (i) to record the gas phase IR absorption spectra of some atmospherically and astronomically important PAHs namely 1, 5-, 1, 6-, and 2, 6-dimethyl naphthalenes (DMNs); 2, 4-, 2, 6-, 2, 7-, and 2,8-dimethyl quinolines (DMQs); and 1, 9-, 2, 4-, and 3, 9-dimethyl phenanthrenes (DMPs) and (ii) unambiguously assign the vibrational bands in the observed spectra. However, the second part of the work is tricky since various theoretical methods of calculation of vibrational spectra are available. I have used scaled harmonic and anharmonic frequencies as well as scaled force fields to fit the experimental spectra. The error limits of each of these assignment methods have also been analyzed.

In another related objective, I have investigated the IR spectra of diols namely 1,2-EG and 1,4-BD in the gas phase and performed DFT calculation in order to look for intramolecular hydrogen bonding in them. These are biologically and industrially important molecules and exist in a mixture of conformers as discussed in section 1.1.3. The most abundant conformer of diols is the *gauche* conformer which is thought to be stabilized by IHB. The existence of IHB in 1,2-EG is still controversial although many papers have been written on it. My hope in this work is to throw some light on this problem.

1.7 References

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Chapter-2

Methods: Experimental and Theoretical

2.1 Introduction

This chapter describes the experimental set-ups and computational methods which were used for the IR spectroscopic studies of PAHs, methyl-PAHs and diols. The FT-IR spectroscopic technique has been used to record IR absorption spectra of PAHs and diols in the gas phase. DFT calculations with valence polarized basis sets have been carried out to obtain the harmonic and anharmonic frequencies and their intensities calculations. In addition to this, I have carried out scaled quantum mechanical (SQM) force field calculations for the unambiguous assignments of the observed bands. The observed spectra can be used for the identification of gaseous PAHs and methylated derivatives of PAHs which are present in the atmosphere at low concentrations. On the other hand, the gas phase IR spectra of diols can be used for the characterization of the nature of hydrogen bonding in diols. In both the cases a variable path-length long-path gas cell was coupled with a FT-IR spectrometer to record the IR spectra at low concentration.

2.2 Experimental technique

2.2.1 Principle of FT-IR spectrometry: Michelson interferometer

The design of interferometers used for IR spectroscopy is based on a two-beam interferometer which was originally designed by Michelson in 1891.[1, 2] The Michelson interferometer is a device that can divide a beam of radiation into two paths and then recombine the two beams after a path difference has been introduced. A condition thereby created under which interference between the beams can occur. The variation of intensity of the beam emerging from the interferometer is measured as a function of the path difference obtained.

The simplest form of Michelson interferometer, interferogram and spectrum (for monochromatic light source) is shown in Figure 2.1. Here a constructive interference will occur only when the distance between the movable mirror and the fixed mirror, δ also called retardation, is an integral multiple of λ, whereas a destructive interference will take place when δ is an integral multiple of $\lambda/2$.
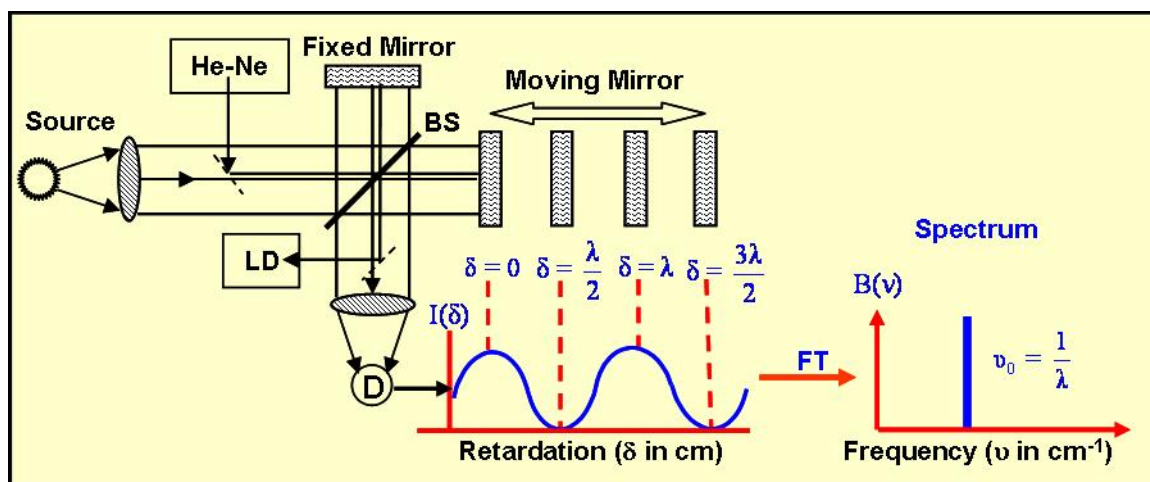
Figure 2.1. Optical diagram of a Michelson interferometer with the He-Ne laser running co-axial, Interferogram and Spectrum for a single frequency light source. The Interferometer consists of four major components: a fixed mirror, a moving mirror, BS: beamsplitter, D: Detector. LD: He-Ne laser detector.

To obtain an interferogram, $I(\delta)$, the detector signal is digitized and recorded as a function of retardation. The interferogram intensity of polychromatic source is mathematically described as:

$$I(\delta) = \int_{-\infty}^{+\infty} B(\nu) \cos(2\pi\nu\delta) d\nu \; ----------- (2.1)$$

where $B(\nu)$ is the spectral intensity at wave number ν (in cm^{-1}).

Fourier transformation (FT) of $I(\delta)$ gives the single-beam IR spectrum expressed as:

$$B(\upsilon) = \int_{-\infty}^{+\infty} I(\delta)\cos(2\pi\upsilon\delta)d\delta \; - - - - - - - - - - - -(2.2)$$

The movable mirror moves continuously in case of continuous scan mode.

2.2.2 Continuous-Scan Interferometry

The continuous-scan is preferably used for the routine static or relatively slow kinetic measurements that require time resolution not faster than 20 ms. In the continuous-scan FT-IR spectrometer, the moving mirror moves continuously at a constant velocity, $V(\text{cm s}^{-1})$, and the optical path difference at time t(s) is given by $\delta = 2Vt(cm)$.
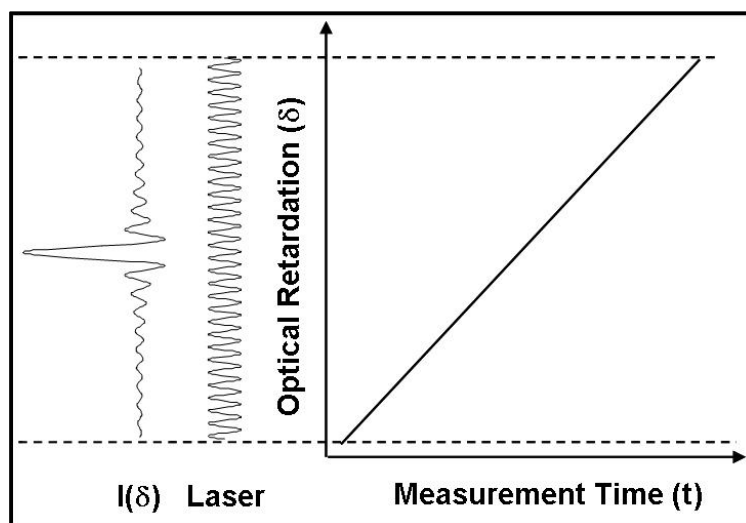
Figure 2.2. Schematic of data collection in continuous-scan interferometer.

The interferogram data points are digitized at the zero crossings of the He-Ne laser signal as shown in Figure 2.2. The use of laser signal ensures that I(δ) is measured at precisely equal intervals of mirror positions and provides an internal wavelength calibration for every scan.

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Because of continuous movement of the mirror, the interferogram I(δ) changes as a function of time. The Fourier frequency (f_F *in Hz*) of IR light at wave number ν is given by:

$$f_F = 2V\nu - - - - - - - - - -(2.3)$$

where V is the mirror velocity in cm s^{-1}. The slow velocities are chosen for thermal detectors; such as deuterated triglycine sulfate (DTGS). The fast velocities are chosen for fast quantum detectors, such as a mercury cadmium telluride (MCT) or indium antimonide (InSb) detector, for routine or kinetic measurements.

2.2.3 Variable Path-length Long Path Gas Cell

In chapter 1, it has been discussed that PAHs and methyl-PAHs have insufficient vapor pressures at room temperature.[3] So, it is difficult to obtain sufficient amount of these compounds in the gas phase for the IR spectroscopic study with a normal gas cell having an optical path length ~10 cm. Kurtz used a stainless steel cell to get the IR spectrum of coronene at elevated temperatures.[4] Later Joblin and coworkers recorded the IR spectra of neutral PAHs in the gas phase using an oven of 7.0 cm^3 which made from nickel-chromium alloy and fitted with IR transparent diamond windows.[5, 6] I have used multi-pass gas cell of 7.2 and 8.0 meters. Figure 2.3 shows the variable path-length long-path gas cell [7] which made according to the "white cell" principle.[8] The cell contains three internal gold-coated mirrors. Out of these, two are immovable and one is movable. Two potassium chloride (KCl)/zinc selenide (ZnSe) windows of 2.5/1.9 cm diameter, respectively, have been used for the entrance and exit of IR radiation into the cell. In addition, there are two plane transfer mirrors. These mirrors guide the

IR light into the cell and then to the detector. The cell can be evacuated by a mechanical pump and the sample holder is connected through a valve to the cell.
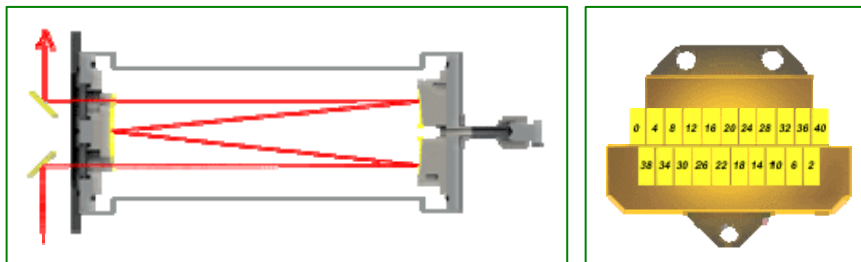
Figure 2.3. Schematic diagram of typical "white cell" and field mirror.

The beam comes through one window (left) and reflects back and forth between the field mirror (left) on the input side and the objective mirror (right) on the other end of the gas cell. After each 4 passes, the beam migrates across the top of the field mirror on the input side until it misses that mirror and exits through the exit window. The field mirror on the left shows the migration of 48 and 40 passes of the IR beam in the gas cell of 7.2 and 8.0 meter, respectively. The IR beam comes in at the position marked 0 and exits at the position marked 40 for the 7.2 meter gas cell (see Figure 2.3). The field mirror has the corners cut out to allow the IR beam to enter and exit the gas cell. These multi-pass gas cells were coupled with a FT-IR spectrometer through homemade aluminum or commercially available cell holders as shown in the subsequent sections.

2.3 Experimental set-up

2.3.1 Set-up for PAHs and diols

The schematic experimental set-up for the gas phase FT-IR spectroscopic studies of PAHs and diols are shown in Figure 2.4. In this figure, I have shown how a multi-pass cell of

7.2 meter has been coupled with the FT-IR spectrometer, the sample-tube, the vacuum pump, and the pressure gauge. The commercially available variable long path-length cell (Model 7.2-V, REFLEX Analytical Corporation, USA) were coupled with the FT-IR spectrometer (Nexus-870, Thermonicolet / Vertex-70, Bruker Optics) by a homemade aluminum cell holder.
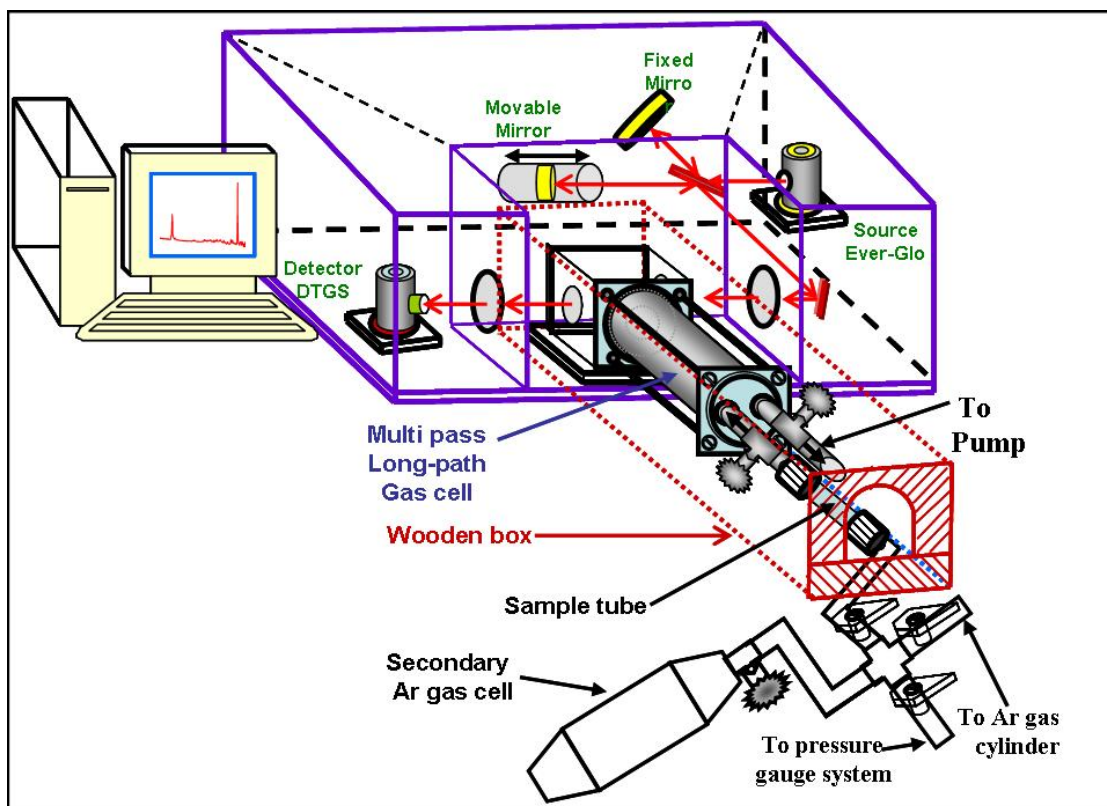
Figure 2.4. Schematic representation of the FT-IR spectrometer coupled with a multi-pass long-path gas cell of 7.2 meter.

The variable path-length cell body is a cylinder of borosilicate glass of length 15 cm, with an inside diameter of 6 cm. It has an optical path adjustable from 0.6 to 7.2 meter in increments of 0.6 meter. This cell is connected to two valves; one side is connected to the sample tube made of pyrex glass and the other side is connected to the vacuum pump. The sample tube was then connected to a four-ways valve system with the help of a homemade

brass coupler and a viton O-ring, which, in turn, is attached with the secondary gas cylinder, the primary Ar gas cylinder and the pressure gauge system (PRM-300MX, IRA). The cell is evacuated by a rotary pump (RV-8, Boc Edward). The cell body and the sample tube were wrapped with a heating tape (Thermolyne Heating Tape, Aldrich) and the temperature was maintained with the help of a temperature controller (DIGITHERM-2000MCX, IRA) fitted with a feedback heat sensor. The multi-pass gas cell along with the sample tube has been kept inside a wooden box covered with a heat-insulating silicon sheet. It maintains the uniformity of temperature of the gas cell along with the sample tube, and also protects the spectrometer from high temperature.
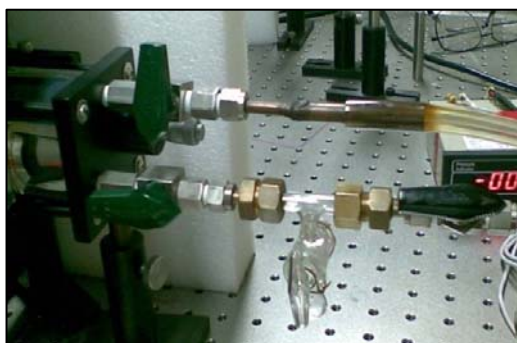
Figure 2.5. A small bulb for liquid samples is connected to the gas cell and the four-ways valve arrangement.

In case of liquid samples, the sample tube was replaced by a small glass bulb of volume 2 ml which is isolated by a valve as shown in Figure 2.5. This set-up has been used to record the IR spectra of compounds which are having vapor pressures up to 10^{-4} mmHg at room temperature.

2.3.2 Standardization of multi-pass gas cell of 7.2 meter path-length coupled with Nexus-870 (Thermonicolet, US) spectrometer

The variable multi-pass gas cell was first standardized with naphthalene. For the standardization, solid naphthalene (~10 mg) was taken in the sample tube which was kept isolated from the cell and the four-ways valve arrangement. The gas cell, along with the sample tube, was then evacuated up to ~ 0 mmHg. The vacuum single-beam spectrum was then recorded with a spectral resolution of 4 cm^{-1} and averaging over 64 scans, which is the reference spectrum.
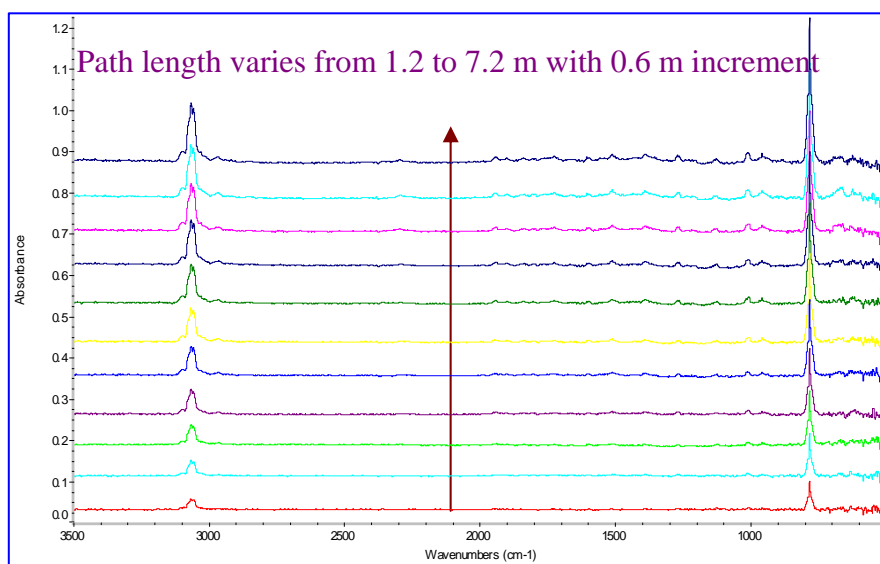
Figure 2.6. Gas phase IR absorption spectra of naphthalene as a function of path length.

After recording the reference spectrum, ultrahigh pure Ar (carrier) gas was allowed to pass through the sample tube to carry naphthalene inside the gas cell. The total pressure of Ar and naphthalene was maintained at 20 mmHg. The spectra of naphthalene were recorded at optical path lengths (OPL) of 1.2, 1.8, 2.4, 3.0 3.6, 4.2, 4.8, 5.4, 6.0, 6.6, and 7.2 meter at room temperature (25 ^{o}C) after normalization with respect to the reference spectrum. The observed

spectra are presented in Figure 2.6. The observed band areas (in cm^{-1}) for the strong bands at 3065 and 782 cm^{-1}, were measured by OMNIC software provided by Thermonicolet.[9] The optical path lengths and band areas with respect to the strong band are listed in Table 2.1.

Table 2.1: Optical path-length (OPL, in m) and integrated band area (in cm^{-1})

OPL (m)	Band area at 3065 cm^{-1}	Band area at 782 cm^{-1}
1.2	0.681	0.928
1.8	1.343	1.263
2.4	1.402	1.753
3.0	2.117	2.35
3.6	2.375	2.683
4.2	2.834	3.002
4.8	3.244	3.548
5.4	3.773	3.950
6.0	3.898	4.235
6.6	4.422	4.893
7.2	4.924	5.406
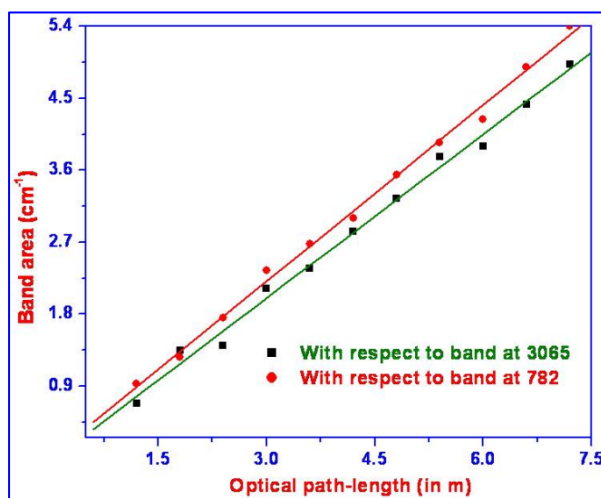
Figure 2.7. Observed band area (in cm^{-1}) vs optical path length (in m) for naphthalene.

The optical path length (in m) *vs* band area (in cm^{-1}) is plotted in Figure 2.7. From this figure it was found that the observed band area follows a linear relationship with the optical path-length. It helps us to set the optical path-length for different compounds having different vapor pressure at a particular temperature.

2.3.3 Standardization of the multi-pass gas cell of 8.0 meter coupled with Vertex-70 (Bruker Optics, Germany) spectrometer

Another experimental set-up has been employed to record the IR spectra of compounds having a vapor pressure of $\sim 10^{-5}$ mmHg at room temperature, where we have used a 8.0 meter path-length white cell (136G/3TQ, Bruker Optics) equipped with a heating jacket.
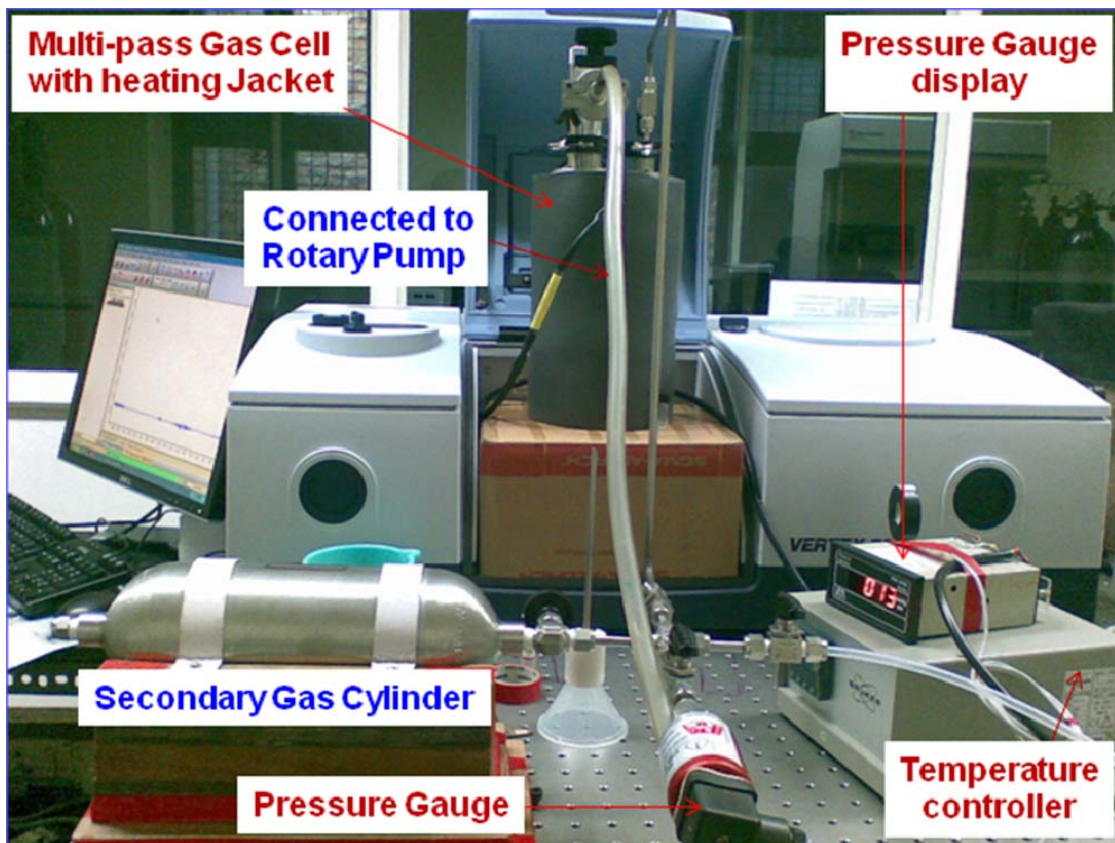
Figure 2.8. Photograph of the FT-IR spectrometer (Vertex-70) coupled with a multi-pass long-path gas cell of 8.0 meter.

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The cell was coupled with the FT-IR spectrometer (Vertex-70, Bruker Optics) as shown in Figure 2.8. The gas cell is made of borosilicate glass tube of (23 cm x 11 cm) and equipped with ZnSe windows. The cell was placed vertically inside the sample chamber of the spectrometer and aligned with the help of an external He-Ne laser before use. The rotary pump and Ar-line were connected to the cell through ball valves. Phenanthrene (90%, Fluka) was used as a standard compound for the optimization of our set-up and purified by vacuum distillation method before use. Compound was thermally vaporized at 100 ^{o}C and the reported spectrum was reproduced (see Figure 2.9).
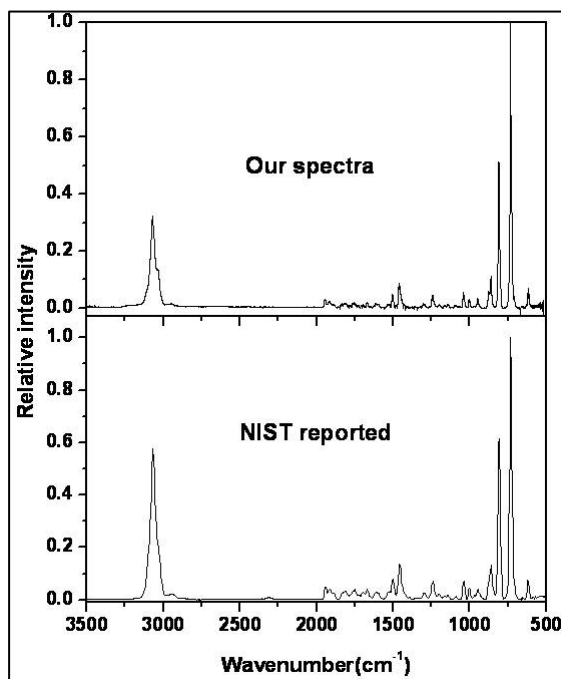
Figure 2.9. Our and NIST reported gas phase IR spectra of phenanthrene.

The total pressure of Ar gas containing phenanthrene in the cell was maintained at 30 mmHg. The mid-IR spectra (4000 - 400 cm^{-1}) were collected using a liquid nitrogen cooled MCT detector and KBr beam splitter combination. The spectrometer was continuously purged with

N_2 gas (UHP grade). The spectra were recorded at 0.5 cm^{-1} resolution with averaging over 2048 scans. Total time required for this number of scans is about one hour. DMPs have low infrared absorbance (OD$_{max}$= 0.03) and small amounts of H_2O vapor present inside the cell give rise to infrared absorption bands that overlap with those of DMPs. We have collected the spectra of Ar at the same pressure without DMP separately and subtracted the same from the sample spectra in order to get H_2O band free spectra of the DMPs. Therefore, the suitable H_2O spectrum was recorded and subtracted from the sample spectra in order to get clear spectra of phenanthrene. This set-up has been used for the gas phase IR spectroscopic study of dimethylphenanthrenes (DMPs).

2.4 Theoretical methods

2.4.1 Harmonic and anharmonic frequency calculations

The potential energy for a polyatomic molecule can be expanded in a Taylor series,[10]

$$V = \frac{1}{2}\sum_i \omega_i q_i^2 + \frac{1}{6}\sum_{ijk} \phi_{ijk} q_i q_j q_k + \frac{1}{24}\sum \phi_{ijkl} q_i q_j q_k q_l + ...,--(2.4)$$

where ω_i s are the harmonic frequencies (in cm^{-1}), q_i s the normal coordinates, and ϕ_{ijk} and ϕ_{ijkl} the third and fourth order force constants of the molecules, respectively. Further ϕ_{ijk} and ϕ_{ijkl} are given by

$$\phi_{ijk} = \frac{\partial^3 E^{el}}{\partial q_i \partial q_j \partial q_k} \quad \text{and} \quad \phi_{ijkl} = \frac{\partial^4 E^{el}}{\partial q_i \partial q_j \partial_k \partial_l} -------(2.5)$$

where E^{el} is the electronic plus the nuclear repulsion energy term in the BO approximation. The total vibrational energy including anharmonicity is then

$$E = \sum_i \omega_i(\upsilon_i + \frac{d_i}{2}) + \sum_{i \leq j} x_{ij}(\upsilon_i + \frac{d_i}{2})(\upsilon_j + \frac{d_j}{2}) + \sum_{i \leq j} l_i l_j g_{ij} ----(2.6)$$

where ω_i and d_i are, repectively, the harmonic frequencies and the degeneracy of the i-th mode; υ_i, the vibrational and l_i, the nuclear vibrational angular-momentum quantum numbers, and x_{ij} and g_{ij} the anharmonic constants, which are related to the third and fourth order force fields as shown in details in Ref.[11]

In this thesis, the optimized geometry, harmonic and anharmonic frequency calculations were carried out at the DFT/B3LYP level of theory and polarized-basis sets such as 6-31G*, 6-311G** and 6-311++G** were used depending on the size of the molecules and time taken to finish a single point calculation. All the calculations have been carried out using G98, G03 and G09 computational codes in an IBM RS/6000, IBM Cluster P720 (IBL-64) and Tesla Cluster (EM64L) computers, respectively.

2.4.2 Scaled quantum mechanical (SQM) force field calculation

The characterization of the observed infrared spectra requires correct identification of the fundamental and non-fundamental vibrational modes. The electronic structure calculations derive harmonic frequencies by diagonalizing the matrix of the second derivative of energy with respect to the nuclear coordinates. But for accuracy we need anharmonic force constants which include the cubic and quartic force constants. Another way to resolve this problem is to consider only the harmonic frequencies and make corrections for errors by means of some scaling procedure.[12, 13]

Most accepted scaling procedure is Pulay's scaled quantum mechanical (SQM) method where force constants were scaled rather frequencies. Therefore, I have carried out scaled force field calculation in order to get calculated frequencies closer to experimental frequencies and potential energy distributions (PEDs) of the normal modes in terms of the local

coordinates of the molecule using a modified UMAT program[14] in the QCPE package.[15] The

QCPE consists of four FORTRAN programs which have been designed to solve Wilson's GF

matrix for a complete vibrational analysis. This method requires the definition of a basis set

which is employed to construct the normal coordinates. The UMAT program allows for the

definition of unsymmetrized or symmetrized basis sets, referred to as internal and symmetry

coordinates, respectively. These are related to Cartesian coordinates via the B and U Matrices

through the following relationships:

$$R = BX \quad - - - - - - - - - - - - - \quad (2.7)$$

$$S = UR = UBX = B^{Sym}X \quad - - - - - -(2.8)$$

where R, S and X represent the column vectors of the internal, symmetry and Cartesian

coordinates, respectively. The inverse Kinetic Energy Matrices, G and G^{Sym} defined by the B

or B^{Sym} as

$$G = BM^{-1}B^t \quad - - - - - - - - - - - - - - - - - -(2.9)$$

$$G^{Sym} = (B^{Sym})M^{-1}(B^{Sym})^t = UBM^{-1}B^tU^t \quad - - - - - (2.10)$$

where the superscript "t" indicates "transpose" and the M^{-1} is a diagonal matrix which contains

the inverses of the masses of the atoms.[16] Using the G or G^{Sym} matrix, in conjunction with the

appropriate Potential Energy (F or F^{Sym}) matrix, the vibrational secular equation has been

formulated in either an unsymmetrized or a symmetrized fashion:

$$GFL = L\Lambda \quad - - - - - - - - - - - - - \quad (2.11)$$

$$G^{Sym}F^{Sym}L^{Sym} = L^{Sym}\Lambda \quad - - - - - - - - - - \quad (2.12)$$

Where Λ is the frequency matrix ($\lambda_i = 4\pi^2 \nu_i^2$) and L is the eigenvector matrix describing the normal modes. Usually F is varied and Λ is calculated until it matches with the experimental frequencies. We modify Λ with small correction $\Delta\Lambda$ given by $\Delta\Lambda = (\Lambda_{expt.} - \Lambda)(iter - 1)/N_{iter}$ where N_{iter} is the total number of iterations. In our fitting I have used $N_{iter}=100$. The details can be found in Ref.[17]

In order to do this analysis, the following steps were followed: First, the internal coordinates were defined for PAHs. Then a set of nonredundant local coordinates were constructed as recommended by Pulay.[12, 13] Force constants in Cartesian coordinates obtained from Gaussian outputs were transformed in terms of nonredundant local coordinates.[18] Finally scaled force constants were obtained by fitting calculated frequencies to the observed frequencies by means of a least square fitting procedure using an algorithm developed by Chakraborty et al.[14] We have done this analysis with the experimental band origin frequencies. The fitting algorithm requires all the experimental frequencies; however, experimentally it was not possible to resolve all the fundamentals in the PAHs studied here. The fitting algorithm requires all the experimental frequencies to obtain a good fit. Therefore, we guessed some of the fundamental frequencies that are not seen in the recorded spectra. The guessed frequencies are chosen to be close to the scaled harmonic frequencies (C-H stretching and non C-H stretching frequencies were multiplied by factors, 0.9588 and 0.9733, respectively) which give minimum RMS errors. Then the PEDs were obtained using fitted force constants using FTRY-ATOM-RMSA-INTY program in the QCPE package.

2.4.3 Error analysis

An error analysis was done in terms of mean deviation, δ (in cm^{-1}), between the observed and calculated (harmonic, anharmonic and force field fitted) frequencies using

$$\delta = \frac{\sum_{i=1}^{n} \left| v_i^{cal.} - v_i^{\exp t.} \right|}{n} \quad - - - - - -(2.13)$$

where $v^{cal.}$ & $v^{\exp t.}$ are calculated and observed frequencies, respectively, and n is the total number of fundamentals assigned in the recorded spectra.

2.5 IR band intensity calculation

2.5.1 Intensity

The quantity of interest in the intensity calculation is the integrated absorption coefficient A (in km mol^{-1}) which can be determined theoretically using the following equation[19]

$$A_i = 42.254 \left| \frac{\partial \mu}{\partial Q_i} \right|^2 \quad - - - - - - - (2.14)$$

where $\partial \mu / \partial Q_i$ are the dipole moment derivatives in D(Å amu$^{1/2}$) evaluated via analytical derivatives computed at the DFT/B3LYP level of theory.

On the other hand, absolute intensity (in cm^{-2} atm^{-1}) can be obtained experimentally by using the following expression given by Galabov et al. [20]

$$A_i = \frac{2.303 \int \log(I_o / I)_i \, dv_i}{P_i l} \quad - - - - - - - (2.15)$$

where l (in cm) is the optical path length and P_i s are the vapor pressures. In our experiment, it is not possible to get the vapor pressure of PAHs or dimethyl-PAHs by conventional pressure gauge system since they are seeded on Ar gas. Therefore, we estimated the vapor pressures

(P_i) under all the bands with the help of the observed band areas and their corresponding calculated intensities by using the same equation (see the next section). The average pressure obtained from all the bands were then calculated using $P = \sum_{i=1}^{n} \dfrac{P_i}{n}$, where n is the total number of observed bands and was used to calculate the observed band intensities (in cm^{-2} atm^{-1}). In order to get the experimental intensities in km mol^{-1}, the values in cm^{-2} atm^{-1} were multiplied by factor of 82.056 (T/K).[21]

2.5.2 Vapor pressure calculation

In section 2.5.1, it has been discussed that the vapor pressure is a necessary parameter for the absolute intensity calculation. The vapor pressures at experimental temperatures under all the observed bands were calculated with the help of the following equation which is obtained by rearranging 2.15

$$P_i(atm) = 2.303 \times 82.056 \times T(K) \times 10^{-5} \tau_i / A_i l ----- (2.16)$$

where $\tau_i = \int \log I_0 / I d\nu$ are the integrated band areas (cm^{-1}) obtained experimentally and A_i are the infrared band intensities (in km mol^{-1}) obtained from DFT calculations. The average value over all the partial pressures is considered as vapor pressure of the PAHs.

2.6 Simulated spectra

From the Gaussian output results we could predict the spectra of PAHs and diols. Simulated spectra were produced with the calculated frequencies and their intensities using FORTRAN code, where each frequency-intensity pair was modeled as a Gaussian function, f(ν), centered at the calculated frequency:[22]

$$f(\upsilon) = \tau \exp\{-(\nu - \nu_o)^2 / 2\sigma^2\} - - - - - - - - - - (2.17)$$

Here, τ is the intensities in km mol^{-1}, ν is the energy in units of cm^{-1}, and σ is the FWHM.

2.7 References

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Chapter-3

Infrared Spectroscopic Studies of Dimethylnaphthalenes (DMNs) in the Gas Phase

3.1 Introduction

In chapter 1, I have discussed that the naphthalene and alkylated naphthalenes are semi volatile polycyclic aromatic hydrocarbons (PAHs) present in the atmosphere in the gas and particle phases.[1] Diesel fuel contains alkyl-PAHs including methyl naphthalenes (MNs) and dimethylnaphthalenes (DMNs).[2, 3] In urban areas emission from diesel-fueled vehicles puts these compounds in the atmosphere.[4, 5] The alkylated PAHs have also been identified in individual interplanetary dust particles (IDPs).[6] The toxicity, carcinogenicity and mutagenicity of DMNs are different, and thus, it is important to identify and distinguish them at low concentrations.[7-9]

In this chapter, I report the infrared spectra at 0.5 cm^{-1} resolution of three dimethylnaphthalenes (DMNs), namely 1,5-DMN, 1,6-DMN, and 2,6-DMN in the gas phase at an elevated temperature recorded with the help of a variable path-length cell. I have carried out DFT calculations to assign the experimentally observed spectral lines. The calculations have been performed at B3LYP level of theory with 6-31G* as basis set to determine the harmonic frequencies and intensities of the DMNs. The motivation to do this work is to identify and distinguish DMNs by IR spectroscopy.

3.2 Materials and Methods

3.2.1 Materials

DMNs used in this investigation are 1,6-dimethylnaphthalene (98.0%, Fluka), 1,5-dimethylnaphthalene (98.0%, Aldrich Chem. Co.), and 2, 6-dimethylnaphthalene (99.8%, Oekanal) which were obtained commercially. Some physical properties of DMNs are listed in Table 3.1.

Table 3.1: Physical properties of DMNs

Name of DMNs	m.p/b.p (^{o}C)	P(in mmHg at 25 ^{o}C)^{est}
1,5-DMN (Solid)	82.0	1.17×10^{-2}
1,6-DMN (Liquid)	-17.0/263.0	1.41×10^{-2}
2,6-DMN (Solid)	109.4	1.66×10^{-2}

^{est}Estimated vapor pressure taken from Ref.[10]

3.2.2 Experimental method

The experimental set-up, which has been used in this study, was discussed in section 2.3.1 of chapter 2. Since the compounds have low vapor pressure at RT (see Table 3.1), ultra high purity (99.999%) argon was used as a carrier gas to get the samples inside the cell. In this study, the optical path length was fixed at 6 meter. The sample DMN vapor mixed with Ar was introduced into the long path-length cell. Including the sample holder, the cell was heated and maintained at 90 ^{o}C. The DMNs were subjected to a repeated freeze/pump thaw procedure before use. The total pressure of argon gas containing DMNs in the cell was maintained at ~25 mmHg. Mid-infrared spectra (4000 – 400) cm^{-1} of DMNs were collected using a Deuterated Triglycine Sulphate (DTGS) detector/KBr beam splitter combination at 0.5 cm^{-1} resolution with averaging over 2048 scans.

3.2.3 Theoretical calculation

Theoretical calculations were carried out using density functional theory (DFT) to determine the harmonic frequencies and intensities of 1,6-DMN, 1,5-DMN, and 2,6-DMN. The geometry optimization was carried out with standard polarization basis set 6-31G* at the B3LYP (Becke 1993; Lee, Yang, & Parr 1988) level of theory using Gaussian 98 codes[11] in an

IBM RS/6000 computers. The frequencies and intensities were determined at the fully optimized C_1 geometry (Figure 3.1). It was reported by Langhoff et al.[12] that many of the methyl PAHs is found to be of lower symmetry (C_1) due to slight rotation of the methyl group, although the true point group of the molecule is C_s. In B3LYP calculations on DMNs, I found at least one imaginary frequency at the C_s optimized structure which is not realistic and thus C_1 symmetry was chosen for calculation. The calculated frequencies were scaled by a factor of 0.9588 for the C-H stretch and 0.9733 for other vibrational modes to compare with experiment.[13]

Figure 3.1. Optimized structure of (A) 1,5-DMN, (B) 1,6-DMN, and (C) 2,6-DMN at B3LYP/6-31G* level.

(A) 1,5-DMN

(B) 1,6-DMN

(C) 2,6-DMN
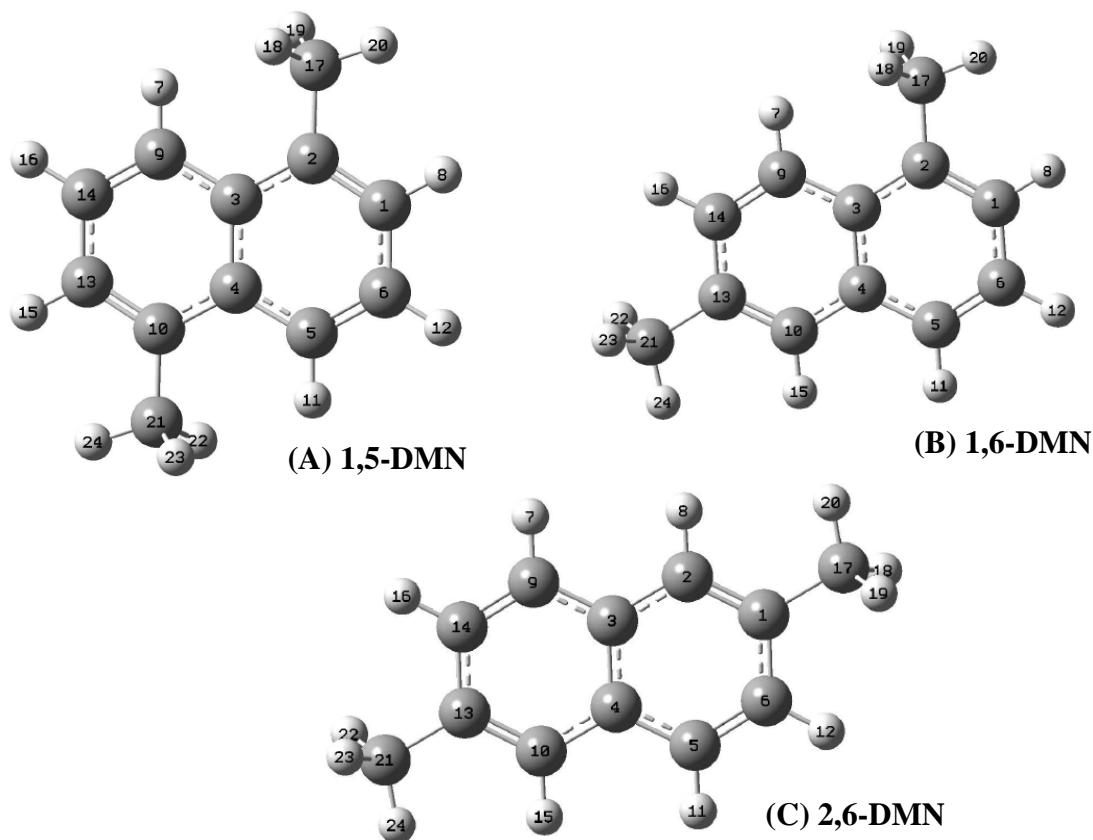
3.2.4 Vapor pressure and absolute intensity calculation

Observed band intensities were calculated with the help of measured band area and DFT calculated intensities as described in section 2.5 of chapter 2. The vapor pressure is a necessary parameter for the intensity calculation. For DMNs, the vapor pressures at 90 $^{\circ}$C under all observed band were calculated with the help of equation 2.16 and result has been presented in Table 3.2. Estimated partial pressure found to be 3.294×10^{-5} atm for 1,5-DMN; 5.590×10^{-5} atm for 1,6-DMN; and 2.743×10^{-5} atm for 2,6-DMN at 90 ^{0}C.

Table 3.2: Calculated intensity (A, km mol^{-1}), observed band area (τ, cm^{-1}) and estimated vapor pressure (P, atm) for individual observed bands at 90 $^{\circ}$C of DMNs.

No	1,5-DMN			1,6-DMN			2,6-DMN		
	A	τ	$P\times10^{-5}$	A	τ	$P\times10^{-5}$	A	τ	$P\times10^{-5}$
1	0.34		--	0.51		--	1.16		--
2	0.00		--	0.47		--	0.00		--
3	0.00		--	0.11		--	0.04		--
4	2.27		--	0.69		--	0.39		--
5	0.00		--	0.61		--	0.00		--
6	0.44		--	1.71		--	0.88		--
7	3.76		--	0.22		--	0.00		--
8	0.00		--	0.05		--	2.91		--
9	0.00		--	3.04		--	0.00		--
10	0.00		--	0.13		--	0.00		--
11	0.00		--	0.89		--	2.31		--
12	1.23		--	2.61		--	5.94		--
13	0.00		--	2.15		--	0.00		--
14	5.30		--	0.39		--	0.00		--
15	0.89		--	1.03		--	1.21		--
16	0.00		--	0.66		--	3.40		--
17	0.00		--	1.03		--	1.35		--
18	0.00		--	0.64		--	0.00		--
19	2.48		--	5.93	0.49	9.446	0.00		--
20	66.58	1.77	3.039	14.14	0.66	5.336	0.00		--
21	0.00		--	31.45	1.39	5.052	31.33	0.80	2.919
22	0.00		--	0.68		--	0.00		--
23	**1.39**	0.17	11.100	**6.73**		--	22.41	0.55	2.806
24	**0.36**		--	**2.80**	0.44	5.277	0.00		--
25	0.00		--	0.41		--	**0.98**		--
26	1.11	0.18	18.538	0.17		--	**0.94**	0.06	3.571
27	0.00		--	0.91		--	0.00		-

Table 3.2: (Continued) calculated intensity (A, km mol^{-1}), observed band area (in cm^{-1}) and estimated vapor pressure (P, atm) for individual observed bands at 90 ^{o}C of DMNs.

No	1,5-DMN			1,6-DMN			2,6-DMN		
	A	τ	P×10^{-5}	A	τ	P×10^{-5}	A	τ	P×10^{-5}
28	0.00		--	2.71		--	0.00		--
29	2.20		--	5.66	0.09	1.817	0.00		--
30	0.00		--	**5.39**		--	13.82	0.04	0.331
31	4.12	0.07	1.942	**1.09**	0.13	2.290	**8.56**	0.20	2.667
32	6.49	0.12	2.113	0.85			**0.01**		
33	0.00		--	2.64	0.12	5.196	1.83	0.10	6.247
34	0.00			0.56		--	0.00		--
35	1.19		--	1.00		--	3.95		
36	0.00		--	2.59	0.13	5.730	0.00		--
37	2.76		--	1.71	0.14	9.357	1.02		--
38	0.00		--	0.30			0.00		--
39	2.43	0.06	2.823	3.18	0.14	5.033	5.22	0.32	7.008
		0.05	--			--	1.69	0.12	--
40	0.92		--	1.45			0.00		--
41	0.00		--	2.03			5.58	0.36	--
42	0.00		--	2.14			1.38		7.375
43	0.48	0.18	--	**0.77**	0.52	47.9	0.01		
44	17.25		1.193	**0.47**		--	0.00		--
45	0.00		--	9.57	0.29	3.463	7.38		--
46	0.00	0.16	--	2.90		--	3.47	0.18	--
47	6.13		2.984	4.16			11.15		5.93
48	6.60		--	7.79	0.18	2.641	0.00		--
49	18.53		--	4.28		--	0.00		--
50	0.00	0.09	--	4.32		--	11.66	0.14	--
51	8.57		1.200	9.85	0.37	4.294	0.00		1.372
52	0.00	0.37	--	1.35		--	25.93	0.48	--
53	12.97		3.261	11.07	0.28	2.891	0.00		2.116
54	0.00	0.19	--	8.73	0.2	2.619		0.51	--
		0.07	--		0.45	--		0.04	--
		0.08	--		0.08	--		0.05	--
		0.04	--		0.19	--			--
			--		0.1	--	**81.85**		--
55	**58.53**	0.26	--	**35.41**		--	**4.79**	0.17	
56	**1.66**		0.493	**35.11**	0.55	0.864	17.05		0.224
57	12.25	0.19	--	9.81		--	27.68	0.44	--
58	29.00		0.526	23.10	0.55	1.910	**16.32**		1.817
59	**18.16**	0.09	--	**16.61**		--	**16.48**	0.01	--
60	**19.24**		0.270	**18.91**	0.11	0.353	21.39	0.15	0.034
61	25.83	0.32	--	16.86	0.56	3.797	0.00		0.802
62	0.00		1.41	**14.64**		--	33.06	0.21	--
63	0.16	0.44	--	**0.76**	0.38	2.820	0.00		0.726
64	49.13		1.023	30.16		--	62.53	0.38	--
65	**41.41**	0.29	--	37.47	0.22	0.671	0.00		0.695
66	**0.03**		0.799	15.71	0.18	1.309			

3.3 Results and Discussion

The gas phase IR spectra of the three DMNs are shown in Figure 3.2 and the experimental and theoretical infrared frequencies and intensities are listed in Tables 3.3 – 3.5. Absolute intensities are listed first while relative intensities are shown in parentheses. The relative intensities are given with respect to the strongest band seen in the range 780 - 815 cm^{-1}. The bands observed at 783.3, 812.8 and 808.5 cm^{-1} in 1,5-, 1,6-, and 2,6-DMN, respectively, correlate with the calculated fundamentals at 786.5, 812.4, and 811.6 cm^{-1} and are assigned to a aromatic C-H out-of-plane bending mode of the DMNs. To compare the experimental, calculated and reported[14] spectra, I have displayed all DMN spectra separately in Figures 3.3 – 3.5. No IR spectrum for 1,6-DMN has been reported and, therefore, only observed and calculated spectra have been displayed in Figure 3.4.
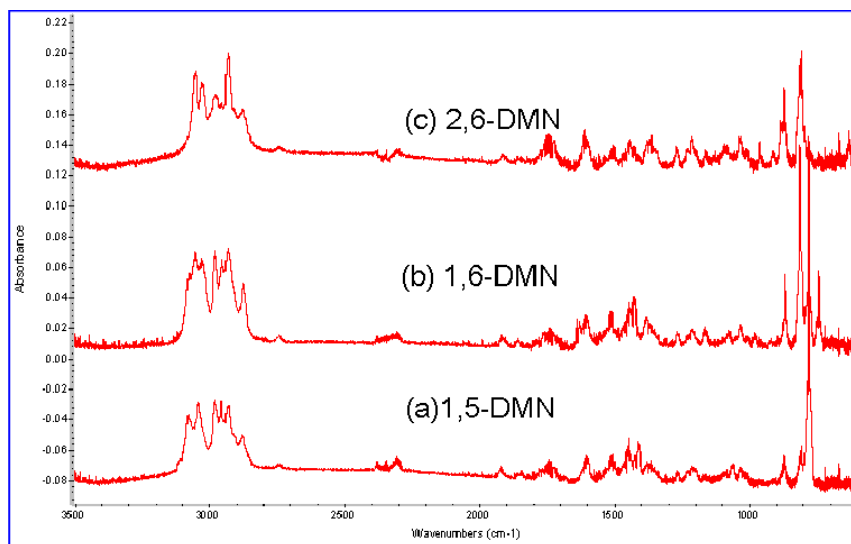
Figure 3.2. IR absorption spectra for (a) 1,5-DMN; (b) 1,6-DMN; and (c) 2,6-DMN at 0.5 cm^{-1} resolution.

Apart from the intense aromatic C-H out-of-plane bending mode mentioned above, many other low frequency aromatic C-H out-of-plane bending modes with lower intensities have been

recorded and assigned in the spectra. Bands observed at 807.5 and 872.2 cm^{-1} in 1,5-DMN; 746.2, 784.1, and 870.2 cm^{-1} in 1,6-DMN; and 873.6 and 914.2 cm^{-1} in 2,6-DMN are assigned to aromatic C-H out-of-plane bending vibrations by comparing with the respective calculated bands at 869.6 and 945.8 cm^{-1} in 1,5-DMN; 747.3, 784.5, and 893.1 cm^{-1} in 1,6-DMN; and 874.7 and 940.4 cm^{-1} in 2,6-DMN. The next low intensity band appears at 1034.7 cm^{-1} in 1,5-DMN, 1038.1 cm^{-1} in 1,6-DMN, and at 1037.9 cm^{-1} in 2,6-DMN.
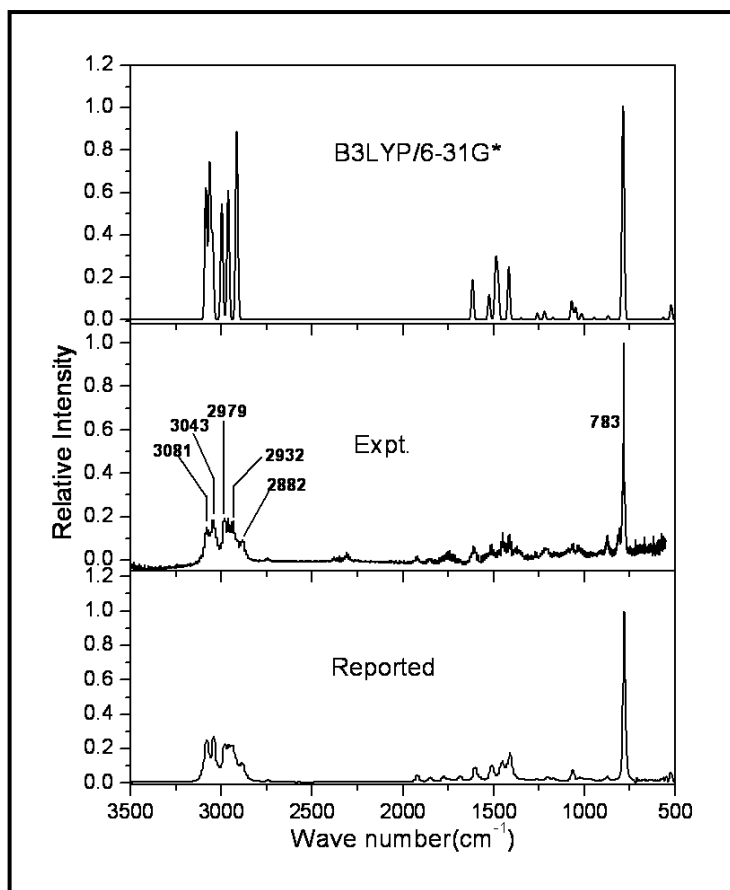
Figure 3.3. Comparison of experimental, theoretical and NIST reported[14] IR reported spectra of 1,5-DMN. In the calculated spectrum, the FWHM is assumed to be 15 cm^{-1}. Prominent peaks are labeled in the observed spectrum. Weak bands such as Me(C-H)$_{asym.\ str.}$ at 2956.9 cm^{-1}, etc. are not labeled in the observed spectrum.

This band has been assigned to a methyl C-H out-of-plane bending mode appearing at 1047.2/1048.5 cm^{-1} in 1,5-DMN, 1048.2/1048.4 cm^{-1} in 1,6-DMN, and 1047.6/1048.3 cm^{-1} in 2,6-DMN in calculation. A methyl C-H in-plane bending vibration of low intensity is seen in 1,6-DMN at 981.9 cm^{-1}. In 2,6-DMN the same band appears at 961.4 cm^{-1}. The methyl C-H in-plane bending vibration is not observed in 1,5-DMN. A weak band at 1062.6 cm^{-1} corresponding to the aromatic ring deformation mode is seen only in 1,5-DMN which match with the calculated band at 1069.7 cm^{-1}. The aromatic C-H in-plane bending as well as ring deformation occurs at a slightly higher frequency. For 1,5-DMN it is observed at 1217.3 cm^{-1}, for 1,6-DMN at 1217.5 cm^{-1} and for 2,6-DMN at 1216.4 cm^{-1}. The calculated positions are 1258.6, 1220.4, and 1267.7 cm^{-1}, respectively.
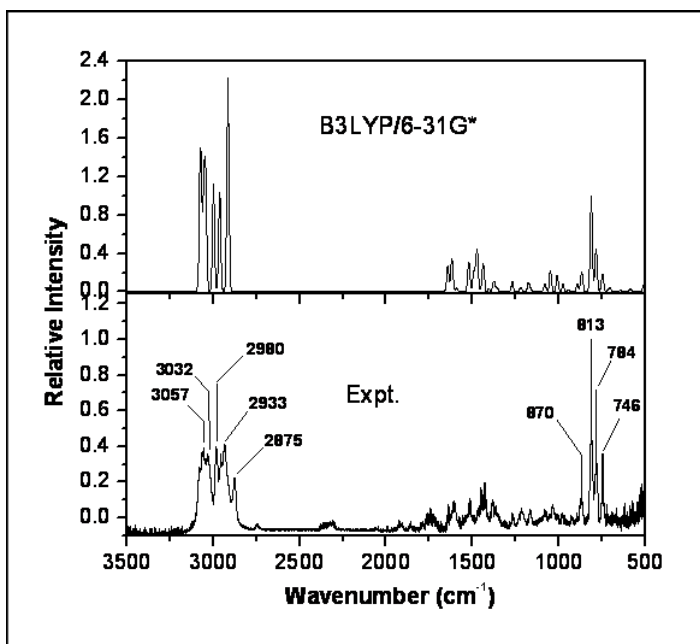
Figure 3.4. Comparison of experimental and calculated IR spectra of 1,6-DMN. In the calculated spectrum the FWHM is assumed to be 15 cm^{-1}. Prominent peaks are labeled in the observed spectrum. Weak bands such as Me(C-H)$_{asym.\ str.}$ at 2953.8 cm^{-1}, Aromatic C-H stretch at 3078.0 cm^{-1}, etc. are not labeled in the observed spectrum.

For the first and last compounds a band at 1264.0 cm^{-1} and a band at 1273.0 cm^{-1}, respectively, have been observed which do not correspond to any harmonic bands in the respective calculated spectrum. They have been tentatively assigned to either a combination or a difference band. For example, the 1264.0 cm^{-1} band in 1,5-DMN may be a difference band arising from the two strong fundamentals (2882.4 – 1606.1) cm^{-1} while the 1273.0 cm^{-1} band in 2,6-DMN may be a difference band from (2880.0 – 1612.9) cm^{-1}.
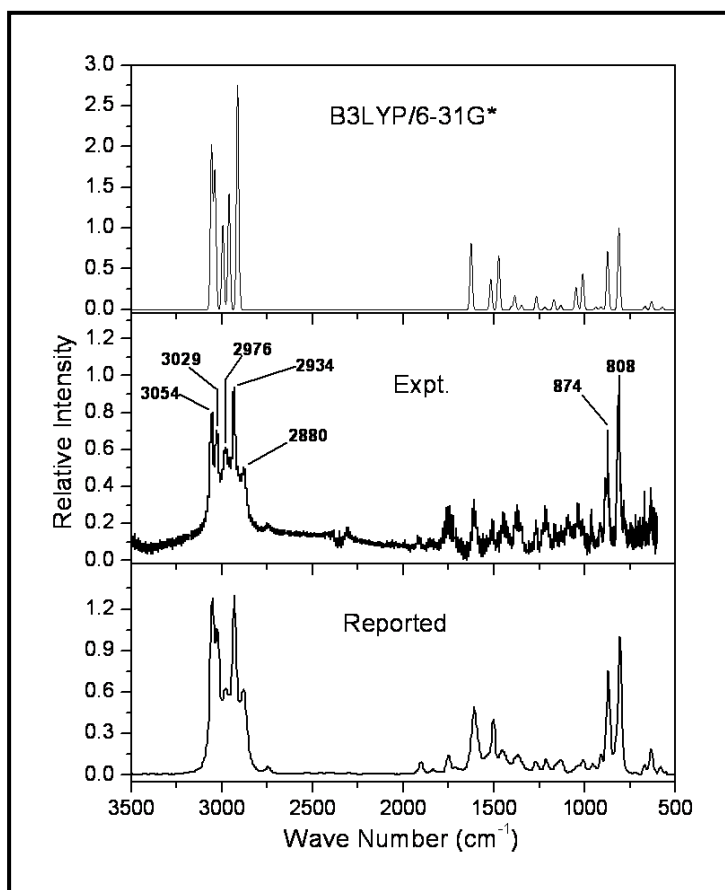
Figure 3.5. Comparison of experimental, theoretical and NIST reported[14] IR spectra of 2,6-DMN. In the calculated spectrum the FWHM is assumed to be 15 cm^{-1}. Prominent peaks are labeled in the observed spectrum. Very weak band such as Me(C-H)$_{asym.\ str.}$ at 2955.2 cm^{-1}, etc. are not labeled in the observed spectrum.

Another weak aromatic C-H in-plane bending occurs at 1413.9 cm^{-1} in 1, 5-DMN, 1426.5 cm^{-1} in 1,6-DMN, and 1365.0 cm^{-1} in 2,6-DMN which correspond to the calculated bands at 1416.2, 1437.9, and 1386.1 cm^{-1}, respectively. In addition, in 1,6-DMN and 2,6-DMN a low intensity band, respectively, at 1076.0 and 1093.1 cm^{-1} have been assigned to aromatic C-H in-plane bending vibration. The next identifiable band in the spectra occurs at 1448.9 cm^{-1} in 1,5-DMN, 1450.0 cm^{-1} in 1,6-DMN, and at 1450.1 cm^{-1} in 2,6-DMN. This band corresponds to the calculated bands in the respective compounds at 1474.0/1474.1, 1473.5/1474.1, and 1472.6/1472.7 cm^{-1} belonging to the methyl C-H out-of-plane twisting. The next set of weak bands appears at 1510.9 and 1606.1 cm^{-1} in 1,5-DMN; 1513.6, 1605.8, and 1638.6 cm^{-1} in 1,6-DMN; and at 1510.9 and 1612.9 cm^{-1} in 2,6-DMN. These bands have been identified as the aromatic C-C stretching vibrations from the calculations.

The next groups of 3 - 4 bands in the spectra of the DMNs do not correspond to any band positions in the calculated spectra and, thus, have been generally identified as combination or difference bands. In 1,5-DMN, the observed band at 1745.3 cm^{-1} matches with a difference band of (2956.9 - 1217.3) cm^{-1} consisting of two fundamentals and that at 1848.6 cm^{-1} is due to a combination of two bands (1062.6 + 807.5) cm^{-1}. Similarly, a combination band at 1922.2 cm^{-1} of fundamental frequencies (1062.6 + 872.2) cm^{-1} has been identified. The observed band at 2744.6 cm^{-1} in 1,5-DMN may be assigned as a difference band originating from the combination of fundamental frequencies (2931.8 – 1217.3 + 1034.7) cm^{-1}. The bands observed at 1741.0, 1858.9, 1922.4, and 2746.6 cm^{-1} in 1,6-DMN do not correspond to any calculated band. The band observed at 1741.0 cm^{-1} could be a difference band of two fundamental frequencies (2953.8 – 1217.5) cm^{-1} whereas the weak 1858.9 cm^{-1} band may originate from a coupled vibration of aromatic C-H in plane bending vibration at 1076.0 cm^{-1} and aromatic C-H

out-of-plane bending vibration at 812.8 cm^{-1}, while the band observed at 1922.4 cm^{-1} is a combination band of frequencies $(1076.0 + 870.2)$ cm^{-1}.

Table 3.3: Calculated and experimental infrared frequencies (in cm^{-1}) and intensities (in km mol^{-1}) for 1,5-DMN.

No	Theoretical		Experimental		NIST Data[b]		Mode of Vibrations
	Freq.[a]	Int. (Rel. Int.)	Freq.	Int. (Rel. Int.)	Freq.(Rel. Int.)[c]		
1	93.89	0.34 (0.005)					
2	162.66	0.00 (0.000)					
3	182.99	0.00 (0.000)					
4	190.28	2.27 (0.034)					
5	202.17	0.00 (0.000)					
6	253.25	0.44 (0.006)					
7	263.59	3.76 (0.056)					
8	323.01	0.00 (0.000)					
9	453.84	0.00 (0.000)					
10	455.30	0.00 (0.000)					
11	469.75	0.00 (0.000)					
12	479.88	1.23 (0.018)					
13	504.95	0.00 (0.000)					
14	521.55	5.30(0.079)					
15	567.17	0.89 (0.013)					
16	626.00	0.00 (0.000)					
17	628.42	0.00 (0.000)					
18	730.99	0.00 (0.000)					
19	777.75	2.48 (0.037)					
20	786.50	66.58 (1.000)	783.3	61.42(1.000)	781.9	(1.000)	$\alpha_{Ar(C-H)}$
21	802.06	0.00 (0.000)					
22	842.89	0.00 (0.000)					
23	869.65	1.39 (0.020)	807.5	5.89(0.096)			$\alpha_{Ar(C-H)}$
24	877.85	0.36 (0.005)					
25	889.48	0.00 (0.000)					
26	945.88	1.11 (0.016)	872.2	6.24(0.101)	873.9	(0.042)	$\alpha_{Ar(C-H)}$
27	947.32	0.00 (0.000)					
28	985.96	0.00 (0.000)					
29	1015.13	2.20(0.033)					
30	1047.22	0.00(0.000)					
31	1048.50	4.12(0.061)	1034.7	2.42(0.039)			$\beta_{Me(C-H)}$
32	1069.71	6.49(0.097)	1062.6	4.16(0.067)	1064.1	(0.075)	$\gamma_{Ar-ring}$
33	1100.39	0.00(0.000)					
34	1135.14	0.00(0.000)					
35	1174.00	1.19(0.017)					
36	1174.16	0.00(0.000)					
37	1218.38	2.76(0.041)					
38	1233.35	0.00(0.000)					
39	1258.63	2.43(0.036)	1217.3	2.08(0.033)			$\delta_{Ar(C-H)} + \gamma_{Ar-ring}$
			1264.0	1.73(0.028)			
40	1348.38	0.92(0.013)					

Table 3.3: (Continued) calculated and experimental infrared frequencies (cm⁻¹) and intensities in km mol⁻¹ for 1,5-DMN.

No	Theoretical		Experimental		NIST Data[b]		Mode of Vibrations
	Freq.[a]	Int. (Rel. Int.)	Freq.	Int. (Rel. Int.)	Freq.(Rel. Int.)[c]		
41	1362.95	0.00(0.000)					
42	1403.11	0.00(0.000)					
43	1404.75	0.48(0.007)					
44	1416.24	17.25(0.259)	1413.9	6.24(0.101)	1410.2	(0.173)	$\delta_{Ar(C-H)}$
45	1416.69	0.00(0.000)					
46	1472.51	0.00(0.000)					
47	1474.06	6.13(0.092)	1448.9	5.55(0.090)	1451.0	(0.068)	$\tau_{Me(C-H)}$
48	1474.19	6.60(0.099)					
49	1486.78	18.53 (0.278)					
50	1494.33	0.00(0.000)					
51	1524.04	8.57(0.128)	1510.9	3.12(0.050)	1510.7	(0.116)	$\nu_{Ar(C-C)}$
52	1598.43	0.00(0.000)					
53	1615.03	12.97(0.194)	1606.1	12.83(0.209)	1600.5	(0.146)	$\nu_{Ar(C-C)}$
54	1629.94	0.00(0.000)					
					1681.8	(0.040)	
			1745.3	6.59(0.107)	1774.1	(0.034)	
			1848.6	2.42(0.039)	1848.8	(0.044)	
			1922.2	2.77(0.045)	1920.0	(0.608)	
			2744.6	1.38(0.022)			
55	2913.59	58.53(0.879)					
56	2913.92	1.66(0.024)	2882.4	9.02(0.146)	2882.6	(0.043)	$\chi_{Me(C-H)\,Sym}$
57	2961.12	12.25(0.183)					
58	2961.25	29.00(0.435)	2931.8	6.59(0.107)	2938.6	(0.055)	$\chi_{Me(C-H)\,Asym}$
59	2995.98	18.16(0.272)					
60	2997.18	19.24(0.288)	2956.9	3.12(0.050)	2957.9	(0.012)	$\chi_{Me(C-H)\,Asym}$
61	3045.84	25.83(0.387)					
62	3046.36	0.00(0.000)	2979.4	11.10(0.180)	2977.2	(0.085)	$\Pi_{Ar(C-H)}$
63	3062.31	0.16(0.002)					
64	3062.45	49.13(0.737)	3043.2	15.26(0.248)	3041.3	(0.175)	$\Pi_{Ar(C-H)}$
65	3083.33	41.41(0.621)					
66	3083.79	0.03(0.000)	3081.0	10.06(0.163)	3079.9	(0.252)	$\Pi_{Ar(C-H)}$

[a]The B3LYP/6-31G* frequencies are scaled by 0.9588 for C-H stretching and 0.9733 for other modes.[13]

[b]adapted from Ref.[14]

[c]In case of the NIST reported spectra, only relative intensities are given in parentheses.

$\alpha_{Ar(C-H)}$= Aromatic C-H out-of-plane, $\beta_{Me(C-H)}$= Methyl C-H out-of-plane bending, $\gamma_{Ar-ring}$= Aromatic ring deformation, $\delta_{Ar(C-H)}$= Aromatic C-H in-plne bending, $\tau_{Me(C-H)}$= Methyl C-H out-

of-plane twist, $\nu_{Ar(C-C)}$= Aromatic (C-C) stretching, $\chi_{Me(C-H)Sym}$= Methyl C-H symmetric stretching, $\chi_{Me(C-H)Asym}$= Methyl C-H asymmetric stretching, $\Pi_{Ar(C-H)}$= Aromatic C-H stretching.

Table 3.4: Calculated and experimental infrared frequencies (in cm^{-1}) and intensities (in km mol^{-1}) for 1,6-DMN.

No	Theoretical		Experimental		Mode of Vibrations
	Freq.[a]	Int. (Rel.Int.)	Freq.	Int. (Rel.Int.)	
1	88.72	0.51(0.016)			
2	107.00	0.47(0.014)			
3	148.54	0.11(0.003)			
4	189.46	0.69(0.022)			
5	233.38	0.61(0.019)			
6	247.55	1.71(0.054)			
7	285.04	0.22(0.007)			
8	328.34	0.05(0.001)			
9	426.34	3.04(0.096)			
10	452.48	0.13(0.004)			
11	463.72	0.89(0.028)			
12	494.88	2.61(0.083)			
13	509.77	2.15(0.068)			
14	561.05	0.39(0.012)			
15	584.63	1.03(0.032)			
16	642.55	0.66(0.021)			
17	703.38	1.03(0.033)			
18	710.37	0.64(0.020)			
19	747.33	5.93(0.188)	746.2	10.02(0.352)	$\alpha_{Ar(C-H)}$
20	784.54	14.14(0.449)	784.1	13.49(0.474)	$\alpha_{Ar(C-H)}$
21	812.42	31.45(1.000)	812.8	28.42(1.000)	$\alpha_{Ar(C-H)}$
22	823.60	0.68(0.021)			
23	867.99	6.73(0.214)			
24	893.11	2.80(0.089)	870.2	8.99(0.316)	$\alpha_{Ar(C-H)}$
25	921.59	0.41(0.013)			
26	939.58	0.17(0.005)			
27	946.68	0.91(0.028)			
28	976.12	2.71(0.086)			
29	1009.17	5.66(0.179)	981.9	1.84(0.064)	$\sigma_{Me(C-H)}$
30	1048.29	5.39(0.171)			
31	1048.44	1.09(0.034)	1038.1	2.65(0.093)	$\beta_{Me(C-H)}$
32	1051.11	0.85(0.027)			
33	1080.50	2.64(0.084)	1076.0	2.45(0.086)	$\delta_{Ar(C-H)}$
34	1162.61	0.56(0.018)			
35	1167.46	1.00(0.032)			
36	1176.66	2.59(0.082)	1167.3	2.65(0.093)	$\delta_{Ar(C-H)}+ \gamma_{Ar-ring}$
37	1220.44	1.71(0.054)	1217.5	2.86(0.101)	$\delta_{Ar(C-H)}+ \gamma_{Ar-ring}$
38	1248.59	0.30(0.009)			
39	1268.85	3.18(0.101)	1269.7	2.86(0.101)	$\delta_{Ar(C-H)}+ \gamma_{Ar-ring}$
40	1357.95	1.45(0.046)			

Table 3.4: (Continued) calculated and experimental infrared frequencies (in cm^{-1}) and intensities (in km mol^{-1}) for 1,6-DMN.

No	Theoretical		Experimental		Mode of Vibrations
	Freq.[a]	Int. (Rel.Int.)	Freq.	Int. (Rel.Int.)	
41	1373.18	2.03(0.064)			
42	1378.15	2.14(0.068)			
43	1404.22	0.77(0.024)	1380.4	10.63(0.374)	$\sigma_{Me(C-H)}$
44	1405.16	0.47(0.015)			
45	1437.97	9.57(0.304)	1426.5	5.93(0.208)	$\delta_{Ar(C-H)}$
46	1467.29	2.90(0.092)			
47	1473.55	4.16(0.132)			
48	1474.13	7.79(0.247)	1450.0	3.68(0.129)	$\tau_{Me(C-H)}$
49	1485.63	4.28(0.136)			
50	1494.07	4.32(0.137)			
51	1520.97	9.85(0.313)	1513.6	7.56(0.266)	$\nu_{Ar(C-C)}$
52	1590.91	1.35(0.043)			
53	1618.56	11.07(0.352)	1605.8	5.72(0.201)	$\nu_{Ar(C-C)}$
54	1642.67	8.73(0.277)	1638.6	4.08(0.143)	$\nu_{Ar(C-C)}$
			1741.0	9.2(0.323)	
			1858.9	1.63(0.057)	
			1922.4	3.88(0.136)	
			2746.6	2.04(0.072)	
55	2913.63	35.41(1.126)			
56	2914.28	35.11(1.116)	2874.8	11.24(0.395)	$\chi_{Me(C-H) Sym}$
57	2960.69	9.81(0.312)			
58	2961.83	23.10(0.734)	2933.3	11.24(0.395)	$\chi_{Me(C-H) Asym}$
59	2997.16	16.61(0.528)			
60	2997.86	18.91(0.601)	2953.8	2.24(0.079)	$\chi_{Me(C-H) Asym}$
61	3040.66	16.86(0.536)	2980.5	11.45(0.402)	$\Pi_{Ar(C-H)}$
62	3044.43	14.64(0.465)			
63	3045.16	0.76(0.024)	3031.8	7.77(0.273)	$\Pi_{Ar(C-H)}$
64	3052.60	30.16(0.958)			
65	3070.49	37.47(1.191)	3056.8	4.49(0.158)	$\Pi_{Ar(C-H)}$
66	3077.56	15.71(0.499)	3078.0	3.68(0.129)	$\Pi_{Ar(C-H)}$

[a]*The B3LYP/6-31G* frequencies are scaled by 0.9588 for C-H stretching and 0.9733 for other modes.*[13]

$\alpha_{Ar(C-H)}$=Aromatic C-H out-of-plane bending, $\sigma_{Me(C-H)}$= Methyl C-H in-plane bending, $\beta_{Me(C-H)}$= Methyl C-H out-of-plane bending, $\gamma_{Ar-ring}$= Aromatic ring deformation, $\delta_{Ar(C-H)}$= Aromatic C-H in-plane bending, $\tau_{Me(C-H)}$= Methyl C-H out-of-plane twist, $\nu_{Ar(C-C)}$= Aromatic (C-C) stretching, $\chi_{Me(C-H)Sym}$= Methyl C-H symmetric stretching, $\chi_{Me(C-H)Asym}$= Methyl C-H asymmetric stretching, $\Pi_{Ar(C-H)}$= Aromatic C-H stretching.

Table 3.5: Calculated and experimental infrared frequencies (in cm^{-1}) and intensities (in km mol^{-1}) for 2,6-DMN.

No	Theoretical		Experimental		NIST Data[b]		Mode of Vibrations
	Freq.[a]	Int. (Rel. Int.)	Freq.	Int. (Rel. Int.)	Freq.(Rel. Int.)[c]		
1	76.86	1.16(0.037)					
2	87.45	0.00(0.000)					
3	95.69	0.04(0.001)					
4	180.07	0.39(0.012)					
5	201.25	0.00(0.000)					
6	215.90	0.88(0.028)					
7	313.50	0.00(0.000)					
8	333.87	2.91(0.093)					
9	395.74	0.00(0.000)					
10	402.16	0.00(0.000)					
11	429.88	2.31(0.074)					
12	482.68	5.94(0.189)					
13	521.53	0.00(0.000)					
14	525.00	0.00(0.000)					
15	574.59	1.21(0.038)					
16	632.80	3.40(0.108)					
17	668.29	1.35(0.043)					
18	747.20	0.00(0.000)					
19	757.53	0.00(0.000)					
20	789.89	0.00(0.000)					
21	811.61	31.33(1.000)	808.5	33.33(1.000)	807.3	(1.00)	$\alpha_{Ar(C-H)}$
22	820.21	0.00(0.000)					
23	874.72	22.41(0.715)	873.6	22.91(0.687)	870.7	(0.61)	$\alpha_{Ar(C-H)}$
24	884.62	0.00(0.000)					
25	911.05	0.98(0.031)					
26	940.49	0.94(0.030)	914.2	2.50(0.075)			$\alpha_{Ar(C-H)}$
27	941.29	0.00(0.000)					
28	957.44	0.00(0.000)					
29	1004.40	0.00(0.000)					
30	1012.35	13.82(0.441)	961.4	1.66(0.049)			$\sigma_{Me(C-H)}$
31	1047.62	8.56(0.273)	1037.9	8.33(0.249)			$\beta_{Me(C-H)}$
32	1048.39	0.01(0.000)					
33	1132.27	1.83(0.058)	1093.1	4.16(0.124)			$\delta_{Ar(C-H)}$
34	1151.69	0.00(0.000)					
35	1170.53	3.95(0.126)					
36	1179.34	0.00(0.000)					
37	1220.40	1.02(0.032)					
38	1258.61	0.00(0.000)					
39	1267.74	5.22(0.166)	1216.4	13.33(0.399)			$\delta_{Ar(C-H)}+ \gamma_{Ar-ring}$
			1273.0	5.00(0.150)			
40	1348.64	1.69(0.054)					
41	1383.14	0.00(0.000)					
42	1386.19	5.58(0.178)	1365.0	15.00(0.450)			$\delta_{Ar(C-H)}$
43	1405.15	1.38(0.044)					

Table 3.5: (Continued) calculated and experimental infrared frequencies (in cm^{-1}) and intensities (in km mol^{-1}) for 2,6-DMN.

No	Theoretical		Experimental		NIST Data[b]		Mode of Vibrations
	Freq.[a]	Int. (Rel. Int.)	Freq.	Int. (Rel. Int.)	Freq.(Rel. Int.)[c]		
44	1405.60	0.01(0.000)					
45	1412.03	0.00(0.000)					
46	1472.61	7.38(0.235)					
47	1472.76	3.47(0.110)	1450.1	7.50(0.225)	1449.9	(0.113)	$\tau_{Me(C-H)}$
48	1476.34	11.15(0.356)					
49	1485.87	0.00(0.000)					
50	1495.08	0.00(0.000)					
51	1518.62	11.66(0.372)	1510.9	5.83(0.175)	1504.7	(0.194)	$\nu_{Ar(C-C)}$
52	1582.20	0.00(0.000)					
53	1627.21	25.93(0.827)	1612.9	20.00(0.600)	1611.3	(0.714)	$\nu_{Ar(C-C)}$
54	1648.64	0.00(0.000)					
			1741.8	21.25(0.637)	1745.3	(0.125)	
			1908.1	1.66(0.049)	1906.0	(0.109)	
			2744.5	2.08(0.062)			
55	2913.68	81.85(2.612)					
56	2914.04	4.79(0.153)	2880.0	7.08(0.212)	2879.4	(0.312)	$\chi_{Me(C-H)\,Sym}$
57	2961.26	17.05(0.544)					
58	2961.40	27.68(0.883)	2933.9	18.33(0.549)	2931.2	(0.727)	$\chi_{Me(C-H)\,Asym}$
59	2995.19	16.32(0.521)					
60	2996.49	16.48(0.526)	2955.2	0.42(0.012)			$\chi_{Me(C-H)\,Asym}$
61	3037.89	21.39(0.682)	2976.5	6.25(0.187)	2978.8	(0.059)	$\Pi_{Ar(C-H)}$
62	3038.20	0.00(0.000)					
63	3040.93	33.06(1.055)	3028.9	8.75(0.262)	3027.8	(0.185)	$\Pi_{Ar(C-H)}$
64	3041.16	0.00(0.000)					
65	3058.03	62.53(1.996)	3054.5	15.83(0.474)	3053.7	(0.589)	$\Pi_{Ar(C-H)}$
66	3058.98	0.00(0.000)					

^{a}The B3LYP/6-31G* frequencies are scaled by 0.9588 for C-H stretching and 0.9733 for other modes.[13]

^{b}adapted from Ref.[14]

^{c} In case of the NIST reported spectrum, only relative intensities are given in parentheses. $\alpha_{Ar(C-H)}$= Aromatic C-H out-of-plane bending, $\sigma_{Me(C-H)}$= Methyl C-H In-plane bending, $\beta_{Me(C-H)}$= Methyl C-H out-of-plane bending, $\gamma_{Ar-ring}$= Aromatic ring deformation, $\delta_{Ar(C-H)}$= Aromatic C-H in-plane bending, $\tau_{Me(C-H)}$= Methyl C-H out-of-plane twist, $\nu_{Ar(C-C)}$= Aromatic (C-C) stretching, $\chi_{Me(C-H)\,Sym}$= Methyl C-H symmetric stretching, $\chi_{Me(C-H)\,Asym}$= Methyl C-H asymmetric stretching, $\Pi_{Ar(C-H)}$= Aromatic C-H stretching.

The observed band at 2746.6 cm^{-1} may be assigned to a difference band of fundamental frequencies (2933.3 − 1217.5 + 1038.1) cm^{-1}. In 2,6-DMN, the observed bands at 1741.8, 1908.1 and 2744.5 cm^{-1} do not match with any band in the calculated spectrum. The band at 1741.8 cm^{-1} is likely to be a difference band of the fundamental frequencies (2955.2 - 1216.4) cm^{-1}. In general, the difference and combination bands are less intense than the fundamental bands.[15] The band observed at 1908.1 cm^{-1} may be a combination band of frequencies (1093.1 + 808.5) cm^{-1}. There is a medium intensity band observed at 2744.5 cm^{-1} which is a difference band of three frequencies (2933.9 − 1216.4 + 1037.9) cm^{-1}.

The next sets of bands observed in the DMNs are at high frequencies (2870 − 3090 cm^{-1}), forms a broad envelope with several peaks and are of moderate intensities. The first three bands in this group are at 2882.4, 2931.8, and 2956.9 cm^{-1} in 1,5-DMN; 2874.8, 2933.3, and 2953.8 cm^{-1} in 1,6-DMN; and 2880.0, 2933.9, and 2955.2 cm^{-1} in 2,6-DMN; which from comparison with calculations have been identified as the methyl C-H symmetric and asymmetric stretching fundamentals. However, the calculated bands at these frequencies are doubly degenerate for each mode due to the presence of two methyl groups in the molecules. At our experimental resolution, these degeneracies cannot be lifted. The next 3 - 4 bands are also of moderate intensities and appear at 2979.4, 3043.2, and 3081.0 cm^{-1} in 1,5-DMN; 2980.5, 3031.8, 3056.8, and 3078.0 cm^{-1} in 1,6-DMN; and 2976.5, 3028.9, and 3054.5cm^{-1} in 2,6-DMN. These bands correspond to 3 pairs of doublets in calculation as shown in Tables 3.3 − 3.5 and are assigned to aromatic C-H stretching modes. In 1,6-DMN the last doublet appears as the doublet in the observed spectrum and is clearly resolved.

Error analysis has done by means of mean deviation as discussed in section 2.4.3. Table 3.6 lists the mean deviations between two types of scaled harmonic frequencies and observed

fundamentals for DMNs. From this table it is clear that (i) the extent of anharmonicity of aromatic and methyl C-H stretching modes is more compared to non C-H stretching modes and (ii) altogether, the deviation is more than 20 cm^{-1} irrespective of different types of vibrations of DMNs. It clearly indicates that the two scaling factors (one for the aromatic C-H stretches and another for all other modes) calculated by Bauschlicher et al.[13] for the non-substituted PAHs is less suitable for the scaling of the harmonic frequencies of substituted PAHs like methyl-PAHs at the B3LYP/6-31G* level of theory.

Table 3.6: Mean deviation, δ (in cm^{-1}) between scaled harmonic and experimental frequencies (in cm^{-1}) for different modes of vibration in DMNs.

Mode of vibration	1,5-DMN	1,6-DMN	2,6-DMN
Non C-H str	25.2	12.4	23.2
Aromatic and methyl C-H str	31.6	28.4	29.9

By comparing the DMN and MN spectra, it has been found that there is only one strong band in the reported spectrum of 1-MN due to the aromatic C-H stretching vibration above 3000.0 cm^{-1} while there are two or more moderate intensity bands in the observed spectrum of the DMNs in that region. In Table 3.7, I have listed four characteristic bands of the DMNs which may help in their identification in an unknown mixture. The aromatic C-H out-of-plane bending vibration is the strongest in intensity among all the bands in DMNs and is easy to identify around 800.0 cm^{-1}. The DMNs are distinguishable from the position of this band which appears with a clear separation in different DMNs. Methyl C-H symmetric and asymmetric stretching set of three bands is the next set of bands which are distinct in all the

DMNs. They appear clearly resolved at the high frequency end of the IR spectrum around 2900.0 cm^{-1} with moderate intensities and can be easily marked.

Table 3.7: Comparison of observed aromatic(C-H) out-of-plane bending and methyl C-H symmetric[a] and asymmetric stretching[b] vibrations in DMNs.

Mode of vibration	1,5-DMN		1,6-DMN		2,6-DMN	
Aromatic C-H out-of-plane	783.2	(1.000)	812.8	(1.000)	808.5	(1.000)
Methyl C-H stretching	2882.4[a]	(0.146)	2874.8[a]	(0.395)	2880.0[a]	(0.212)
	2931.8[b]	(0.107)	2933.3[b]	(0.395)	2933.9[b]	(0.549)
	2956.9[b]	(0.050)	2953.8[b]	(0.079)	2955.2[b]	(0.012)

The band positions are given in cm^{-1} and the relative intensities in parentheses.

3.4 Conclusion

In this chapter, I have reported the gas phase IR spectra of 1, 5-DMN, 1, 6-DMN, and 2, 6-DMN and assigned their vibrational modes using harmonic DFT calculation. In general experimental spectra are in good agreement with calculated spectra. However, deviations between calculated and observed frequencies are more than 20 cm^{-1} which is less reliable for the quantitative analysis of experimental spectra. From the experimentally observed spectra it is possible to distinguish the DMNs based on the intensity and position of the aromatic C-H out-of-plane bending and methyl C-H symmetric and asymmetric stretching vibrations which are well resolved in frequency among various DMNs. These spectra at 0.5 cm^{-1} resolution have many more features over the previously reported low resolution spectra of the DMNs. Further

studies with isotope substitution along with anharmonic analysis of the data are necessary to fully assign the vibrations of these differently substituted DMNs.

3.5 References

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Chapter-4

Infrared Spectra of Dimethylquinolines (DMQs) in the Gas Phase: Experiment and Theory

4.1 Introduction

Methylated quinolines belong to a class of polycyclic aromatic hydrocarbons (PAHs) present in ambient air, in lake and marine sediments, in coal-tar, and in coker gas oil.[1 - 4] Synthetic fuel contains methylated quinolines, including methyl quinolines (MQs) and dimethylquinolines (DMQs).[5] MQs and DMQs have been found in ground water adjacent to an underground coal gasification site and in low-Btu coal gasifier tar.[6 - 7] They have also been identified in petroleum and petroleum substitutes.[8 - 11] In section 1.1.2 of chapter 1, I have discussed that many of these compounds have been reported to be mutagenic, toxic, and carcinogenic, they also act as tumor initiating agent.[12 - 14]

A few experimental techniques have been employed for the identification and detection of PAHs including alkylquinolines in the gas phase (see section 1.2, chapter 1). The infrared spectra of MQs are available in the NIST - IR spectral library.[15] Ozel et al. have carried out DFT calculation for the assignment of the vibrational bands of MQs.[16] Infrared spectra of 2,8-DMQ and trimethylquinolines (TMQs) have been recorded in CS_2 solution.[17]

In this chapter, I present the IR absorption spectra of DMQs in the gas phase which were recorded at low pressures using a heated multi-pass long-path gas cell. I have carried out DFT calculations to calculate harmonic and anharmonic frequencies and their intensities. Then SQM force field vibrational analysis have done to get fitted frequencies closer to the experimental frequencies and potential energy distributions (PEDs) of normal modes in terms of nonredundant local coordinates using a modified version of the UMAT program in the QCPE package.

4.2 Experimental: Materials and Methods

4.2.1 Materials

DMQs used in this investigation were obtained commercially and used as received. They are 2,4-dimethylquinoline (98.0%, Chiron AS), 2,6-dimethylquinoline (98.0%, Aldrich Inc), 2,7-dimethyquinoline (99.0%, Aldrich Inc) and 2,8-dimethylquinoline (99.9%, Chiron AS). Some physical properties of the DMQs are listed in Table 4.1. Ultra high purity (99.999%) argon was used in these experiments as a carrier gas.

Table 4.1: Physical properties of DMQs

Name	State at 25 ^{o}C	m.p/b.p (in ^{o}C)	P(in mmHg)^a at 25 ^{o}C
2,4-DMQ	Liquid (98.0%)	b.p = 265	1.64×10^{-2}
2,6-DMQ	Solid-powder (98.0%)	m.p = 58	1.42×10^{-2}
2,7-DMQ	Solid -powder (99.0%)	m.p = 61	1.82×10^{-2}
2,8-DMQ	Liquid (99.9%)	b.p = 255	2.63×10^{-2}

^{a}Since experimental vapor pressures are not available, calculated values are given[18] in column 4.

4.2.2 Methods

Infrared spectra of polycyclic aromatic compound (PAHs) have been reported mostly in Ar/He matrix because of their low vapor pressures at room temperature. I have used a multi-pass long-path gas cell to record the gas phase IR spectra of DMQs. The details of the experimental set-up have been discussed in section 2.2.4.1 of chapter 2. The FT-IR spectrometer, Vertex-70 (Bruker Optic), equipped with the liquid N_2 cooled HgCdTe (LN - MCT) detector/KBr beam splitter was used in this study. The optical path-length of gas cell was fixed at 6 meter. Temperature of the cell and sample tube was maintained at 80 ^{o}C with

the help of a temperature controller fitted with a feedback heat sensor. The total pressure of argon gas in the cell containing DMQs was maintained at ~30 mmHg. The spectral band areas $\int \log(I_0/I) \, dv$ (in cm^{-1}) were calculated with the help of OPUS software provided by Bruker Optics.

The observed IR band intensities were calculated with the help of equation 2.15. Vapor pressure was calculated in similar fashion as was done for DMNs in chapter 3. The estimated vapor pressure found to be 1.47 $x10^{-5}$, 1.23 $x10^{-5}$, 2.01 x 10^{-5}, and 2.52 x 10^{-5} atm at 80 ^{o}C for 2,4-, 2,6-, 2,7-, and 2,8-DMQ, respectively. The detail of the intensity calculation was discussed in section 2.5 of chapter 2.

4.3 Theoretical calculation

4.3.1 Harmonic and anharmonic calculation

DFT calculations were carried out to determine the harmonic and anharmonic frequencies of the vibrational modes and their intensities for the DMQs. The geometry optimization was carried out with standard polarization basis set 6-31G* at the B3LYP (Becke 1993; Lee, Yang, & Parr 1988) level of theory using Gaussian 03 codes[19] in an IBM Cluster P720 (IBL-64) computers. The frequencies and intensities were determined at the fully optimized C_s geometry of the DMQs (see Figure 4.1).

4.3.2 Force field calculation

In section 2.4.2 of chapter 2, I have discussed that SQM vibrational analysis is the alternative way to resolve the discrepancy between observed fundamentals and calculated harmonic frequencies by means of some scaling procedure. Therefore, I have carried out SQM

force field calculation which was described in section 2.4.2 of chapter 2. Cartesian Force constants matrix obtained from DFT calculations were transformed to the nonredundant local coordinate matrix of the DMQs using modified version of UMAT program in the QCPE package.[20] All the 63 nonredundant internal coordinates of the DMQs are shown in Table 4.2. The symbolic force constant matrix, unscaled and scaled force constants in term of nonredundant local coordinates can be found in supporting information of Ref.[21] For completeness, the same has been shown for one representative molecule 2,4-DMQ in the Appendix at the end of the thesis.

An error analysis have been done in terms of mean deviation, δ (in cm^{-1}), between the observed and calculated (harmonic, anharmonic and fitted) frequencies using equation 2.13. The mean deviations between the calculated (harmonic, anharmonic and force field fitted) and observed frequencies for three different types of vibrations in DMQs are listed in Table 4.3. From this table it is clear that the aromatic and methyl C-H stretching frequencies deviate more than non-C-H stretching vibrations vis-a-vis the calculated harmonic and anharmonic frequencies. It also indicates that the extent of anharmonicity is not the same for the different modes of vibrations. Overall, the force field fitted frequencies are closest to the observed frequencies. This gives us more confidence in unambiguous and correct assignments of the observed bands although for non C-H vibrations, the differences between the calculated anharmonic frequencies and observed frequencies are less significant.

Figure 4.1. Optimized B3LYP/6-31G* structure and internal coordinates of (a) 2,4-DMQ, (b) 2,6-DMQ, (c) 2,7-DMQ, and (d) 2,8-DMQ.

(a) 2,4-DMQ

(b) 2,6-DMQ
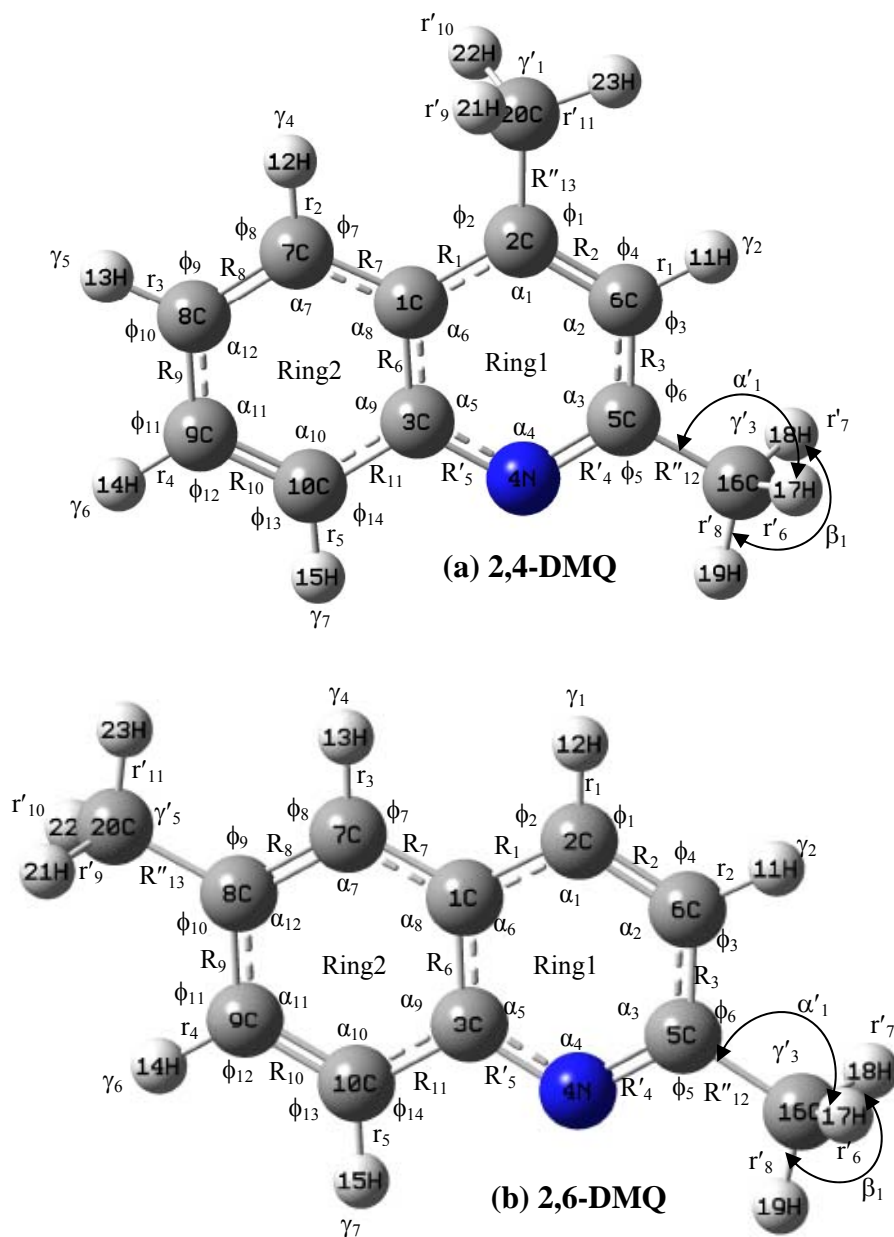
Figure 4.1. (Continued)

(c) 2,7-DMQ

(d) 2,8-DMQ
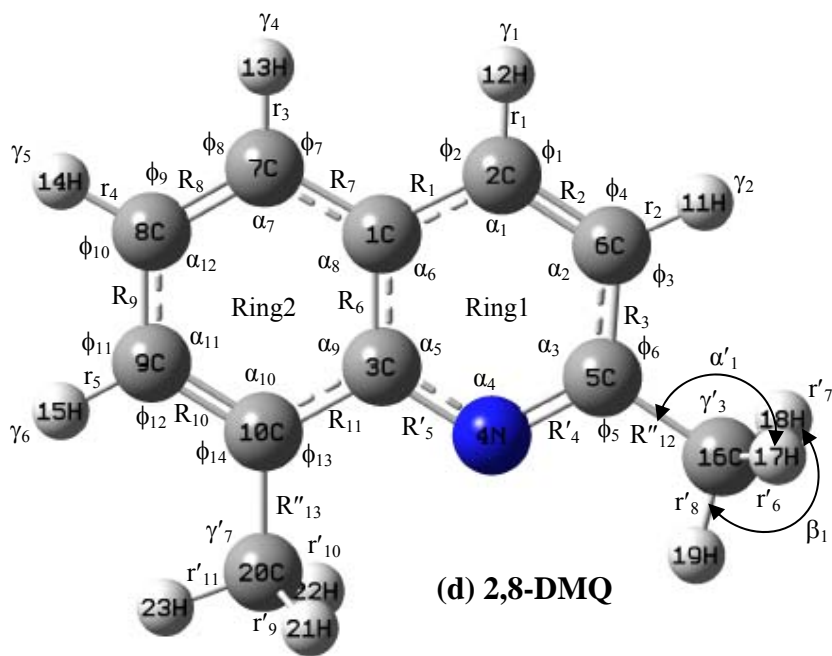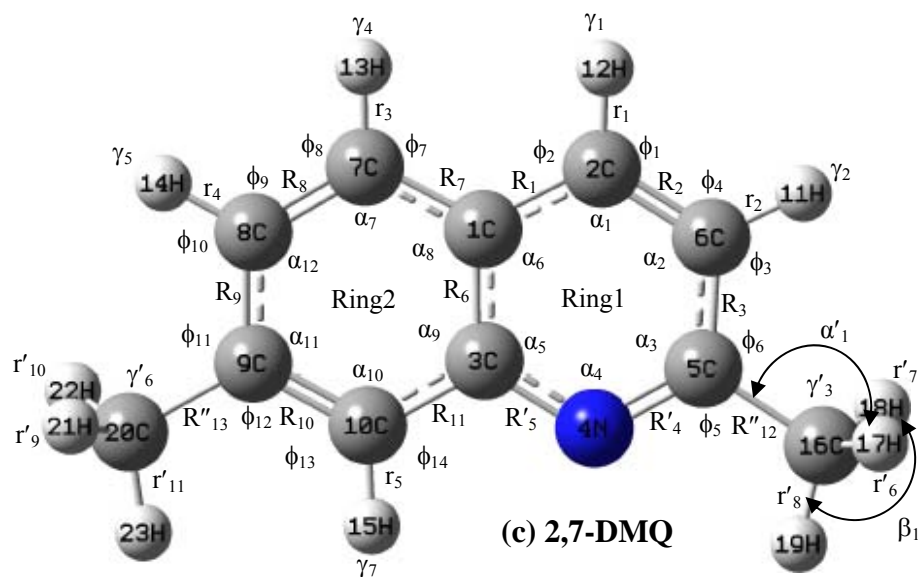
Twist coordinates, τ's numbering are the same as defined for R (the C-C bond coordinates). $\alpha_1{'}$ is one of the C-C-H angle coordinate of the CH$_3$ groups. The other C-C-H angle coordinates, $\alpha_2{'}$, $\alpha_3{'}$, etc. are defined similarly. β_1 is one of the H-C-H angle coordinate of CH$_3$ groups. The other H-C-H angle coordinates, β_2, β_3, etc. are defined similarly.

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Table 4.2: Nonredundant local coordinates of the DMQs studied in this thesis.

Compound	Nonredundant local coordinates
2,4-DMQ **See Fig 4.1 (a) for the internal-coordinates**	$S_{1\text{-}3,\,6\text{ -}11} = R$ (Ar, C-C stretch) (R_i) ; $S_{4,5} = R($Ar, C-N stretch$)$ (R'_i) $S_{12,\,14} = R($Ar-CH$_3$, C-C stretch$)$ (R''_i) $S_{13,\,15\text{ -}18} = r($Ar, C-H stretch$)$ (r_i) ; $S_{19\text{ -}24} = r($CH3, C-H stretch$)$ (r'_i) $S_{25,\,27} = (\phi_1\text{-}\phi_2)$; $(\phi_5\text{-}\phi_6)$ (C-CH$_3$ def.)(β'_i) $S_{26,\,28\text{-}31} = (\phi_3\text{-}\phi_4)$; $(\phi_7\text{-}\phi_8)\ldots$ (Ar, C-H def.)(β_i) $S_{32,\,35} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)(δ_1, δ_4) $S_{33,\,36} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)(δ_2, δ_5) $S_{34,\,37} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$ (ring def.)(δ_3, δ_6) $S_{38,\,43} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{39,\,44} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{40,\,45} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{41,\,46} = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) $\rho($CH$_3)$ $S_{42,\,47} = 2^{-1/2} (\beta_2 - \beta_3)$ (CH$_3$ rock) $\rho($CH$_3)$ $S_{48,\,50} = \gamma$ (Ar-CH$_3$, C-C wag) γ_i $S_{49,\,51\text{-}54} = \gamma$ (Ar, C-H wag) γ'_i $S_{55,\,58} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4) $S_{56,\,59} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion)(τ_2, τ_5) $S_{57,\,60} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion)(τ_3, τ_6) $S_{61} = 2^{-1/2}(\tau_{2\text{-}1\text{-}3\text{-}10} - \tau_{7\text{-}1\text{-}3\text{-}4})$ (τ_{ring}) $S_{62,\,63} = \tau_{5\text{-}16}$; $\tau_{2\text{-}20}$ (C-CH$_3$ twist) (τ''_i)
2,6-DMQ **See Fig 4.1 (b) for the internal-coordinates**	$S_{1\text{-}3,\,6\text{-}11} = R($Ar, C-C stretch$)$ (R_i) ; $S_{4,5} = R($Ar, C-N stretch$)$ (R'_i) $S_{14,\,16} = R($Ar-CH$_3$, C-C stretch$)$ (R''_i) $S_{12,\,13,15,17,\,18} = r($Ar, C-H stretch$)$ (r_i) ; $S_{19\text{ -}24} = r($CH$_3$, C-H stretch$)$ (r'_i) $S_{25,26,28,30,\,31} = (\phi_1\text{-}\phi_2)\ldots$; $(\phi_7\text{-}\phi_8)$; $(\phi_{11}\text{-}\phi_{12})\ldots$ (C-H def.)(β_i) $S_{27,29} = (\phi_5\text{-}\phi_6)$; $(\phi_9\text{-}\phi_{10})$ (C-CH$_3$ def.)(β'_i) $S_{32,\,35} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)(δ_1, δ_4) $S_{33,\,36} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)(δ_2, δ_5) $S_{34,\,37} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$ (ring def.)(δ_3, δ_6) $S_{38,\,43} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{39,\,44} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{40,\,45} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{41,\,46} = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) $\rho($CH$_3)$ $S_{42,\,47} = 2^{-1/2} (\beta_2 - \beta_3)$ (CH$_3$ rock) $\rho($CH$_3)$ $S_{48,49,51,53,\,54} = \gamma$ (Ar, C-H wag) γ_i $S_{50,\,52} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i $S_{55,\,58} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4) $S_{56,\,59} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion)(τ_2, τ_5) $S_{57,\,60} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion)(τ_3, τ_6) $S_{61} = 2^{-1/2}(\tau_{2\text{-}1\text{-}3\text{-}10} - \tau_{7\text{-}1\text{-}3\text{-}4})$ (τ_{ring}) $S_{62,\,63} = \tau_{5\text{-}16}$; $\tau_{8\text{-}20}$ (C-CH$_3$ twist) (τ''_i)

Table 4.2: (Continued) nonredundant local coordinates of the DMQs studied in this thesis.

Compound	Nonredundant local coordinates
2,7-DMQ **See Fig 4.1 (c)** **for the internal-** **coordinates**	$S_{1-3, 6-11} = R$ (Ar, C-C stretch) (R_i) ; $S_{4,5} = R$(Ar, C-N stretch) (R'_i) $S_{14, 17} = R$ (Ar-CH$_3$, C-C stretch) (R''_i) $S_{12, 13, 15, 16, 18} = r$ (Ar, C-H stretch) (r_i); $S_{19-24} = r$ (CH$_3$, C-H stretch) (r'_i) $S_{25, 26, 28, 29, 31} = (\phi_1-\phi_2)\ldots; (\phi_7-\phi_8)\ldots.. (\phi_{13}-\phi_{14})$ (C-H def.)(β_i) $S_{27, 30} = (\phi_5-\phi_6); (\phi_{11}-\phi_{12})$ (C-CH$_3$ def.)(β'_i) $S_{32, 35} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)(δ_1, δ_4) $S_{33, 36} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)(δ_2, δ_5) $S_{34, 37} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$ (ring def.)(δ_3, δ_6) $S_{38, 43} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{39, 44} = 6^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{40, 45} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{41, 46} = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{42, 47} = 2^{-1/2} (\beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{48, 49, 51, 52, 54} = \gamma$ (Ar, C-H wag) γ_i $S_{50, 53} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i $S_{55, 58} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4) $S_{56, 59} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion)(τ_2, τ_5) $S_{57, 60} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion)(τ_3, τ_6) $S_{61} = 2^{-1/2}(\tau_{2-1-3-10} - \tau_{7-1-3-4})$ (τ_{ring}) $S_{62, 63} = \tau_{5-16}; \tau_{9-20}$ (C-CH$_3$ twist) (τ''_i)
2,8-DMQ **See Fig 4.1 (d)** **for the internal-** **coordinates**	$S_{1-3, 6-11} = R$(Ar, C-C stretch) (R_i) ; $S_{4, 5} = R$(Ar, C-N stretch) (R'_i) $S_{14, 18} = R$(Ar-CH$_3$, C-C stretch) (R''_i) $S_{12, 13, 15-17} = r$(Ar, C-H stretch) (r_i) ; $S_{19-24} = r$(CH$_3$, C-H stretch) (r'_i) $S_{25, 26, 28-30} = (\phi_1-\phi_2)\ldots; (\phi_7-\phi_8)\ldots$ (C-H def.)(β_i) $S_{27, 31} = (\phi_5-\phi_6); (\phi_{13}-\phi_{14})$ (C-CH$_3$ def.)(β'_i) $S_{32, 35} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)(δ_1, δ_4) $S_{33, 36} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)(δ_2, δ_5) $S_{34, 37} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$ (ring def.)(δ_3, δ_6) $S_{38, 43} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{39, 44} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{40, 45} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{41, 46} = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{42, 47} = 2^{-1/2} (\beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{48, 49, 51-53} = \gamma$ (Ar, C-H wag) γ_i $S_{50, 54} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i $S_{55, 58} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4) $S_{56, 59} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion)(τ_2, τ_5) $S_{57, 60} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion)(τ_3, τ_6) $S_{61} = 2^{-1/2}(\tau_{2-1-3-10} - \tau_{7-1-3-4})$ (τ_{ring}) $S_{62, 63} = \tau_{5-16}; \tau_{10-20}$ (C-CH$_3$ twist) (τ''_i)

Table 4.3: Mean deviation, δ (in cm⁻¹) between the calculated (harmonic, anharmonic and force field fitted) and observed frequencies for different modes of vibration in the DMQs.

δ/Mode of vibration	Harmonic				Anharmonic				Force Field Fitted			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
Aromatic C-H str	166.9	139.4	165.6	167.9	26.2	7.6	40.8	25.4	0.16	0.15	0.36	0.36
Methyl C-H str	176.9	176.2	176.6	186.8	41.1	49.1	48.7	57.4	3.1	1.7	2.5	8.3
Non-C-H str	31.7	31.0	32.6	31.1	14.6	12.9	11.1	9.8	1.7	1.8	2.6	1.5

(a), (b), (c), and (d) represents the 2,4-, 2,6-, 2,7-, and 2,8-DMQ, respectivel.

4.4 Results and discussion

The gas phase IR spectra of the DMQs are shown in Figure 4.2. The experimental and theoretical infrared frequencies, intensities and potential energy distributions (PEDs) of vibrational modes of the DMQs are listed in Tables 4.4 – 4.7. Observed non-fundamental and corresponding calculated non-fundamental anharmonic bands are listed in Table 4.8. To compare the experimental and calculated spectra, we have displayed spectra of all the four DMQs separately in Figure 4.3. For the calculated spectra, force field fitted frequencies were used and FWHM of each band was assumed to be 15 cm⁻¹ (see section 2.5 in chapter 2). Each DMQ molecules has 23 atoms; and thus 63 normal modes which belong to the irreducible representation 41A′ + 22A″ under the C_s point group. The observed spectra have been divided in three distinct regions: (A) aromatic and methyl C-H stretching region, (B) non C-H stretching region including aromatic C-C/C-N, aromatic-methyl C-C stretch, C-H in-plane and

out-of-plane, methyl C-H symmetric and asymmetric deformations, etc. and (C) non-fundamental vibration region: combination and overtone bands. Initially, fundamental bands are tentatively assigned using calculated anharmonic frequencies. The assignment is then confirmed by fitted frequencies obtained by scaled force field calculations since some of the observed frequencies, particularly aromatic and methyl C-H stretching frequencies differ by as much as 50 cm^{-1} from the calculated anharmonic frequencies. The fitting by the force field method is extremely good and RMS errors (in cm^{-1}) with 100 iterations remain within a few wavenumbers, 3 cm^{-1}. Details of the assignment have been discussed in the subsequent sections.
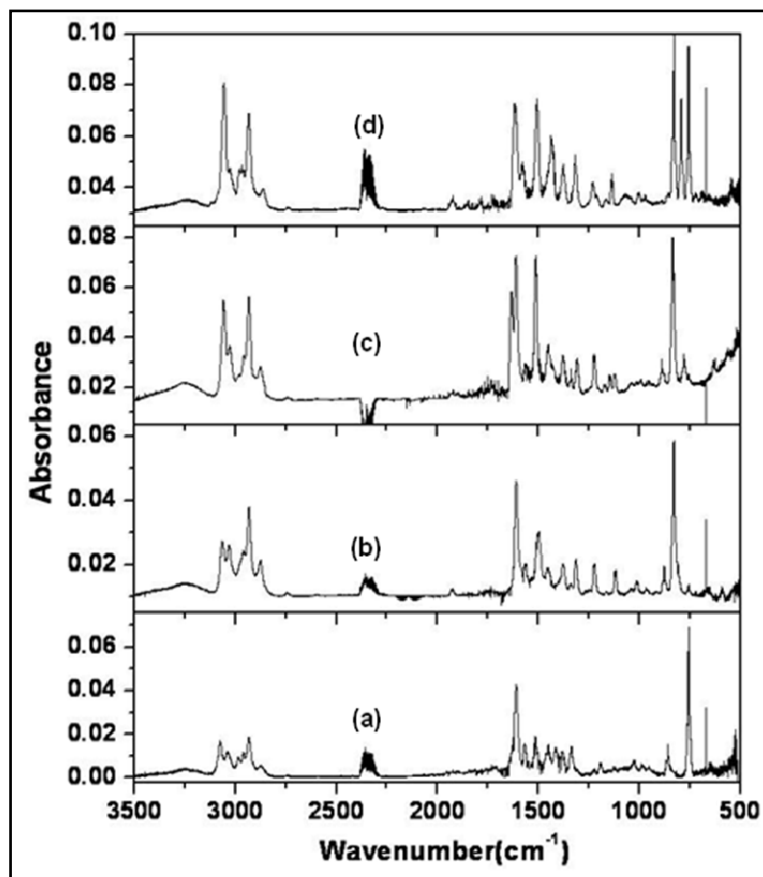
Figure 4.2. Experimental gas phase IR absorption spectra of (a) 2,4-DMQ, (b) 2,6-DMQ, (c) 2,7-DMQ, and (d) 2,8-DMQ at 0.5 cm^{-1} resolution.

4.4.1 C-H stretching Vibrations:

The aromatic C-H stretching region in the experimental spectra is always more complex than that predicted by DFT due to the occurrence of Fermi resonances and the presence overtone and combination modes.[22] However, we could assign the bands observed in this region with the help of PEDs. Groups of two to three bands in the spectral range of (2980 – 3070) cm^{-1} are assigned to aromatic C-H stretching vibrations. Bands observed at 3075.8, 3039.2, and 2984.9 cm^{-1} in 2,4-DMQ; 3066.1 and 3032.9 cm^{-1} in 2,6-DMQ; 3059.3, 3028.2, and 2987.7 cm^{-1} in 2,7-DMQ and 3056.8, 3027.3, and 2978.9 cm^{-1} in 2,8-DMQ correspond to the calculated anharmonic fundamental bands at 3079.4, 3052.2, and 3046.9 cm^{-1} in 2,4-DMQ; 3057.3 and 3026.4 cm^{-1} in 2,6-DMQ; 3064.1, 3053.5, and 3020.0 cm^{-1} in 2,7-DMQ; 3069.3, 3049.4, and 3020.6 cm^{-1} in 2,8-DMQ, respectively. On the other hand, their respective fitted frequencies are 3076.3, 3039.2, and 2984.9 cm^{-1} in 2,4-DMQ; 3066.0 and 3032.7 cm^{-1} in 2,6-DMQ; 3059.3, 3028.2, and 2988.8 cm^{-1} in 2,7-DMQ; 3056.8, 3027.3, and 2980.0 cm^{-1} in 2,8-DMQ. The force field fitted frequencies match very well with the observed bands which add evidence to our assignment.

The next three bands observed in the spectral range of 2860 – 2970 cm^{-1} are assigned to antisymmetric and symmetric C-H stretching vibrations of methyl groups. The interpretation of the methyl C-H stretching regions of the vibrational spectra of methylated compounds is normally hindered by a Fermi resonance which occurs between the methyl C-H symmetric stretch and an overtone involving two quanta of a methyl deformation mode.[23] For large aromatic hydrocarbons such as the DMQs, it is difficult to ascertain the presence or absence of such resonances in the methyl C-H stretching region, however, the closeness of our fitted frequencies to the observed ones provides the basis of our assignment. Bands observed at

2961.0 and 2933.5 cm^{-1} in 2,4-DMQ; 2959.9 and 2933.3 cm^{-1} in 2,6-DMQ; 2958.6 and 2934.4 cm^{-1} in 2,7-DMQ; 2966.3 and 2934.7 cm^{-1} in 2,8-DMQ are assigned to asymmetric stretching vibrations of the methyl C-H by comparing with the force field fitted frequencies at 2959.7 and 2930.4 cm^{-1} in 2,4-DMQ; 2959.3 and 2931.9 cm^{-1} in 2,6-DMQ; 2957.7 and 2932.6 cm^{-1} in 2,7-DMQ; 2963.5 and 2925.5 cm^{-1} in 2,8-DMQ, respectively. Their corresponding anharmonic frequencies at 3007.3 and 2955.8 cm^{-1} in 2,4-DMQ; 3013.1 and 2944.0 cm^{-1} in 2,6-DMQ; 3007.2 and 2945.1 cm^{-1} in 2,7-DMQ; 3007.3 and 2958.1 cm^{-1} in 2,8-DMQ which deviate by ~ 30 cm^{-1}. The symmetric methyl C-H stretching band of moderate intensity appears at 2873.8 cm^{-1} in 2,4-DMQ, 2876.0 cm^{-1} in 2,6-DMQ, 2875.8 cm^{-1} in 2,7-DMQ, and 2863.1 cm^{-1} in 2,8-DMQ. This band can be correlated with the calculated anharmonic frequencies at 2928.5 cm^{-1} in 2,4-DMQ, 2959.6 cm^{-1} in 2,6-DMQ, 2962.8 cm^{-1} in 2,7-DMQ, and 2971.4 cm^{-1} in 2,8-DMQ, respectively. DFT calculated asymmetric and symmetric anharmonic frequencies are generally overestimated, whereas the force field fitted frequencies are quite close to the observed frequencies as seen from Tables 4.4 – 4.7. It is also found that the absolute intensities of the C-H stretching bands do not match well with the calculated band intensities perhaps partially due to the occurrence of Fermi resonances in the region.

4.4.2 Non C-H stretching Vibrations:

Except aromatic C-H out-of-plane bending vibrations, most of the non C-H stretching vibrations belong to the irreducible representation, A′. A highly intense band observed at 1609.7 cm^{-1} in 2,4-DMQ, at 1610.3 cm^{-1} in 2,6-DMQ, at 1612.5 cm^{-1} in 2,7-DMQ and at 1615.1 cm^{-1} in 2,8-DMQ is assigned to the aromatic C-C stretching vibration.

Table 4.4: Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMQ$.

Sym	B3LYP/6-31G^*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
1	3218.3	14.954	3079.4	3075.8	16.327	3076.3	r_2 (48) + r_5 (47)
2	3210.0	27.665	3072.2	(3075.0)		3074.5	r_2 (50) + r_5 (47)
3	3197.5	14.608	3052.2	3039.2	8.577	3039.2	r_4 (92)
4	3185.1	1.440	3046.9	2984.9	3.009	2984.9	r_3 (96)
5	3180.9	19.449	3041.6	(2984.0)		2984.0	r_1 (98)
6	3157.6	8.121	3007.3	2961.0	2.106	2959.7	r'_7 (77)+ r'_6 (23)
7	3131.4	16.314	2985.1	(2960.0)		2958.8	r'_9 (80)+ r'_8 (18)
8	3044.8	17.224	2928.5	2873.8	5.643	2878.8	r'_8 (81)+ r'_9 (18)
9	3044.1	25.493	2942.6	(2873.0)		2877.2	r'_6 (77)+ r'_7 (23)
10	1672.5	4.589	1633.2	(1627.0)		1626.2	R_8 (26)+ R_{10} (18)+ R_{11} (11)
11	1661.7	76.208	1619.5	1609.7	73.664	1610.9	R_2 (36)
12	1617.6	23.918	1577.2	1566.9	14.371	1568.2	R'_4 (23)+ R_9 (13)+ R_{10} (13)
13	1561.7	19.393	1525.8	1512.8	18.510	1513.0	R_9 (17)
14	1529.7	10.823	1472.0	(1488.0)		1489.1	$\delta_s CH_3(2)$ (67)
15	1514.7	9.856	1498.1	(1474.0)		1470.2	$\delta_s CH_3(1)$ (16)+ $\delta_s CH_3(2)$ (14) + β_4 (10)
16	1499.6	3.227	1464.6	(1449.0)		1450.8	$\delta_s CH_3(1)$ (58)
17	1457.7	20.604	1423.8	1413.8	11.136	1412.6	β_2 (18)
18	1440.1	0.491	1433.7	(1401.0)		1401.1	$\rho CH_3(1)$ (86)
19	1431.2	5.113	1422.1	1380.1	8.201	1381.3	δ_5 (63)+ R''_{12} (17)
20	1411.0	2.956	1375.5	(1373.0)		1371.4	R_6 (30)+ R'_5 (14)
21	1386.6	3.509	1358.5	(1349.0)		1347.5	R'_4 (12)+ R_{10} (12)+ R_2 (10)
22	1370.0	16.948	1341.7	1336.9	12.415	1332.1	R_3 (18)+ R'_5 (12)
23	1300.0	0.247	1279.6	(1265.0)		1263.3	β_6 (17)+ β_2 (15)+ R_{11} (13) β_5 (11)
24	1268.5	1.101	1246.6	1223.3	2.106	1226.6	R_7 (23)+ R'_5 (15)+ R_1 (13) + r'_{11} (12)
25	1223.6	6.944	1202.0	1192.9	4.966	1192.1	r'_{11} (34)+ R''_{12} (14)
26	1192.8	0.750	1177.9	(1160.0)		1161.0	β'_3 (39)+ β_2 (16)+ R_8 (11
27	1157.6	1.904	1142.4	1121.2	2.332	1122.9	β_4 (30)+ β_5 (22)+ R_{10} (12)
28	1093.0	0.707	1078.3	(1063.0)		1063.2	δ_2 (16)+ R''_{13} (14) + $\delta_a CH_3(2)$ (14)+ R_{11} (12)
29	1053.6	4.610	1035.0	(1025.0)		1025.6	R_9 (38)+ R_{10} (12)
30	1042.4	2.048	1028.2	1024.0	3.837	1021.0	$\delta_a CH_3(1)$ (24)+ $\delta_a CH_3(2)$ (14) + R_9 (12)
31	1003.3	6.645	989.2	982.5	2.558	980.4	δ_2 (21)+ $\delta_a CH_3(2)$ (17) + R''_{13} (16)+ R''_{12} (11)
32	977.3	1.703	966.0	951.2	1.655	953.2	R_3 (29)+ β_6 (18)+ δ_1 (10)
33	877.3	4.283	863.9	(853.0)		855.3	δ_2 (33)
34	758.3	2.064	750.0	(738.0)		737.4	R_1 (15)+ R_7 (15)+ δ_1 (12) + δ_3 (11)+ R_6 (11)+ β_6 (11)
35	657.9	4.115	650.4	645.8	3.837	645.3	δ_3 (44)+ β_6 (12)
36	546.9	1.913	540.5	531.0	1.882	531.2	β_7 (27)+ δ_4 (16)+ R''_{13} (11) + δ_1 (10)

Table 4.4:(Continued) Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMQ$.

Sym	B3LYP/6-31G^*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
37	533.0	1.397	529.4	(518.0)		518.7	δ_3 (25)+ δ_4 (19)
38	501.6	2.765	500.9	(488.0)		487.9	δ_1 (24)+ r'_{10} (21)+ β'_1 (20)
39	452.7	2.050	449.6	(440.7)		439.8	β_7 (30)+ δ_1 (29)
							+ δ_4 (13)
40	280.6	0.932	285.1	(273.0)		273.1	r'_{10} (43)+ β'_1 (37)
41	266.9	1.142	267.2	(259.0)		259.0	β'_1 (30)+ δ_4 (25)+ r'_{10} (15)
A''							
42	3097.2	15.845	2955.8	2933.5	15.500	2930.4	r'_6 (100)
43	3094.4	18.237	2947.2	(2933.0)		2928.9	r'_8 (100)
44	1513.7	3.042	1508.6	(1473.3)		1472.6	$\delta_s CH_3(1)$ (92)
45	1512.2	10.639	1504.7	1450.7	11.813	1450.3	$\delta_s CH_3(2)$ (92)
46	1076.8	1.079	1053.0	(1048.0)		1052.3	δ_6 (55) + $\delta_a CH_3(1)$ (19)
47	1069.0	3.989	1049.2	(1040.0)		1044.1	$\rho CH_3(1)$ (48)+ $\delta_a CH_3(2)$ (17)
							+ $\rho CH_3(2)$ (10)
48	996.2	0.136	982.2	(969.0)		968.6	γ_5 (35)+ γ_4 (24)+ γ'_3 (15)
							+ τ_2 (12)
49	961.4	1.579	953.1	(950.0)		949.2	γ_2 (34)+ γ'_3 (30)+ γ_5 (25)
50	895.2	2.926	877.2	(871.0)		872.0	$\rho CH_3(2)$ (23)+ γ_2 (22)+
							γ_4 (15)+ γ'_3 (10)
51	882.7	8.855	866.7	857.1	9.932	856.4	$\rho CH_3(2)$ (59)
52	799.9	0.986	791.3	(778.0)		780.6	τ_2 (38)+ γ_6 (35)
53	778.8	47.456	766.0	755.7	63.256	756.2	γ'_3 (29)+ γ_4 (23)+ γ_2 (22)
							+ γ_5 (12)
54	664.9	0.130	656.4	(647.0)		645.2	τ_2 (33)+ γ_6 (25)+ γ'_1 (18)
55	573.3	0.124	568.1	(558.0)		556.4	$\rho CH_3(2)$ (26)+ τ_1 (17)
							+ τ_5 (17)+ γ_7 (11)
56	533.5	0.100	526.3	(519.0)		519.7	τ_4 (21)+ γ'_1 (14) + τ_2 (13)
							+ γ_6 (11)
57	434.7	2.376	429.5	(427.0)		427.2	τ_3 (32)+ τ_4 (25)
							+ $\rho CH_3(2)$ (13)
58	309.9	0.848	304.6	(301.0)		300.7	τ_4 (42)+ γ'_1 (11)
59	206.6	0.493	207.8	(201.0)		200.9	τ_1 (39)+ τ_{ring} (19)
							+ $\rho CH_3(2)$ (12)
60	163.0	0.070	186.5	(158.0)		158.0	τ_{ring} (67)+ τ_1 (14)
61	153.9	2.721	153.6	(149.0)		149.0	τ_5 (29)+ $\rho CH_3(2)$ (19)
							+ τ_3 (17)
62	114.3	0.191	103.9	(111.0)		111.1	γ_7 (49) + τ_4 (15) + τ_3 (11)
63	81.0	0.624	49.8	(78.0)		78.0	τ_6 (72)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $2,4-DMQ$ and do not have any other significance. RMS error is 1.9720 for the fitting of experimental frequencies.

Table 4.5: Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol)at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,6-DMQ$.

Sym	B3LYP/6-31G^*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
1	3215.0	9.908	3073.9	(3066.0)		3066.3	r_2 (46) + r_5 (46)
2	3199.7	23.718	3057.3	3066.1	16.737	3066.0	r_5 (47) + r_2 (46)
3	3178.7	12.350	3024.2	(3033.0)		3033.4	r_4 (34) + r_1 (32)+ r_3 (27)
4	3178.2	15.913	3026.4	3032.9	10.258	3032.7	r_4 (56) + r_1 (32)
5	3169.8	16.336	3008.7	(3030.0)		3029.8	r_3 (67) + r_1 (28)
6	3158.9	8.269	3013.1	2959.9	4.409	2959.3	r'_7 (76)+ r'_6 (24)
7	3126.1	15.737	2980.7	(2959.0)		2958.2	r'_9 (81)+ r'_8 (19)
8	3044.4	23.522	2959.6	2876.0	13.497	2879.3	r'_8 (81)+ r'_9 (18)
9	3041.1	40.044	2982.6	(2876.0)		2877.9	r'_6 (76)+ r'_7 (24)
10	1685.0	2.275	1648.0	(1640.0)		1639.9	R_8 (23)+ R_{10} (20)+ δ_4 (11)
11	1661.8	63.725	1624.8	1610.3	62.269	1609.1	R_2 (36)
12	1614.0	13.368	1571.9	1565.5	8.098	1568.6	R'_4 (18) + R_6 (12) + R_1 (11) + R_{10} (11)
13	1552.0	29.518	1516.4	1498.6	33.024	1503.7	$\delta_s CH_3(2)$ (16) + R_9 (13)
14	1537.8	0.596	1502.0	(1496.0)		1493.5	R_{11} (13) + $\delta_s CH_3(2)$ (12)
15	1514.5	14.448	1511.4	(1474.0)		1473.1	$\delta_s CH_3(2)$ (53)+ r'_{11} (10)
16	1506.5	8.419	1499.0	1453.1	8.278	1453.3	$\delta_s CH_3(1)$ (75)
17	1445.2	0.275	1427.4	(1406.0)		1406.1	$\rho CH_3(1)$ (88)
18	1440.9	4.430	1411.5	(1402.4)		1398.7	R_{10} (17) + R_7 (14) + β_2 (13) + δ_5 (10)
19	1431.1	2.951	1415.5	(1392.0)		1392.7	δ_5 (76)
20	1413.4	3.843	1380.5	1378.6	14.037	1381.4	R_6 (27) + R_8 (13)
21	1394.9	10.995	1358.8	1340.0	1.709	1341.7	R'_4 (26) + R_2 (20)
22	1349.3	11.198	1326.3	1313.1	13.587	1311.2	R'_5 (28) + β_4 (14)+ δ_2 (13)
23	1295.6	1.855	1279.0	1266.8	0.899	1265.4	β_6 (23)+ β_2 (19)+ β'_5 (13)
24	1260.7	5.395	1235.6	1223.0	12.507	1221.7	R'_5 (15)+ R_7 (14)+ R''_{12} (14)
25	1252.5	5.537	1223.7	(1219.1)		1217.4	R''_{13} (14)+ δ_2 (13)+ R_{11} (12) + r'_{11} (11) + R_9 (11)
26	1201.8	1.263	1182.7	1162.0	0.899	1162.8	r'_{10} (22)+ β_2 (17)+ R''_{13} (16) + R_1 (13)
27	1174.7	0.602	1157.7	(1143.0)		1143.9	β'_5 (28)+ β_4 (17)+ R_{10} (12) r'_{11} (12)
28	1151.2	6.650	1136.8	1118.2	8.998	1118.6	r'_{11} (17)+ r'_{10} (12) + R'_5 (11)
29	1040.3	15.703	1022.0	1013.1	4.859	1013.1	$\delta_a CH_3(2)$ (30)+ $\delta_a CH_3(1)$ (14)
30	1030.6	2.056	1016.1	(1003.0)		1002.9	$\delta_a CH_3(1)$ (28)+ $\delta_a CH_3(2)$ (19)
31	976.3	1.277	962.0	(950.0)		948.9	β_6 (21)+ δ_2 (19)+ R_3 (13)
32	935.6	0.795	922.9	(910.0)		908.4	R_3 (16)+ R_9 (14)
33	842.5	3.581	829.6	(820.0)		824.0	β_6 (20)+ δ_2 (15)+ R_6 (11)
34	765.4	0.285	754.1	755.0	1.709	744.1	R_6 (20)+ δ_3 (15)+ β_7 (10)
35	678.0	1.062	670.0	(659.0)		663.9	β_7 (26)+ δ_3 (25)
36	599.3	4.151	593.4	592.4	4.139	589.4	β_7 (30)+ δ_3 (20)+ R''_{12} (10)
37	545.5	0.120	540.4	(530.0)		530.2	δ_1 (38)+ δ_4 (20)

Table 4.5:(Continued) Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,6-DMQ$.

Sym	B3LYP/6-31G^*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
38	457.8	6.570	456.9	(445.0)		444.9	δ_4 (26)+ β_1 (25)+ β_3' (13) + δ_1 (11)
39	419.2	0.184	416.2	(408.0)		408.9	δ_3 (16)+ δ_1 (14) + δ_4 (14)+ β_7 (11)
40	328.7	0.259	330.3	(319.0)		318.8	β_3' (37)+ β_1 (32)
41	226.9	1.338	226.7	(220.0)		220.1	β_3' (29)+ β_1 (26)
A''							
42	3094.6	19.309	2944.0	2933.3	27.265	2931.9	r_6' (100)
43	3091.5	20.426	2946.2	(2933.0)		2927.3	r_8' (100)
44	1514.2	5.39	1514.4	(1473.8)		1473.8	$\delta_s CH_3(1)$ (93)
45	1513.8	6.609	1521.2	(1473.0)		1473.0	$\delta_s CH_3(2)$ (92)
46	1077.9	3.969	1050.9	(1049.0)		1049.0	$\rho CH_3(1)$ (52)+ $\delta_a CH_3(2)$ (18)
47	1069.9	3.886	1045.5	1042.0	1.079	1042.6	δ_6 (55)+ $\delta_a CH_3(1)$ (19) + γ_1 (12)
48	987.9	1.514	973.3	968.2	2.159	967.9	$\rho CH_3(2)$ (59)+ $\rho CH_3(2)$ (28)
49	983.5	0.100	965.9	(957.0)		957.1	γ_5' (47)+ γ_4 (39)
50	902.6	7.831	887.9	877.9	8.458	877.7	γ_2 (65)+ τ_2 (12)
51	853.4	39.968	838.7	830.3	65.418	830.2	γ_4 (30)+ γ_5' (28)+ γ_6 (11) + $\rho CH_3(2)$ (10)
52	830.4	2.229	818.1	(808.0)		808.6	$\rho CH_3(2)$ (34)+ $\rho CH_3(2)$ (27) + γ_2 (14)
53	789.3	0.065	778.1	(768.0)		768.1	γ_6 (34)+ τ_2 (28)+ γ_4 (11)
54	668.4	0.727	658.2	(650.0)		649.9	τ_2 (33)+ γ_6 (21)+ γ_1 (17)
55	551.0	1.014	542.6	(536.0)		535.4	γ_3' (26)+ τ_4 (23)+ γ_1 (17) + γ_7 (14)
56	501.8	0.462	490.9	(488.0)		488.3	τ_5 (35)+ τ_3 (27) + τ_1 (20)
57	410.5	1.894	404.1	(399.0)		399.0	τ_3 (44)+ τ_1 (31)
58	348.1	3.157	339.1	(338.0)		337.8	γ_1 (23)+ γ_3' (23)+ τ_2 (11)
59	211.1	0.815	200.0	(205.0)		205.2	τ_4 (30)+ γ_3' (15)+ γ_1 (15)
60	173.6	1.947	171.4	(169.0)		169.0	τ_1 (26)+ γ_7 (16)+ τ_5 (15)+ τ_4 (12)+ τ_3 (12)
61	101.0	0.010	56.8	(98.0)		98.1	τ_{ring} (59)+ γ_7 (11)
62	89.3	0.330	58.2	(86.9)		86.7	τ_{ring} (29)+ τ_6 (23)
63	75.6	0.828	60.7	(73.6)		73.7	τ_6 (58)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $2,6-DMQ$ and do not have any other significance. RMS error is 1.6618 for the fitting of experimental frequencies.

Table 4.6: Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,7-DMQ$.

Sym	B3LYP/6-31G^*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
1	3203.3	5.150	3064.1	3059.3	33.825	3059.3	r_5 (93)
2	3200.5	25.686	3054.6	(3059.0)		3059.0	r_2 (91)
3	3190.2	33.904	3053.5	3028.2	7.572	3028.2	r_4 (94)
4	3178.6	6.619	3020.0	2987.7	0.829	2988.8	r_1 (49)+ r_3 (47)
5	3172.0	4.946	3025.8	(2987.0)		2985.9	r_1 (49)+ r_3 (47)
6	3159.3	8.184	3007.2	2958.6	1.989	2957.7	r_7' (74)+ r_6' (25)
7	3130.7	15.511	2981.8	(2958.0)		2956.6	r_9' (78)+ r_8' (21)
8	3044.5	22.728	2962.8	2875.8	9.175	2880.0	r_8' (79)+ r_9' (21)
9	3041.0	37.099	2976.1	(2875.0)		2877.6	r_6' (74)+ r_7' (25)
10	1683.7	37.525	1644.9	1633.0	22.716	1633.8	R_{10} (21)+ R_8 (15)+ R_{11} (11) + δ_4 (11)
11	1663.7	55.653	1625.8	1612.5	33.991	1612.9	R_2 (34)
12	1611.3	11.888	1574.2	1563.6	11.275	1563.3	R_4' (16)+ R_{10} (15)+ R_6 (12)
13	1562.0	41.169	1525.9	1513.5	44.216	1518.4	R_9 (18)+ R_7 (11)+ β_3' (11)
14	1528.3	2.965	1464.9	(1487.0)		1486.8	$\delta_s CH_3(2)$ (61)
15	1509.9	10.262	1494.3	(1469.0)		1469.4	$\delta_s CH_3(1)$ (66)+ $\delta_s CH_3(2)$ (16)
16	1497.9	10.566	1469.4	1450.6	13.375	1454.0	β_2 (19)+ r_{11}' (15)+ r_{10}' (14) + R_8 (11)
17	1460.8	5.779	1430.7	1425.4	1.602	1422.8	R_{11} (13)+ $\delta_s CH_3(1)$ (12)+ R_5' (11)
18	1441.2	0.284	1434.5	(1402.0)		1402.1	$\rho CH_3(1)$ (89)
19	1429.1	3.010	1419.6	(1390.0)		1390.1	δ_5 (89)
20	1413.7	7.207	1380.3	1380.1	11.551	1378.0	R_6 (30)+ R_8 (12)+ R_{11} (10)
21	1394.3	7.627	1363.4	1340.6	2.708	1343.5	R_4' (24)+ R_2 (16)
22	1341.5	9.909	1318.8	1308.7	11.993	1310.5	R_5' (19)+ δ_2 (14)
23	1291.0	0.493	1265.6	(1256.6)		1253.8	β_2 (26)+ β_5 (17)+ β_6' (17)
24	1254.7	12.347	1230.2	1222.6	16.083	1218.6	R_{12}'' (16)+ R_7 (13)+ R_3 (13)
25	1247.1	0.375	1221.3	(1213.0)		1210.7	R_1 (21)+ r_{10}' (17)+ R_{11} (13)
26	1201.7	3.384	1177.9	1172.2	2.542	1170.2	R_{13}'' (27)+ β_5 (25)
27	1183.5	4.870	1172.9	1145.8	4.366	1145.6	β_3' (28)+ β_2 (18)+ R_8 (16)+ r_{11}' (10)
28	1153.6	2.837	1134.2	1121.8	5.029	1120.6	r_{11}' (26)+ β_3' (14)
29	1055.9	1.447	1038.0	1014.6	0.497	1024.1	$\delta_a CH_3(2)$ (21)+ $\delta_a CH_3(1)$ (16)
30	1018.5	16.659	1006.1	993.4	1.602	987.6	$\delta_a CH_3(2)$ (28)+ $\delta_a CH_3(1)$ (22)
31	969.0	2.740	956.9	952.7	1.823	949.7	δ_2 (28)+ β_6' (19)+ R_9 (14)
32	956.9	1.827	941.4	929.8	0.552	930.8	R_3 (24)+ $\delta_a CH_3(1)$ (14)+ β_6' (13)
33	789.9	2.027	779.7	(768.0)		768.1	R_6 (32)+ R_1 (13)+ R_7 (11)
34	782.9	1.276	768.7	(762.0)		762.5	R_{12}'' (18)+ R_{13}'' (17) + δ_2 (17) + β_6' (15)
35	689.2	0.901	681.4	(670.0)		670.7	R_{12}'' (14)+ β_6' (14)+ δ_2 (12) + δ_3 (10)
36	643.2	3.884	636.5	(629.6)		629.2	β_7 (47)+ δ_3 (36)
37	482.0	0.266	479.8	(469.0)		469.2	δ_1 (52)+ δ_4 (11)

Table 4.6:(Continued) Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,7-DMQ$.

Sym	B3LYP/6-31G*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
38	464.1	1.301	462.2	(451.0)		451.3	δ_4 (30)+ β_1 (18)+ β_7 (15)
39	436.2	1.655	433.3	(424.0)		424.0	δ_4 (25)+ δ_3 (17)
40	332.9	2.589	338.6	(324.0)		323.9	β_4 (38)+ β_1 (32)
41	222.5	1.211	224.6	(216.0)		216.5	$\beta4$ (30)+ β_1 (27)
A''							
42	3094.8	19.158	2945.1	2934.4	27.303	2932.6	r_6' (100)
43	3091.0	20.452	2945.1	(2934.0)		2930.3	r_8' (100)
44	1513.9	7.285	1504.0	(1473.0)		1473.1	$\delta_s CH_3(1)$ (93)
45	1513.0	4.978	1512.9	(1472.0)		1472.1	$\delta_s CH_3(2)$ (93)
46	1076.9	5.034	1052.1	1041.5	1.658	1041.0	$\rho CH_3(1)$ (50)+ $\delta_a CH_3(2)$ (17)
47	1069.3	3.100	1046.8	(1040.0)		1038.6	δ_6 (53)+ $\delta_a CH_3(1)$ (18) $+ \gamma_1$ (12)
48	987.1	1.198	972.2	968.1	0.276	968.5	$\rho CH_3(2)$ (60)+ $\rho CH_3(2)$ (26)
49	963.6	0.214	959.3	(937.0)		937.1	γ_3' (44)+ γ_2 (42)
50	919.2	6.222	893.6	888.9	8.511	889.4	γ_5 (71)+ τ_2 (12)
51	860.0	36.431	845.5	835.6	56.266	835.8	$\rho CH_3(2)$ (32)+ $\rho CH_3(2)$ (15) $+ \gamma_2$ (14)+ γ_3' (13)
52	803.7	2.470	790.4	(782.0)		782.0	γ_3' (30)+ γ_2 (26)+ $\rho CH_3(2)$ (12) $+ \rho CH_3(2)$ (11)
53	796.4	4.847	790.1	780.0	8.788	777.0	γ_6' (45)+ $\tau_2(ring1)$ (23) $+ \rho CH_3(2)$ (15)
54	665.5	0.830	660.2	(647.0)		648.0	τ_2 (37)+ γ_6' (18)+ γ_1 (15) $+ \gamma_4$ (10)
55	574.6	2.968	569.9	562.7	1.879	559.3	τ_4 (20)+ γ_4 (19) $+ \gamma_1$ (15)+ τ_1 (10)
56	492.2	2.575	483.5	(479.0)		478.2	τ_3 (28)+ τ_5 (27) $+ \tau_1$ (14)
57	420.5	1.112	415.1	(409.0)		408.9	τ_3 (36)+ τ_1 (25)
58	295.4	1.193	291.5	(287.0)		287.5	γ_1 (21)+ τ_4 (17)+ τ_3 (15)+ γ_6' (10)
59	270.6	0.078	269.8	(263.4)		263.4	τ_1 (29)+ γ_4 (19)
60	123.7	0.001	120.0	(120.0)		120.1	γ_7 (45)+ τ_4 (33)
61	119.4	2.413	116.5	(116.0)		116.2	τ_5 (26)+ τ_3 (18) $+\gamma_5$ (12)
62	87.3	0.221	15.8	(84.9)		84.8	$\tau_{(ring)}$ (68)+ τ_6 (11)
63	79.4	1.176	-1.0	(77.0)		77.0	τ_6 (64)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good for $2,7-DMQ$ and do not have any other significance. RMS error is 2.1157 for the fitting of experimental frequencies.

Table 4.7: Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,8-DMQ$.

Sym	B3LYP/6-31G*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
1	3203.8	31.229	3069.3	3056.8	33.585	3056.8	r_2 (96)
2	3200.5	27.074	3055.8	(3056.0)		3056.0	r_4 (89)
3	3184.0	26.451	3049.4	3027.3	1.909	3027.3	r_5 (90)
4	3179.1	4.992	3020.6	2978.9	2.343	2980.0	r_1 (49)+r_3 (49)
5	3176.5	1.497	3021.4	(2978.0)		2976.8	r_1 (49)+r_3 (49)
6	3156.8	8.124	3007.3	2966.3	0.998	2963.5	r'_7 (78)+ r'_6 (18)
7	3129.3	20.645	2980.9	(2966.0)		2963.0	r'_9 (79)+ r'_8 (17)
8	3055.0	26.142	2971.4	2863.1	4.642	2876.5	r'_8 (82)+ r'_9 (17)
9	3044.4	24.186	2967.7	(2863.0)		2874.5	r'_6 (81)+ r'_7 (18)
10	1671.6	17.805	1631.4	(1626.0)		1626.4	R_{10} (19)+ R_7 (13)+ R_2 (11)
11	1662.3	39.932	1623.8	1615.1	34.149	1615.8	R_2 (27)+ R_8 (16)
12	1625.6	11.462	1583.4	1578.2	6.335	1579.3	R'_4 (16)+ R_8 (12)+ R_9 (12) + R_6 (10)
13	1553.6	37.373	1516.6	1506.4	32.631	1504.4	β'_3 (13)+ R_3 (11) + R_9 (10) $\delta_s CH_3(2)$ (10)
14	1529.9	1.326	1493.2	(1489.0)		1489.7	$\delta_s CH_3(2)$ (58)
15	1517.8	1.023	1486.9	(1477.0)		1474.5	$\delta_s CH_3(1)$ (15)+ R'_4 (14)+ $\delta_s CH_3(2)$ (13)+ R_{11} (10)
16	1490.5	22.922	1454.8	1434.3	27.510	1434.8	$\delta_s CH_3(1)$ (62)
17	1477.2	11.949	1445.6	(1430.0)		1430.8	r'_{10} (13) + β_2 (12)+ β'_3 (11) + R_7 (10)
18	1444.4	0.657	1432.5	(1405.0)		1405.0	$\rho CH_3(1)$ (87)
19	1430.9	2.578	1417.4	1378.1	11.455	1377.9	δ_5 (84)
20	1408.7	4.682	1372.5	(1371.0)		1371.9	R_6 (33)
21	1377.3	7.638	1345.1	(1340.0)		1339.6	R_2 (14)+ R'_4 (13)+ R_{10} (12)
22	1353.8	10.832	1326.3	1318.7	13.321	1317.5	R'_5 (25)+ δ_2 (18)
23	1290.3	0.338	1263.1	(1255.0)		1256.1	β_4 (26)+ β_6 (12)+ R_{11} (11) β_2 (10)
24	1261.4	5.952	1233.5	1231.5	4.382	1234.0	R''_{12} (21)+ r'_{10} (16)+ δ_2 (11)
25	1250.2	5.628	1226.2	1207.0	0.911	1213.5	R_1 (18)+ R_7 (18)+R'_5 (14) + β'_3 (12)
26	1197.9	1.932	1183.0	1164.0	1.562	1161.5	β'_3 (32)+ β_2 (19)
27	1173.6	3.832	1155.2	1135.3	5.207	1133.7	r'_{11} (33)+ r'_{10} (23)+ R_2 (12)
28	1113.1	1.794	1092.3	(1083.0)		1081.4	R_9 (13)+β_4 (13)+ $\delta_a CH_3(2)$ (13) + β_6 (12)
29	1095.0	3.601	1073.5	1066.9	7.246	1068.4	R_9 (22)+β_6 (14)+ β_2 (12) R_8 (11)+ R''_{13} (11)
30	1030.4	11.371	1008.6	1002.5	2.386	1003.2	$\delta_a CH_3(1)$ (40)+ δ_6 (13)
31	999.6	2.432	978.2	970.0	0.477	972.4	$\delta_a CH_3(2)$ (31)+ δ_2 (11)
32	922.4	0.213	906.4	(897.0)		894.7	R_3 (25)+ δ_1 (14)
33	870.2	4.122	854.3	858.1	0.998	858.2	δ_2 (34)
34	730.2	2.969	720.2	721.0	1.518	718.3	δ_4 (18)+β_6 (14)+R_7 (11)
35	703.1	0.699	692.9	687.6	1.518	689.9	β'_7 (37)+ β_6 (11)

Table 4.7:(Continued) Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,8-DMQ$.

Sym	B3LYP/6-31G*			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
36	553.2	4.581	546.3	544.2	3.514	541.2	δ_3 (31)+ β_7' (29)+ $R''13$ (10)
37	535.7	0.195	528.6	(512.0)		515.1	δ_1 (28)+ δ_3 (22) + δ_4 (16)
38	490.5	1.453	485.1	(477.0)		477.4	δ_1 (39)+ β_1 (19)+ β_5 (13)
39	440.2	0.803	435.3	(428.0)		426.6	δ_1 (41)+ δ_3 (18)
40	346.7	3.800	341.3	(337.0)		337.4	β_1 (43)+ β_5 (33)
41	221.2	0.672	215.4	(215.0)		214.6	β_1 (28)+ β_5 (28)+ δ_4 (18)
A''							
42	3112.9	13.690	2958.1	2934.7	23.952	2925.5	r_6' (100)
43	3094.8	18.313	2949.5	(2934.0)		2923.1	r_8' (100)
44	1513.8	5.458	1512.2	(1473.0)		1473.1	$\delta_s CH_3(1)$ (93)
45	1504.4	5.865	1474.7	(1464.0)		1464.3	$\delta_s CH_3(2)$ (93)
46	1079.4	4.245	1053.5	(1050.0)		1045.2	$\rho CH_3(1)$ (39)+ $\delta_a CH_3(2)$ (13) + δ_6 (12)
47	1069.1	2.024	1043.9	(1040.0)		1040.1	δ_6 (42)+ $\delta_a CH_3(1)$ (14) + $\rho CH_3(1)$ (12)
48	989.4	1.126	970.5	(963.0)		963.0	$\rho CH_3(2)$ (56)+ $\rho CH_3(2)$ (28)
49	974.0	0.259	962.4	(948.0)		947.8	γ_3' (49)+ γ_4 (23)+ γ_2 (13)
50	913.1	0.950	896.3	(888.0)		888.2	γ_4 (47)+ γ_2 (37)
51	853.8	30.146	835.6	829.3	27.207	829.7	$\rho CH_3(2)$ (27)+ + τ_2 (20) + $\rho CH_3(2)$ (18)
52	813.6	10.504	802.5	792.3	16.662	791.4	γ_6 (32)+ τ_2 (30) + $\rho CH_3(2)$ (16)
53	779.8	17.015	762.9	756.2	19.569	756.4	γ_2 (39)+ γ_3' (34)
54	670.3	0.092	659.7	(652.0)		651.9	γ_6 (29)+ τ_2 (24)+ γ_1 (19)
55	564.4	0.002	555.3	(549.0)		549.3	τ_3 (29)+ $\tau_2(ring2)$ (21) + τ_2 (13)
56	520.1	0.631	511.4	(506.0)		505.4	τ_4 (23)+ γ_7' (20)+ γ_1 (18) + γ_5 (14)
57	424.1	0.035	417.2	(412.0)		412.0	τ_1 (48)+ γ_5 (12) +τ_3 (12)
58	311.3	0.003	306.0	(302.0)		302.4	τ_4 (32)+ γ_1 (21)+ γ_5 (11) +γ_6 (10)
59	212.2	0.974	203.4	(206.0)		206.0	τ_3 (48)
60	168.4	5.545	163.9	(163.0)		163.0	τ_5 (33)+ τ_1 (24) + γ_5 (13)
61	136.5	0.090	27.7	(132.0)		132.0	τ_{ring} (81)
62	101.4	0.074	106.7	(98.0)		98.0	γ_7' (39)+ τ_4 (17) + τ_3 (16)
63	74.7	0.426	211.0	(72.0)		72.0	τ_6 (72)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $2,8-DMQ$ and do not have any other significance. RMS error is 3.3118 for the fitting of experimental frequencies.
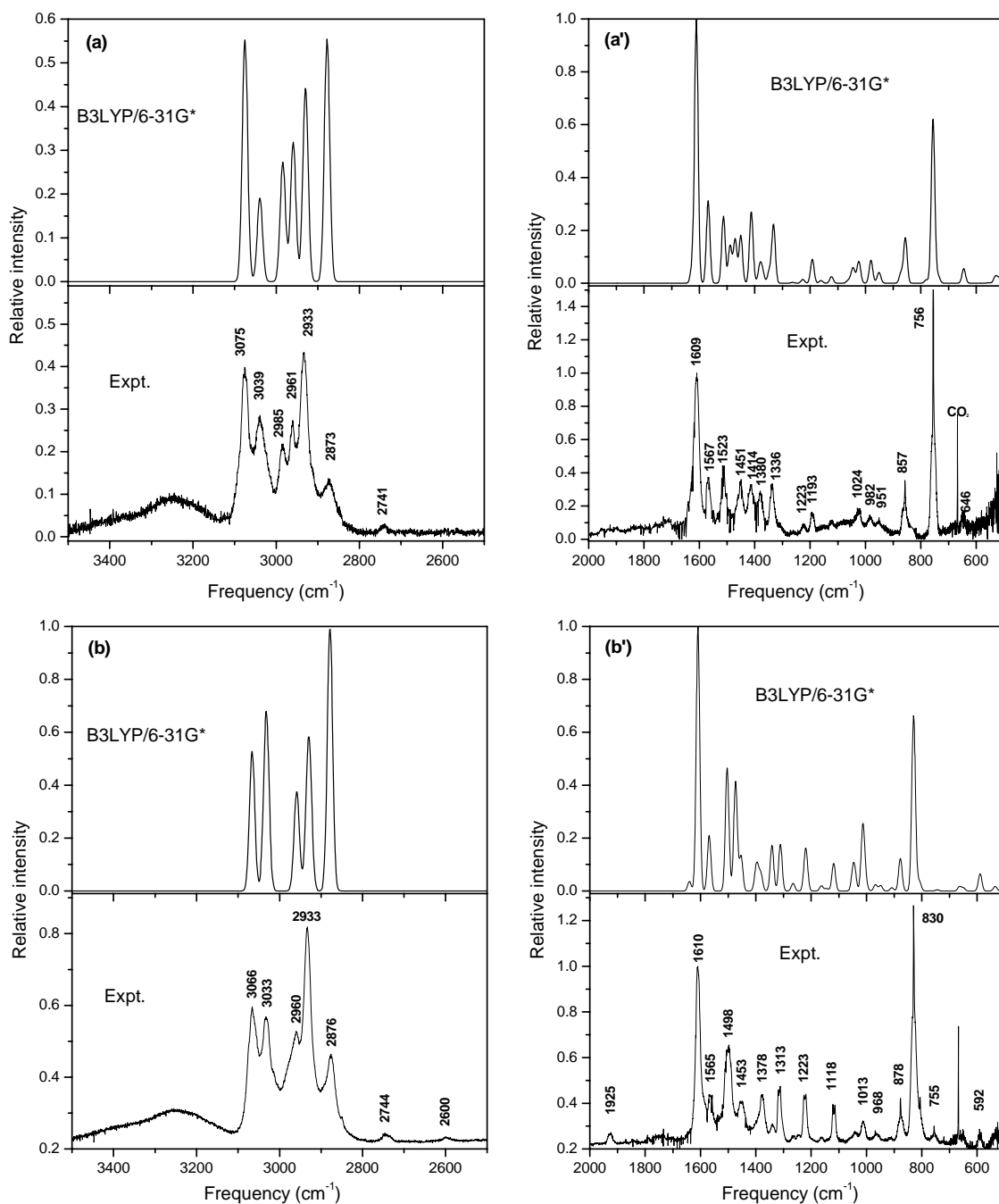
Figure 4.3. Comparison of observed and calculated IR spectra of (a, a′) 2,4-DMQ and (b, b′) 2,6-DMQ. In the calculated spectrum, FWHM assumed to be 15 cm⁻¹. Prominent peaks are labeled in the observed spectrum.
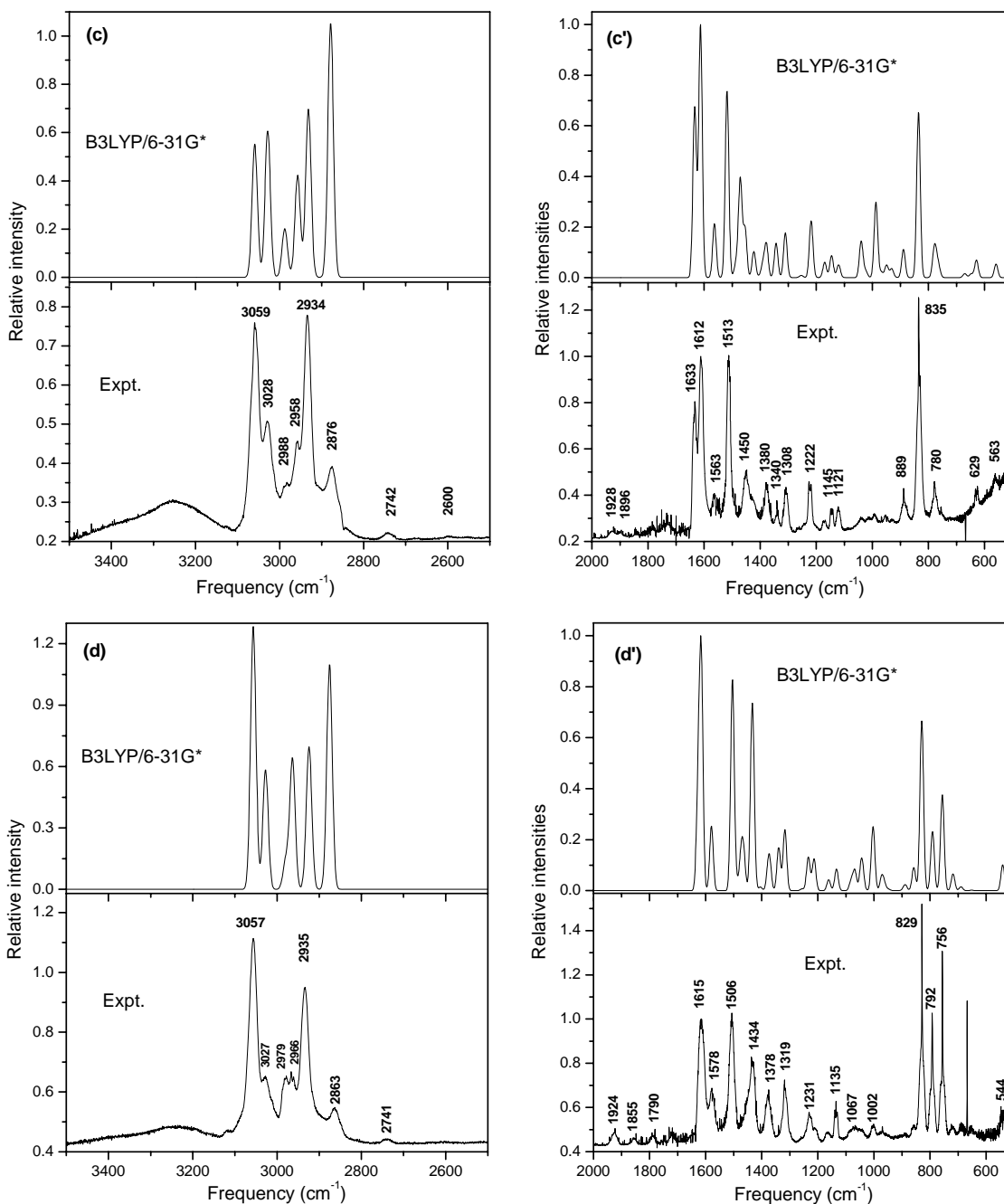
Figure 4.3. (Continued) Comparison of observed and calculated IR spectra of (c, c′) 2,7-DMQ and (d, d′) 2,8-DMQ. In the calculated spectrum, FWHM assumed to be 15 cm⁻¹. Prominent peaks are labeled in the observed spectrum.

The corresponding force field fitted frequency is 1610.9 cm^{-1} in 2,4-DMQ, 1609.1 cm^{-1} in 2,6-DMQ, 1612.9 cm^{-1} in 2,7-DMQ, and 1615.8 cm^{-1} in 2,8-DMQ. The relative intensity of this band in DMQs is more intense compared to that in dimethylnaphthalenes (DMNs).[24] The larger intensity result from a large change in dipole moment as the ring is stretched. In 2,7-DMQ one extra band observed at 1632.2 cm^{-1} which is not clearly resolved from the adjacent band at 1612.5 cm^{-1}. This band is not observed for the rest of the isomers of DMQ. In the calculated spectra of 2,8-DMQ, this band is moderately intense however in the experimental spectra it is not observed. Perhaps this band is masked by the adjacent band found at 1615.1 cm^{-1}. A low intensity band observed at 1566.9 cm^{-1} in 2,4-DMQ, at 1565.5 cm^{-1} in 2,6-DMQ, at 1563.6 in cm^{-1} in 2,7-DMQ, and at 1578.2 cm^{-1} in 2,8-DMQ is assigned as a mixture of local coordinate vibration of aromatic C-N stretching (R′) and aromatic C-C stretching (R) by comparing with the force field fitted frequency calculated at 1568.2 cm^{-1} in 2,4-DMQ, 1568.6 cm^{-1} in 2,6-DMQ, 1563.3 cm^{-1} in 2,7-DMQ, and 1579.3 cm^{-1} in 2,8-DMQ, respectively. A moderately intense band observed at 1512.8, 1498.6, 1513.5, and 1506 cm^{-1} for 2,4-, 2,6-, 2,7- and 2,8-DMQ, respectively, is unique for different isomers of DMQ. The agreement between the calculated anharmonic frequencies and observed frequencies is satisfactory for these non C-H stretching vibrations.

A band observed at 1450.7 cm^{-1} in 2,4-DMQ and 1453.1 cm^{-1} in 2,6-DMQ is of low intensity whereas the same band observed at 1450.6 cm^{-1} in 2,7-DMQ and 1434.3 cm^{-1} in 2,8-DMQ is of moderate intensity. This band is correlated with the calculated anharmonic frequency at 1504.7 cm^{-1} in 2,4-DMQ, 1499.0 cm^{-1} in 2,7-DMQ, 1469.4 cm^{-1} in 2,7-DMQ, and 1454.8 cm^{-1} in 2,8-DMQ, respectively, which is responsible for methyl C-H antisymmetric deformation (δ_s). In 2,4-DMQ this band can also be correlated with the fundamental

anharmonic band at 1464.4 cm^{-1} instead of that at 1504.7 cm^{-1} since its corresponding fitted frequency and the nature of vibration is the same. In such a case assignment is confirmed with the help of the intensity. A band observed at 1413.8 cm^{-1} in 2,4-DMQ corresponds to the force field fitted frequency at 1412.6 cm^{-1} which is responsible for aromatic C-H in-plane bending (β) vibration. A pair of aromatic C-C stretching/aromatic ring deformation bands found at 1380.1 and 1336.9 cm^{-1} in 2,4-DMQ; at 1376.8 and 1313.1 cm^{-1} in 2,6-DMQ; at 1380.1 and 1308.7 cm^{-1} in 2,7-DMQ; at 1378.1 and 1318.7 cm^{-1} in 2,8-DMQ correspond to the DFT calculated anharmonic frequencies at 1422.1 and 1341.7 cm^{-1} in 2,4-DMQ; at 1380.5 and 1326.3 cm^{-1} in 2,6-DMQ; at 1380.3 and 1318.8 cm^{-1} in 2,7-DMQ; at 1417.4 and 1326.3 cm^{-1} in 2,8-DMQ, respectively. In this region the agreement between observed and calculated anharmonic frequencies are not very good for 2,4-DMQ and 2,8-DMQ. They deviate by more than 10 cm^{-1}, however, the force field fitted frequencies are quite close and calculated at 1381.3 and 1332.1 cm^{-1} in 2,4-DMQ; at 1381.4 and 1311.2 cm^{-1} in 2,6-DMQ; at 1378.0 and 1310.5 cm^{-1} in 2,7-DMQ; at 1377.9 and 1317.5 cm^{-1}, respectively.

A band observed at 1223.3 cm^{-1} in 2,4-DMQ, at 1223.0 cm^{-1} in 2,6-DMQ, at 1222.6 cm^{-1} in 2,7-DMQ, and at 1231.5 cm^{-1} in 2,8-DMQ match well with the calculated fundamental anharmonic band at 1246.6 cm^{-1} in 2,4-DMQ, 1223.7/1235.6 cm^{-1} in 2,6-DMQ, 1230.2 cm^{-1} in 2,7-DMQ, and 1233.5 cm^{-1} in 2,8-DMQ. In 2,4-DMQ this band is assigned to a mixture of local coordinate vibration of aromatic C-C stretch (R) and aromatic C-N stretch (R′); whereas for other three isomers it is assigned to a mixture of local coordinate vibration of aromatic-methyl C-C stretch (R″) and aromatic C-C stretch (R) as obtained from PEDs. A low intensity aromatic C-C/C-N stretching vibration appears at 1207.0 cm^{-1} in 2,8-DMQ which is close to the calculated anharmonic band at 1226.2 cm^{-1} and with the force field fitted frequency at

1213.5 cm⁻¹. This band is not observed in other three isomers. In 2,7-DMQ two extra bands observed at 1172.2 and 1145.8 cm⁻¹ are assigned to aromatic-methyl C-C stretching (R″) and aromatic C-H in-plane bending (β) vibrations with the help of force field fitted frequencies at 1170.2 and 1145.6 cm⁻¹, respectively. A band observed at 1121.2, 1118.2, 1121.8, and 1135.3 cm⁻¹ for 2,4-, 2,6-, 2,7-, and 2,8-DMQ, respectively, is assigned to aromatic C-H in-plane bending vibrations (β) by comparing with the calculated anharmonic bands at 1142.4, 1136.8, 1134.2, and 1155.2 cm⁻¹ which differ by ~20 cm⁻¹ from their respective observed frequencies.

In 2,8-DMQ, one moderately intense band observed at 1066.9 cm⁻¹ is identified as a mixture of local coordinate vibration of aromatic C-H in-plane bending (β), aromatic C-C stretching (R) and aromatic-methyl C-C stretching (R″) by correlating with the DFT calculated anharmonic frequency at 1073.5 cm⁻¹. A low intensity band observed at 1024.3 cm⁻¹ in 2,4-DMQ is assigned to a mixture of local-coordinate vibration of aromatic C-C stretching (R) and methyl C-H symmetric deformation (δ_a) by comparing with the calculated anharmonic band at 1028.2 cm⁻¹. Next one set of band observed at 1013.1, 1014.6, and 1002.5 cm⁻¹ for 2,6-, 2,7- and 2,8-DMQ, respectively, is assigned to the methyl C-H symmetric deformation (δ_a). This band is correlated with the calculated anharmonic band at 1022.0, 1038.0, and 1008.6 cm⁻¹ in 2,6-, 2,7-, and 2,8-DMQ, respectively. In 2,4- and 2,8-DMQ one extra band observed at 982.5 and 970.0 cm⁻¹, respectively, correspond to the DFT calculated anharmonic band at 989.2 and 978.2 cm⁻¹. This band is assigned as a mixture of local coordinate vibration of aromatic ring deformation (δ) and methyl C-H symmetric deformation (δ_a).

The next groups of two to three intense bands in the recorded spectra at 857.1 and 755.7 cm⁻¹ in 2,4-DMQ; at 877.9 and 830.3 cm⁻¹ in 2,6-DMQ; at 888.9, 835.6, and 780.0 cm⁻¹ in 2,7-DMQ; at 829.3, 792.3, and 756.2cm⁻¹ in 2,8-DMQ are assigned to aromatic C-H out-of-plane

bending vibrations (γ) by comparing with the anharmonic frequencies calculated at 866.7 and 766.0 cm^{-1} in 2,4-DMQ; 887.9 and 838.7 cm^{-1} in 2,6-DMQ; 893.6, 845.5, and 790.4 cm^{-1} in 2,7-DMQ; 835.6, 802.5, and 762.9 cm^{-1} in 2,8-DMQ, respectively. In the lower frequency region bands observed at 645.8 and 531.0 cm^{-1} in 2,4-DMQ; at 755.0 and 592.4 cm^{-1} in 2,6-DMQ; at 562.7 cm^{-1} in 2,7-DMQ; at 721.0, 687.6, and 544.2 cm^{-1} in 2,8-DMQ are assigned to aromatic ring deformation (δ) vibrations. Their corresponding anharmonic frequencies are 650.4 and 540.5 cm^{-1} in 2,4-DMQ; 754.1 and 593.4 cm^{-1} in 2,6-DMQ; 569.9 cm^{-1} in 2,7-DMQ; 720.2, 692.9, and 546.3 cm^{-1} in 2,8-DMQ, respectively.

4.4.3 Non-fundamental bands

In DMQs a few weak bands are seen in the spectral range of (2800 - 1780) cm^{-1} which do not correspond to any calculated fundamentals. They are identified as non-fundamental (combination/overtone) bands (see Table 4.8). I have assigned these bands with the help of calculated force field fitted frequencies. There are many possibilities for the assignment of the observed non-fundamental bands with the calculated ones, and we have assigned them by correlating with those whose corresponding fundamental bands are intense. The band observed at 2741.2 cm^{-1} in 2,4-DMQ, at 2744.0 cm^{-1} in 2,6-DMQ, at 2743.9 cm^{-1} in 2,7-DMQ, and at 2741.0 cm^{-1} in 2,8-DMQ is assigned to the first overtone band of ν_{19} in 2,4- and 2,8-DMQ and to the first overtone of ν_{20} in 2,6- and 2,7-DMQ by comparing with the force field fitted band at 2762.2 cm^{-1} in 2,4-DMQ, at 2762.8 cm^{-1} in 2,6-DMQ, at 2756.0 cm^{-1} in 2,7-DMQ, and at 2755.8 cm^{-1} in 2,8-DMQ. The low intensity band observed at 2600.0 cm^{-1} in 2,6-DMQ and at 2599.8 cm^{-1} in 2,7-DMQ is compared with the force field fitted frequencies at 2622.4/2603.1 and 2621.0/2596.6 cm^{-1}, respectively. It could be a first overtone of ν_{22} or a combination of the

fundamentals, ν_{24} and ν_{20}. A non-fundamental band observed at 1925.0 cm^{-1} in 2,6-DMQ, 1928.9 cm^{-1} in 2,7-DMQ and 1923.9 cm^{-1} in 2,8-DMQ corresponds to the non-fundamental band at 1948.8 cm^{-1} in 2,6-DMQ, at 1956.4 cm^{-1} in 2,7-DMQ, and at 1963.4 cm^{-1} in 2,8-DMQ, respectively, which is a combination of ν_{51} and ν_{27} in 2,8-DMQ, and $\nu_{51} + \nu_{28}$ in 2,6-, and 2,7-DMQs. Combination bands are not seen in the 2,4-DMQ spectrum perhaps due to lower absorbances of the fundamentals compared to the other dimethylquinolines.

Table 4.8: Observed and calculated fitted and anharmonic non-fundamental bands in DMQs. All frequencies are in cm^{-1}.

Compound	Observed Non-fundamental bands		Force Field Fitted		Anharmonic Non-fundamental Bands	
	Freq.	Int.	Overtone	Combination	Overtone	Combination
2,4-DMQ	2741.2	1.053	2762.6($2\nu_{19}$)		2817.1	
2,6-DMQ	2744.0	1.709	2762.8($2\nu_{20}$)		2757.5	
	2600.0	0.539	2622.4($2\nu_{22}$)	2603.1($\nu_{24}+\nu_{20}$)	2649.0	2616.6
	1925.0	3.149		1948.8($\nu_{51}+\nu_{28}$)		1955.5
2,7-DMQ	2743.9	1.713	2756.0($2\nu_{20}$)		2756.5	
	2599.8	0.386	2621.0($2\nu_{22}$)	2596.6($\nu_{24}+\nu_{20}$)	2631.4	2609.0
	1928.9	1.602		1956.4($\nu_{51}+\nu_{28}$)		1980.0
	1896.0	0.663		1897.6($\nu_{53}+\nu_{28}$)		1924.1
2,8-DMQ	2741.0	0.968	2755.8($2\nu_{19}$)		2805.1	
	1923.9	4.313		1963.4($\nu_{51}+\nu_{27}$)		1991.8
	1855.8	1.628		1859.8($\nu_{52}+\nu_{29}$)		1879.0
	1789.7	2.205		1824.8($\nu_{53}+\nu_{29}$)		1874.9

In parentheses frequency, ν_i refers to the i-th fundamental vibration. For description see Tables 4.4 - 4.7.

One band observed at 1896.0 cm^{-1} in 2,7-DMQ corresponds to the calculated band at 1897.6 cm^{-1} which is a combination band of fundamental vibrations, ν_{53} and ν_{28}. In 2,8-DMQ two non-fundamental bands observed at 1855.8 and 1789.7 cm^{-1} can be correlated with the non-fundamental bands at 1859.8 and 1824.8 cm^{-1} which are assigned to a combination band of (ν_{52} + ν_{29}) and (ν_{53} + ν_{29}), respectively. It is worth noting that the assignment of the non-fundamental modes may be done as well by comparison with calculated anharmonic frequencies in the region. However, the mismatch between the observed and calculated anharmonic frequencies is much more than that found between the observed and force field fitted frequencies. For comparison, we have included the corresponding calculated anharmonic frequencies in Table 4.8 for all the nonfundamental modes.

In 2,4-, 2,6-, and 2,7-DMQs the comparison of the observed and calculated spectra indicates that the intense vibrations in the experimental spectra are also intense in the theoretical spectra except for bands that are present in the lower frequency region which are generally intense in the observed spectra compared to those in the calculated spectra.

4.5 Conclusion

In this chapter, I have reported the gas phase IR spectra of 2,4-, 2,6-, 2,7-, and 2,8-DMQ recorded at low concentrations and assigned their vibrational spectra using force field fitted frequencies and their PEDs of normal modes and DFT calculated anharmonic frequencies. The anharmonic frequencies match well with the observed frequencies at lower frequency region. Unambiguously, I have assigned the aromatic C-H and methyl C-H stretching bands with the help of force field fitted frequencies. The error in fitting is within 3 cm^{-1} between the observed fundamental vibrations and the force field fitted frequencies. PEDs help identify the type of

vibrations in terms of the activity in the local coordinate motion. For nonfundamental

vibrations such as combinations or overtones, however, the error in fitting is higher than 3 cm^{-1}

but still better than that found between the calculated anharmonic and observed frequencies.

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Chapter-5

An Experimental and Theoretical investigation of Infrared spectra of Dimethylphenanthrenes (DMPs) in the Gas Phase

5.1 Introduction

In chapter 3 and 4, I have investigated the gas phase IR spectra of dimethyl polycyclic aromatic compounds having two fused benzene/nitrogen substituted benzene rings in the gas phase.[1] By combining IR spectroscopy and theory, I have assigned the fundamental and non-fundamental bands in the observed spectra. Here, I continue with tricyclicaromatic compounds namely dimethylphenanthrenes (DMPs) and report their IR spectra. They are present in interplanetary dust particles (IDPs), meteorites individual, diesel fuels, and sugar cane soot.[2-6] The residential wood combustion and motor vehicle exhaust emissions contribute to mono-methylphenanthrene (MMPs) and DMPs to the lower atmosphere.[7-11] The isomer of DMPs have different biological activities, e.g., 4,10-DMP acts as a tumor initiating agent and 9,10-DMP is mutagenic whereas 1,4-DMP exhibits both the activities.[12] Another interesting feature of these molecules is that they are known to be the reasons behind unidentified infrared bands (UIR) in the interstellar medium (ISM).[13] Therefore, it is necessary to find accurate frequencies and intensities for DMPs and to identify different isomers of DMP in the gas phase.

In section 1.2 of chapter1, I have discussed that a few experimental techniques employed for the analysis and identification of PAHs including DMPs.[2, 10] Pakdel et al. used FTNMR and FT-IR technique for the analysis of aromatic fractions of pyrolysis oil containing DMPs along with other methylated PAHs.[14] In 1997, Cane et al. recorded the gas phase IR spectra of anthracene and phenanthrene with the help of a multi-pass gas cell of 4.2 meter.[15] There is no literature report on the infrared spectroscopy of DMPs in the gas phase.

In this chapter, I report the mid-IR spectra of DMPs at low concentrations using a long-path gas cell and assign the observed vibrational frequencies unambiguously using scaled force field calculation at the B3LYP/6-311G** level of theory as discussed in chapter 2.

5.2 Experimental section

5.2.1 Materials

DMPs chosen in this study are 1, 9-dimethylphenanthrene (Chiron, 99.1 %), 2,4-dimethylphenanthrene (Chiron, 99.9 %), and 3,6-dimethylphenanthrene (Chiron, 99.9 % purity) and they were used as received.

Table 5.1: Some physical properties of phenanthrene and DMPs.

Compound	State at 25 ^{o}C	m.p (in ^{o}C)	P (at 25 ^{o}C in mmHg)
Phenanthrene	Solid powder	100	[a]1.25×10^{-4}
1,9-DMP	Solid powder	88	[b]2.89×10^{-5}
2,4-DMP	Solid powder	80	[b]2.60×10^{-5}
3,9-DMP	Solid powder	62	[b]2.49×10^{-5}

[a] *Experimentally measured value.*[16]

[b]*Since experimental vapor pressures are not available, calculated values found through SciFinder search are given.*[17]

5.2.2 Methods

Experimental set-up employed for this study has been discussed in section 2.3.3 of chapter 2. DMPs have very low vapor pressures (~10^{-5} mmHg) at room temperature [see Table 5.1]. I have thermally vaporized the DMPs by placing them inside a gas cell at 110 ^{o}C. During the vaporization, UHP Ar gas was introduced through a ball valve to seed the DMPs. The total pressure of Ar gas containing DMPs in the cell was maintained at 30 mmHg. For this study optical path length was fixed at 7.2 meter. The mid-IR spectra (4000 - 400 cm^{-1}) were collected using a liquid nitrogen cooled mercury cadmium telluride or HgCdTe (MCT) detector and KBr beam splitter combination. The spectra were recorded at 0.5 cm^{-1} spectral

resolution with averaging over 2048 scans. The suitable H_2O spectrum was recorded and subtracted from sample spectra in order to get clear spectra of DMPs. The integrated band area $\int \log(I_0/I) \, dv$ (in cm^{-1}) for each band was obtained with the help of OPUS software provided by Bruker. Levenberg Marquardt algorithm is used in the OPUS software to calculate single component band area in the region of overlapping bands particularly in the C-H stretching region.

Intensity of observed was calculated for DMPs using experimental band area and DFT calculated intensity. The detail of the intensity calculation was discussed in section 2.5 of chapter 2. The estimated vapor pressures found to be 1.069×10^{-5}, 0.913×10^{-5}, and 0.533×10^{-5} atm at 110 ^{o}C for 1,9-, 2,4-, and 3,9-DMP, respectively, when B3LYP/6-311G** calculated intensities were considered in the vapor pressure calculation under all the bands.

5.3 Theoretical calculations

I followed the approach which was applied to DMQs (see section 4.3 of chapter 3). At first the molecular geometry of DMPs were optimized at Cs point group with the B3LYP/6-31G* and B3LYP/6-311G** levels of theory using the Gaussian 09 program.[18] At the computed equilibrium geometry, the harmonic and anharmonic frequencies and their intensities were calculated in a Tesla Cluster (EM64L) system. For 2,4-DMP, I found one imaginary frequency due to the interaction between an aromatic C-H bond and the methyl group present in the adjacent ring. For the quantitative fitting of observed bands with calculated spectra, I have performed scaled quantum mechanical force field calculation as described in section 2.4.2 of chapter 2. The internal coordinates were defined for DMPs as shown in Figure 5.1. Then the set of nonredundant local coordinates were constructed (see

Table 5.2). The symbolic force constant matrix, unscaled and scaled force constants in term of nonredundant local coordinates was calculated for DMPs in a similar manner as was done for DMQs (data not shown).

Calculations were carried out with 6-311G** and 6-31G* basis sets and mean deviation between calculated (harmonic, anharmonic and scaled force field fitted) and observed frequencies were evaluated using equation 2.13. Table 5.3 lists the mean deviation between calculated and observed frequencies for three different types of vibration. It is clear that (i) the extent of anharmonicty is different for different types of vibration, (ii) fundamental anharmonic frequencies obtained with 6-31G* basis set differ by ~10 cm^{-1} from that with 6-311G** whereas for the non-fundamental frequencies the difference is more significant and (iii) the force field fitted frequencies obtained by the SQM method are more reliable in the C-H stretching region irrespective of the basis sets. It should be noted that the SQM approach relies on minimizing the fitting error and it can be applied with confidence to the methylated polycyclic compounds.

Figure 5.1. Optimized B3LYP/6-311G** structure and internal coordinates of (a) 1,9-DMP (b) 2,4-DMP and (c) 3,9-DMP.
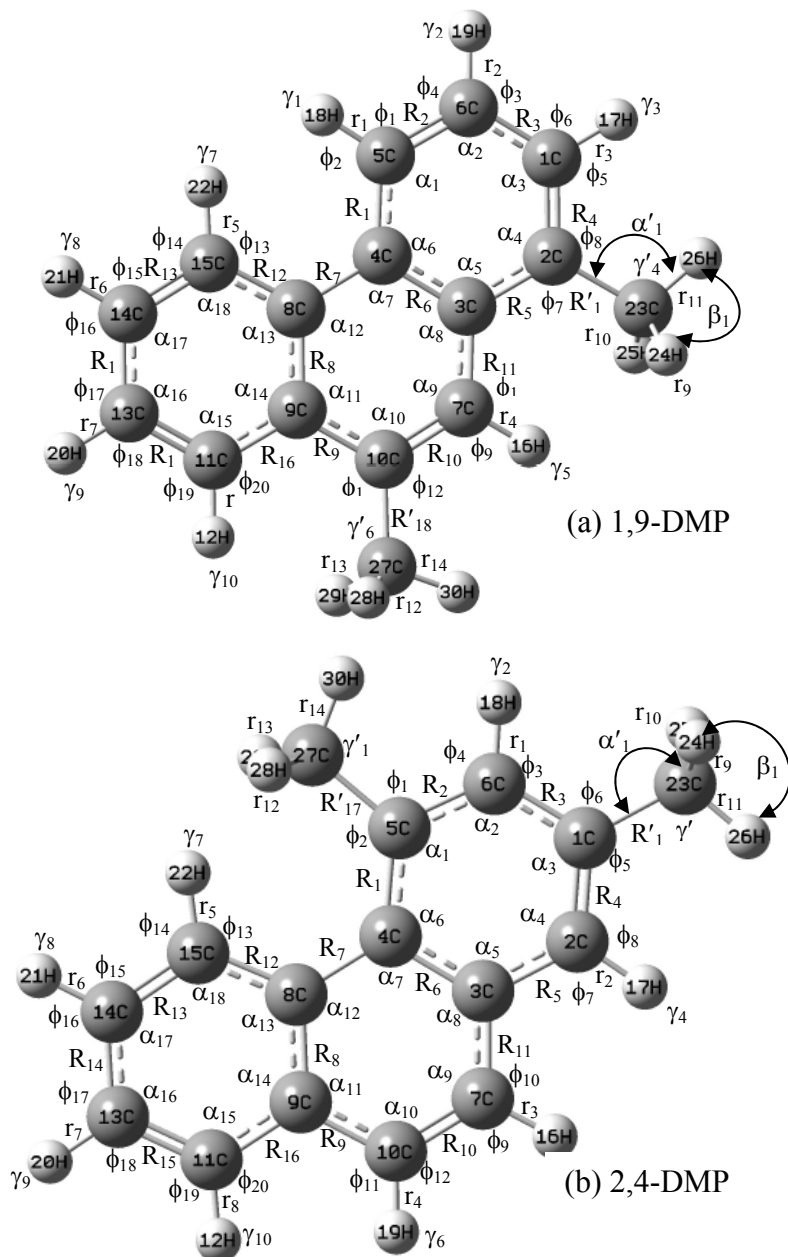
(a) 1,9-DMP

(b) 2,4-DMP

Twist coordinates, τ's numbering are the same as defined for R (the C-C bond coordinates). α_1' and β_1 is one of the C-C-H and H-C-H angle coordinate of the CH$_3$ groups, respectively. The other C-C-H and H-C-H angle coordinates, α_2', α_3', etc. and β_2, β_3, etc., respectively, are defined similarly.

Figure 5.1. (Continued)

(c) 3,9-DMP
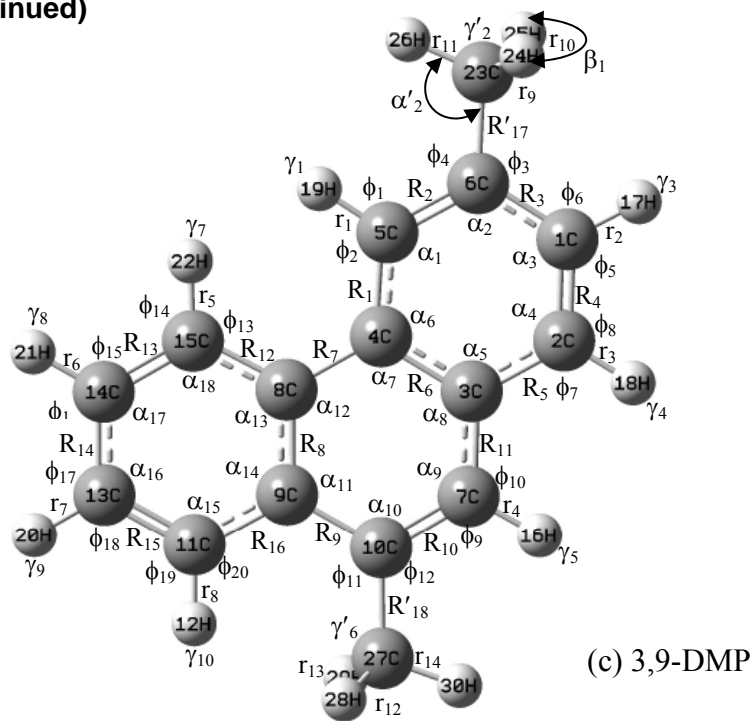
Table 5.2: Nonredundant local coordinates of DMPs used in this thesis.

Compound	Nonredundant local coordinates
1,9-DMP **See Fig 5.1 (a) for the internal-coordinates**	In-plane $S_{1-16} = R$ (Ar, C-C stretch) (R_i) ; $S_{20, 22} = R$(Ar-CH$_3$, C-C stretch) (R'_i) $S_{17-19, 21, 23-26} = r$(Ar, C-H stretch) (r_i) ; $S_{27-32} = r$(CH$_3$, C-H stretch) (r'_i) $S_{33-35, 37, 39-42} = 2^{-1/2}(\phi_3-\phi_4); (\phi_7-\phi_8)\dots$ (Ar, C-H def.)(β_i) $S_{36, 38} = 2^{-1/2}(\phi_1-\phi_2); (\phi_5-\phi_6)$ (C-CH$_3$ def.)(β'_i) $S_{43, 46, 49} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)$(\delta_1, \delta_4, \delta_7)$ $S_{44, 47, 50} = 3^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)$(\delta_2, \delta_5, \delta_8)$ $S_{45, 48, 51} = 1/2(\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)$ (ring def.) $(\delta_3, \delta_6, \delta_9)$ Out-of-plane $S_{52, 57} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{53, 58} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{54, 59} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{55, 60} = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{56, 61} = 2^{-1/2} (\beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{62, 64, 65, 68-71} = \gamma$ (Ar, C-H wag) γ_i ; $S_{65, 67} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i $S_{72, 75, 78} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4, τ_7) $S_{73, 76, 79} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion) (τ_2, τ_5, τ_8) $S_{74, 77, 80} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion) (τ_3, τ_6, τ_9) $S_{81} = 2^{-1/2}(\tau_{5-4-3-7} - \tau_{8-4-3-2})$ (τ_{ring}); $S_{82} = 2^{-1/2}(\tau_{4-8-9-11} - \tau_{15-8-9-10})$ (τ_{ring}) $S_{83, 84} = \tau_{2-23}; \tau_{10-17}$ (C-CH$_3$ twist) (τ''_i)

Table 5.2: Continued……..

Compound	Nonredundant local coordinates
2,4-DMP **See Fig 5.2 (b) for the internal-coordinates**	In-plane $S_{1\text{-}16} = R$ (Ar, C-C stretch) (R_i) ; $S_{17,\,19} = R$(Ar-CH$_3$, C-C stretch) (R'_i) $S_{18,\,22\text{-}26} = r$(Ar, C-H stretch) (r_i) ; $S_{27\text{-}32} = r$(CH$_3$, C-H stretch) (r'_i) $S_{33,\,35} = 2^{-1/2}(\phi_1\text{-}\phi_2);\ (\phi_5\text{-}\phi_6)$ (C-CH$_3$ def.)(β'_i) $S_{34,\,36\text{-}42} = 2^{-1/2}(\phi_3\text{-}\phi_4);\ (\phi_7\text{-}\phi_8)\dots$ (Ar, C-H def.)(β_i) $S_{43,\,46,\,49} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)$(\delta_1,\,\delta_4,\,\delta_7)$ $S_{44,\,47,\,50} = 3^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)$(\delta_2,\,\delta_5,\,\delta_8)$ $S_{45,\,48,\,51} = 1/2(\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)$ (ring def.) $(\delta_3,\,\delta_6,\,\delta_9)$ Out-of-plane $S_{52,\,57} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{53,\,58} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{54,\,59} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{55,\,60} = 6^{-1/2}(2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{56,\,61} = 2^{-1/2}(\beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{62,\,64} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i ; $S_{63,\,65\text{-}71} = \gamma$ (Ar, C-H wag) γ_i $S_{72,\,75,\,78} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4, τ_7) $S_{73,\,76,\,79} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion) (τ_2, τ_5, τ_8) $S_{74,\,77,\,80} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion) (τ_3, τ_6, τ_9) $S_{81} = 2^{-1/2}(\tau_{5\text{-}4\text{-}3\text{-}7} - \tau_{8\text{-}4\text{-}3\text{-}2})$ (τ_{ring}); $S_{82} = 2^{-1/2}(\tau_{4\text{-}8\text{-}9\text{-}11} - \tau_{15\text{-}8\text{-}9\text{-}10})$ (τ_{ring}) $S_{83,\,84} = \tau_{1\text{-}23};\ \tau_{5\text{-}27}$ (C-CH$_3$ twist) (τ''_i)
3,9-DMP **See Fig 5.2 (c) for the internal-coordinates**	In-plane $S_{1\text{-}16} = R$ (Ar, C-C stretch) (R_i) ; $S_{18,\,22} = R$(Ar-CH$_3$, C-C stretch) (R'_i) $S_{17,\,19\text{-}21,\,23\text{-}26} = r$(Ar, C-H stretch) (r_i) ; $S_{27\text{-}32} = r$(CH$_3$, C-H stretch) (r'_i) $S_{33,\,35\text{-}37,\,39\text{-}42} = 2^{-1/2}(\phi_3\text{-}\phi_4);\ (\phi_7\text{-}\phi_8)\dots$ (Ar, C-H def.)(β_i) $S_{34,\,38} = 2^{-1/2}(\phi_1\text{-}\phi_2);\ (\phi_5\text{-}\phi_6)$ (C-CH$_3$ def.)(β'_i) $S_{43,\,46,\,49} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ (ring def.)$(\delta_1,\,\delta_4,\,\delta_7)$ $S_{44,\,47,\,50} = 3^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ (ring def.)$(\delta_2,\,\delta_5,\,\delta_8)$ $S_{45,\,48,\,51} = 1/2(\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)$ (ring def.) $(\delta_3,\,\delta_6,\,\delta_9)$ Out-of-plane $S_{52,\,57} = 6^{-1/2}(\alpha'_1 + \alpha'_2 + \alpha'_3 - \beta_1 - \beta_2 - \beta_3)$ (CH$_3$ sym. def.) (δ_a) $S_{53,\,58} = 6^{-1/2}(2\alpha'_1 - \alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{54,\,59} = 2^{-1/2}(\alpha'_2 - \alpha'_3)$ (CH$_3$ antisym. def.) (δ_s) $S_{55,\,60} = 6^{-1/2}(2\beta_1 - \beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{56,\,61} = 2^{-1/2}(\beta_2 - \beta_3)$ (CH$_3$ rock) ρ(CH$_3$) $S_{62,\,64\text{-}66,\,69\text{-}71} = \gamma$ (Ar, C-H wag) γ_i ; $S_{63,\,68} = \gamma$ (Ar-CH$_3$, C-C wag) γ'_i $S_{72,\,75,\,78} = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$ (ring torsion)(τ_1, τ_4, τ_7) $S_{73,\,76,\,79} = 1/2(\tau_1 - \tau_3 + \tau_4 - \tau_6)$ (ring torsion) (τ_2, τ_5, τ_8) $S_{74,\,77,\,80} = 12^{-1/2}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$ (ring torsion) (τ_3, τ_6, τ_9) $S_{81} = 2^{-1/2}(\tau_{5\text{-}4\text{-}3\text{-}7} - \tau_{8\text{-}4\text{-}3\text{-}2})$ (τ_{ring}); $S_{82} = 2^{-1/2}(\tau_{4\text{-}8\text{-}9\text{-}11} - \tau_{15\text{-}8\text{-}9\text{-}10})$ (τ_{ring}) $S_{83,\,84} = \tau_{6\text{-}23};\ \tau_{10\text{-}27}$ (C-CH$_3$ twist) (τ''_i)

Table 5.3: Mean deviation, δ (in cm^{-1}), between the calculated (harmonic, anharmonic and force field fitted) and observed band position of DMPs.

δ\Mode of Vibration	Basis set	Harmonic			Anharmonic			Fitted		
		(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
AromaticC-H str	6-31G*	181.5	149.4	178.9	43.6	19.0	41.6	0.1	0.8	0.2
	6-311G**	161.6	125.5	161.6	36.8	20.0	36.8	<0.1	0.7	<0.1
Methyl C-H str	6-31G*	181.3	161.3	180.0	34.5	13.8	61.0	7.6	0.7	6.5
	6-311G**	160.2	140.4	160.2	23.5	13.8	23.5	6.4	1.0	6.4
Non-C-H str	6-31G*	35.3	33.7	30.6	14.3	15.9	15.5	1.3	1.7	1.5
	6-311G**	24.1	23.7	24.1	8.6	8.0	8.6	0.8	1.7	0.8
Non-Fundam.	6-31G*				84.8	97.6	170.2			
	6-311G**				48.8	79.5	67.3	57.1	71.9	60.9

(a), (b) and (c) represent the 1,9-, 2,4- and 3,9-DMP, respectively.

5.4 Results and discussion

The gas phase IR absorption spectra of DMPs are shown in Figures 5.2 – 5.4. The DMP molecule in C$_s$ symmetry has 84 normal modes which belong to the irreducible representation 55A′ + 29A″. The recorded band-origin frequencies and their intensities, calculated (harmonic, anharmonic and force field fitted) frequencies of DMPs with 6-311G** and 6-31G* basis sets are presented in Tables 5.4 (a - c) and 5.5 (a - c), respectively. A few observed non-fundamental and corresponding calculated anharmonic and force field fitted frequencies are listed in Table 5.6. Observed bands are assigned with the help of scaled force field fitted frequencies and PEDs at the B3LYP/6-311G** level of theory. From Tables 5.4 (a - c) and 5.5 (a - c) it is clear that the description of PEDs of normal modes remains the same for the 6-31G* and 6-311G** basis sets, although, percent contribution of coordinates to PEDs change by a small extent. The observed spectra of DMPs can be divided into five distinct regions: (1)

aromatic C-H and methyl C-H stretching, (2) aromatic C-C stretching (3) methyl C-H symmetric and asymmetric and aromatic in-plane ring deformation, (4) aromatic C-H out-of-plane and aromatic out-of-plane ring deformation, and (5) non-fundamental modes: overtone and combination. Details of the assignment have been discussed region wise in the following section.

5.4.1 Spectral region of 2800 – 3200 cm^{-1}

Two types of bands appear in this region. They are aromatic C-H and methyl C-H stretching vibrations. The assignment of the observed bands in this region is always difficult because of the presence of Fermi resonances.[1b, 19]
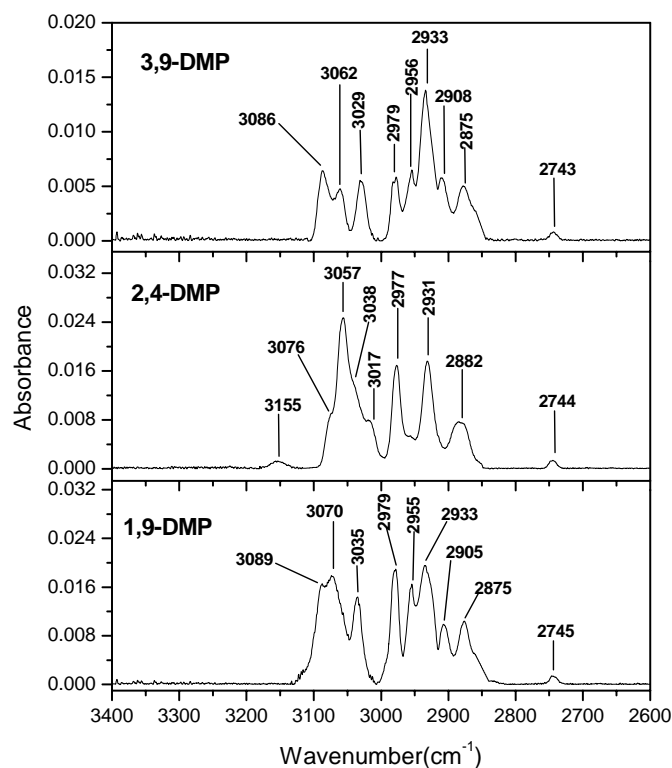
Figure 5.2. Expanded gas phase IR absorption spectra of 1,9-, 2,4-, and 3,9 - DMPs from 2600 to 3400 cm^{-1} at 0.5 cm^{-1} resolution.

In the aromatic C-H stretching region, this occurs due to interaction of a fundamental mode with an overtone or a combination of lower frequency modes. On the other hand in the methyl C-H stretching region, Fermi resonance occurs between the methyl C-H symmetric stretch and an overtone involving two quanta of a methyl deformation mode. Therefore, an assignment of the observed bands in this region with the help of force fitted frequencies and their PEDs is tentative. We have tried to use intensity criteria to resolve this but it is not straightforward.

A group of five bands observed at 3089.1, 3069.7, 3035.3, 2979.6, and 2955.2 cm^{-1} in 1,9-DMP; 3155.1, 3076.5, 3057.2, 3038.0, and 3017.1 cm^{-1} in 2,4-DMP; 3085.7, 3062.5, 3029.1, 2978.9, and 2956.3 cm^{-1} in 3,9-DMP match well with the scaled force field frequencies at 3089.1, 3069.8, 3035.3, 2979.8, and 2955.2 cm^{-1} in 1,9- DMP; 3155.1, 30765.2, 3057.7, 3039.3, and 3018.1 cm^{-1} in 2,4-DMP; 3085.8, 3062.5, 3030.6, 2978.9, and 2957.0 cm^{-1} in 3,9-DMP, respectively. Their respective anharmonic frequencies deviate by 40 and 25 cm^{-1} with 6-31G* and 6-311G** basis sets, respectively. These bands are assigned to aromatic C-H stretching vibration.

A groups of three bands of methyl C-H stretching vibration is seen in the experimental spectra of DMPs. Bands at 2933.5 and 2905.0 cm^{-1} in 1,9-DMP; 2976.7 and 2930.8 cm^{-1} in 2,4-DMP; 2933.5 and 2908.2 cm^{-1} in 3,9-DMP correspond to the force field fitted frequencies at 2936.1 and 2912.4 cm^{-1} in 1,9-DMP; 2976.3 and 2930.6 cm^{-1} in 2,4-DMP; 2936.0 and 2914.1 cm^{-1} in 3,9-DMP, respectively. These bands are assigned to the asymmetric C-H stretching vibrations of methyl group. The symmetric C-H stretching band observed at a lower frequency region such as 2875.3, 2882.3, and 2875.0 cm^{-1} for 1,9-, 2,4-, and 3,9-DMP, respectively, is correlated with the fitted frequency at

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Table 5.4(a): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PEDs of $1,9-DMP$.

Sym	B3LYP/6-311G^{**}			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3210.7	23.82	3069.7	3089.1	14.454	3089.1	r_5 (70)+ r_1 (28)
ν_2	3198.3	23.42	3064.8	3069.7	31.830	3069.8	r_1 (54)+ r_8 (25)+ r_5 (19)
ν_3	3194.1	0.78	3069.0	(3069.0)		3069.0	r_8 (73)+ r_1 (17)
ν_4	3184.7	12.70	3043.7	3035.3	11.215	3035.3	r_4 (99)
ν_5	3179.1	14.98	3053.9	2979.6	14.454	2979.8	r_2 (43)+ r_6 (43)
ν_6	3175.1	33.10	3034.2	(2979.0)		2979.4	r_2 (43)+ r_6 (43)
ν_7	3164.2	2.11	3033.1	2955.2	8.293	2955.2	r_7 (81)+ r_6 (43)
ν_8	3157.9	11.45	3036.8	(2955.0)		2954.9	r_3 (79)+ r_2 (11)
ν_9	3105.4	17.77	2971.9	2933.5	34.121	2936.1	$r'12$ (77)+ $r'11$ (21)
ν_{10}	3104.5	22.23	2961.5	(2933.0)		2935.6	$r'10$ (76)+ $r'9$ (20)
ν_{11}	3021.1	32.70	2895.4	2875.3	14.533	2866.0	$r'11$ (65)+ $r'12$ (17)+ $r'9$ (14)
ν_{12}	3019.5	34.69	2903.5	(2875.0)		2865.6	$r'9$ (65)+ $r'10$ (16)+ $r'11$ (14)
ν_{13}	1659.8	9.84	1620.0	1626.5	9.952	1626.9	R_{10} (36)
ν_{14}	1651.4	1.34	1613.6	(1619.0)		1619.6	R_{15} (21)+ R_{13} (16)+ δ_7 (11)
ν_{15}	1642.4	7.32	1605.3	1604.6	7.819	1604.9	R_4 (25)+ R_2 (14)+ R_1 (12)
ν_{16}	1614.5	1.72	1578.5	1584.5		1583.0	R_2 (13)+ R_3 (13)+ R_6 (11)
ν_{17}	1567.1	4.28	1533.4	(1536.2)		1535.5	R_{14} (21)
ν_{18}	1523.9	10.68	1491.6	1495.4	3.791	1495.3	R_9 (14)
ν_{19}	1507.7	11.54	1459.7	1471.2		1473.9	$\delta_s(1)$ (40)+ $\delta_s(2)$ (21)
ν_{20}	1497.9	4.44	1459.7	(1469.0)		1465.8	$\delta_s(1)$ (33)+ $\delta_s(2)$ (14)
ν_{21}	1487.9	16.63	1458.1	1456.0	25.433	1455.7	$\delta_s(2)$ (34)
ν_{22}	1475.2	0.14	1445.0	(1446.0)		1445.8	β_5 (17)+ R_{10} (11)+ R_{15} (10)
ν_{23}	1440.8	11.59	1414.8	1412.4	6.713	1413.5	β_8 (15)+ R_{11} (11)
ν_{24}	1419.1	5.78	1379.8	1389.5	5.213	1390.6	δ_8 (36)+ $\rho(1)$ (33)
ν_{25}	1427.0	0.16	1373.5	(1389.0)		1388.2	δ_8 (44)+ $\rho(1)$ (44)
ν_{26}	1405.6	0.33	1374.9	(1378.0)		1377.9	R_9 (16)+ β_3 (11)
ν_{27}	1374.1	0.27	1344.9	(1347.0)		1347.9	R_6 (16)+ R_7 (14)+ R_2 (11)
ν_{28}	1362.4	0.59	1332.7	(1336.0)		1337.0	R_8 (19)
ν_{29}	1319.6	2.33	1293.7	1296.1	1.263	1295.2	R_7 (15)+ β_9 (14)+ R_{11} (12)
ν_{30}	1299.9	1.33	1281.3	1273.2	0.868	1274.6	δ_2 (19)+ β_1 (14)+ β_5 (13)+ β_8 (11)
ν_{31}	1271.5	2.22	1253.9	1249.5	3.712	1247.7	R_{16} (14)+ β_3 (14)+ β_8 (13)
ν_{32}	1253.1	3.98	1233.5	(1228.0)		1228.1	β_3 (23)+ R'_{17} (15)+ β_1 (15)+ R_5 (15)
ν_{33}	1236.0	2.55	1217.3	1213.0	0.789	1213.4	R_1 (18)+ R_{11} (16)
ν_{34}	1203.1	0.54	1192.8	(1179.0)		1179.4	$r'14$ (31)+ $r'13$ (12)
ν_{35}	1191.2	0.46	1185.4	(1168.0)		1168.6	β_7 (26)+ β'_6 (22)+ β_8 (11)+ β_5 (10)
ν_{36}	1173.4	1.57	1160.9	1152.7	0.631	1151.7	R_{15} (4)+ β_7 (13)+ β'_6 (11)+ δ_2 (10)
ν_{37}	1110.8	3.96	1097.5	1089.9	2.290	1089.9	R_3 (35)+ β_1 (16)
ν_{38}	1089.3	0.15	1070.5	(1068.0)		1068.5	$\delta_a(2)$ (11)
ν_{39}	1082.7	0.14	1063.4	(1061.0)		1061.6	δ_5 (41)
ν_{40}	1058.6	7.41	1040.0	1036.4	7.108	1036.5	R_{14} (42)
ν_{41}	1018.6	0.85	989.8	(998.0)		998.7	$\delta_a(1)$ (19)+ β_9 (16)+ $\delta_a(2)$ (13)
ν_{42}	1012.4	4.98	985.4	995.3	2.843	993.6	$\delta_a(1)$ (22)+ $\delta_a(2)$ (18)+ δ_5 (13)
ν_{43}	891.3	2.22	879.2	(874.0)		873.5	δ_5 (16)+ δ_4 (11)+ R'_{17} (11)
ν_{44}	867.9	0.31	854.0	(851.0)		851.0	β_9 (31)

Table 5.4(a): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $1,9-DMP$.

Sym	B3LYP/6-311G^{**}			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{45}	778.9	0.19	767.5	(763.0)		763.3	δ_7 (26)+ δ_5 (12)+ R_9 (12)
ν_{46}	710.7	3.66	702.2	698.5	3.633	697.8	δ_6 (22)+ δ_1 (15)+ δ_2 (13)
ν_{47}	635.7	0.54	630.7	(623.0)		623.5	δ_6 (35)+ δ_1 (22)+ δ_2 (14)
ν_{48}	574.2	0.58	569.8	(563.0)		562.7	δ_7 (25)+ β'_4 (22)+ δ_1 (20)
ν_{49}	552.4	5.63	548.4	539.5	1.816	539.6	β_{10} (37)+ R'_{17} (12)+ δ_3 (11)
ν_{50}	513.8	1.71	508.0	(503.0)		502.8	δ_4 (23)+ β_{10} (16)+ δ_7 (11)
ν_{51}	447.2	0.82	443.6	(438.0)		437.9	δ_4 (29)+ β_2 (25)+ δ_3 (14)
ν_{52}	425.7	0.21	423.1	(417.0)		417.0	δ_3 (38)+ β_{10} (12)
ν_{53}	334.0	0.57	330.6	(327.0)		327.7	β_2 (28)+ β'_4 (19)
ν_{54}	282.4	0.24	281.1	(277.0)		277.0	β'_4 (47)+ δ_7 (18)
ν_{55}	221.7	0.43	223.3	(217.0)		217.1	δ_1 (24)+ β_2 (22)
A''							
ν_{56}	3067.9	21.34	2917.2	2905.0	3.554	2912.4	r'_9 (81) + $r'11$ (18)
ν_{57}	3065.2	18.34	2919.7	(2905.0)		2912.1	r'_{11} (82) + $r'9$ (18)
ν_{58}	1490.3	5.47	1432.3	(1461.0)		1460.9	$\delta_s(1)$ (90)
ν_{59}	1487.2	9.70	1442.7	(1458.0)		1457.9	$\delta_s(2)$ (90)
ν_{60}	1063.8	0.99	1034.2	(1043.0)		1043.5	$\rho(1)$ (51)+ $\delta_a(2)$ (18)
ν_{61}	1061.9	1.94	1030.9	(1041.0)		1042.3	δ_9 (50)+ $\delta_a(1)$ (18)
ν_{62}	990.7	0.00	987.1	(971.0)		970.7	γ_7 (38)+ γ_8 (28)+ γ'_6 (18)
ν_{63}	972.7	0.49	977.8	(954.0)		954.1	$\rho(2)$ (48)+ γ_1 (16)+ $\rho(2)$ (15)
ν_{64}	954.0	0.58	957.9	(935.0)		934.6	γ'_6 (33)+ γ_5 (26)+ γ_8 (19)
ν_{65}	902.1	4.12	911.3	(884.0)		883.8	γ_1 (42)+ $\rho(2)$ (31)+ γ_3 (11)
ν_{66}	890.5	11.95	882.4	871.4	17.692	871.5	γ_3 (66)
ν_{67}	873.0	0.26	886.4	(856.0)		856.9	γ_5 (26)+ γ_8 (18)+ τ_2 (13)+ γ_7 (11)
ν_{68}	815.9	5.82	846.3	803.5	9.952	801.9	γ_9 (26)+ τ_2 (22)+ τ_5 (10)
ν_{69}	768.5	41.94	767.3	748.3	105.602	749.0	γ'_6 (30)+ γ_5 (19)+ γ_7 (16)+ γ_8 (12)
ν_{70}	761.5	49.77	764.0	746.0		746.7	$\rho(2)$ (31)+ $\rho(2)$ (25)+ τ_5 (13)+ τ_2 (11)
ν_{71}	744.2	0.23	745.9	(729.0)		729.3	γ_9 (36)+ τ_5 (30)
ν_{72}	610.7	0.13	619.5	(598.0)		598.2	τ_5 (28)+ τ_2 (17)+ γ'_4 (14)
ν_{73}	578.5	1.32	577.0	(567.0)		565.2	τ_8 (17)+ γ_2 (14)+ τ_9 (11)
ν_{74}	538.5	0.55	538.6	(528.0)		527.8	τ_1 (29)+ γ_9 (14)
ν_{75}	482.9	0.12	476.8	(473.0)		472.9	τ_7 (23)+ γ_2 (17)+ γ_{10} (13)+ τ_3 (11)
ν_{76}	420.9	4.21	414.8	(412.0)		411.9	τ_6 (54)
ν_{77}	328.6	0.95	322.3	(322.0)		322.1	γ_2 (16)+ γ'_4 (16)+ τ_8 (16)+ τ_1 (12) + τ_7 (11)
ν_{78}	245.6	0.64	243.5	(240.0)		240.2	γ_{10} (27)+ τ_6 (23)+ τ_9 (11)
ν_{79}	212.0	0.07	195.7	(207.0)		207.0	τ_{ring} (64)
ν_{80}	192.3	0.00	163.3	(188.0)		187.9	τ_{ring} (38)+ τ_1 (17)+ τ_{ring} (15)
ν_{81}	183.7	1.33	167.8	(180.0)		180.0	τ_{ring} (44)+ γ_2 (16)+ τ_1 (10)
ν_{82}	140.6	2.71	146.5	(137.0)		137.0	γ'_4 (20)+ τ_9 (16)+ τ_8 (14)+ τ_7 (14)
ν_{83}	93.2	0.39	98.7	(91.0)		91.1	τ_3 (39)+ τ_7 (23)+ τ_8 (11)
ν_{84}	59.1	0.03	71.5	(57.0)		57.0	τ_4 (33)+ τ_3 (13)+ γ_{10} (12)+ τ_1 (12)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $1,9-DMP$ and do not have any other significance. RMS error is 1.9880 for the fitting of experimental frequencies.

Table 5.4(b): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMP$.

Sym	B3LYP/6-311G^{**}			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3309.7	3.69	3159.7	3155.1	2.350	3155.1	r_5 (98)
ν_2	3185.9	33.46	3048.3	3076.5	2.644	3075.2	r_7 (70)+ r_6 (25)
ν_3	3176.8	36.94	3030.4	3057.2	41.917	3057.7	r_4 (47)+ r_3 (23)+ r_6 (21)
ν_4	3168.2	13.30	3032.5	(3057.0)		3056.7	r_6 (52)+ r_7 (17)+r_4 (16)+ r_3 (10)
ν_5	3159.5	7.58	3011.1	3038.0	17.237	3039.3	r_8 (50)+ r_3 (32)
ν_6	3156.9	7.63	3018.9	(3038.0)		3036.3	r_8 (38)+ r_3 (32) + r_4 (25)
ν_7	3154.1	4.46	3007.9	3017.1	6.072	3018.1	r_2 (50)+ r_1 (48)
ν_8	3151.1	26.29	3002.8	(3017.0)		3016.1	r_1 (50)+ r_2 (48)
ν_9	3103.6	18.24	2963.4	2976.7	20.273	2976.3	r'_{10} (87)+ r'_9 (12)
ν_{10}	3102.5	22.85	2957.8	(2976.0)		2976.0	r'_{12} (89)
ν_{11}	3026.6	21.74	2862.3	2882.3	18.902	2884.9	r'_9 (88)+ r'_{10} (11)
ν_{12}	3021.8	43.87	2905.4	(2882.0)		2883.6	r'_{11} (91)
ν_{13}	1668.3	0.72	1632.3	(1636.0)		1635.0	R_{10} (36)+ R_4 (13)
ν_{14}	1659.9	24.46	1618.4	1621.4	28.206	1624.0	R_4 (15)+ R_2 (12)+ R_5 (12)
ν_{15}	1648.2	8.53	1614.8	1609.1		1609.9	R_{15} (20)+ R_{13} (17)+ R_{16} (11) + δ_7 (11)
ν_{16}	1604.7	2.56	1563.3	(1573.0)		1570.8	R_{14} (14)+ R_3 (10)
ν_{17}	1562.7	1.45	1521.6	(1532.0)		1531.1	R_{14} (15)+ R_3 (12)
ν_{18}	1527.8	3.25	1492.6	(1498.0)		1495.7	R_9 (17)
ν_{19}	1518.7	18.47	1407.0	1470.9	40.742	1471.5	$\delta_s(2)$ (66)
ν_{20}	1492.6	13.15	1468.8	1457.4		1460.2	$\delta_s(1)$ (36)+ β_5 (11)
ν_{21}	1484.9	13.46	1450.0	1456.0		1454.4	$\delta_s(1)$ (28)+ β_5 (11)
ν_{22}	1458.1	2.28	1428.5	1431.8	1.567	1429.6	β_7 (15)+ β_6 (11)
ν_{23}	1430.0	0.10	1399.1	(1402.0)		1399.0	R_5 (14)+ r'_{14} (12)+ β_2 (12)
ν_{24}	1425.3	0.39	1391.5	(1390.0)		1389.0	R_2 (11)
ν_{25}	1419.9	2.08	1361.9	1384.4	2.644	1384.4	$\rho(1)$ (76)
ν_{26}	1414.3	0.17	1403.3	(1380.0)		1380.2	δ_8 (79)
ν_{27}	1361.4	1.28	1326.3	(1335.0)		1331.7	R_8 (21)+ R_{13} (14)+ R_{15} (14)+ R_{16} (12)
ν_{28}	1356.9	4.85	1321.3	1324.7	1.371	1321.1	R_6 (21)+ R_2 (12)
ν_{29}	1325.0	2.35	1294.8	1300.0	1.469	1298.6	R_7 (12)+ β_5 (12)+ β_9 (10)
ν_{30}	1298.2	1.81	1268.4	1270.6	0.976	1271.7	r'_{14} (27)+ R_7 (17)
ν_{31}	1275.1	0.86	1251.3	(1250.0)		1250.1	R_1 (11)+ β_8 (10)
ν_{32}	1242.8	3.26	1213.2	1217.4	2.546	1218.2	β_6 (13)+ β_5 (12)
ν_{33}	1227.6	0.09	1204.1	(1203.0)		1203.9	R_9 (20)+ R_{12} (17)+ β_7 (11)
ν_{34}	1208.1	1.37	1186.5	(1184.0)		1185.0	β_2 (25)+ β'_3 (13)+ r'_{14} (11)
ν_{35}	1191.7	2.41	1168.8	1170.6	2.056	1169.8	β_6 (19)
ν_{36}	1176.4	1.33	1166.3	1148.6	0.391	1150.3	β_4 (19)+ β'_3 (15)+ β_8 (11)
ν_{37}	1148.7	0.66	1128.6	(1126.0)		1126.7	β_7 (18)+ δ_5 (12)+ R_{15} (10)
ν_{38}	1077.3	5.00	1057.7	1053.2	3.525	1053.9	R_{14} (47)+ R_{15} (11)
ν_{39}	1057.0	0.54	1015.8	(1036.0)		1032.1	$\delta_a(2)$ (39)+ $\rho(1)$ (12)
ν_{40}	1040.5	3.53	1026.2	(1020.0)		1019.6	$\delta_a(1)$ (38)+ δ_9 (12)
ν_{41}	1010.2	3.40	995.1	996.4	4.896	995.1	β_9 (32)+ δ_5 (24)
ν_{42}	983.7	1.32	968.9	968.8	0.587	967.1	R'_{18} (23)+ R'_{17} (17)+ δ_5 (12)
ν_{43}	979.6	2.27	955.5	944.9	0.489	952.2	$\delta_a(2)$ (12)+ δ_1 (11)+ R_6 (11)+ R_{11} (10)

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Table 5.4(b): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMP$.

Sym	B3LYP/6-311G^{**}			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{44}	857.9	1.78	846.6	(841.0)		843.7	δ_5 (19)+ δ_3 (11)+ R_8 (11)+ δ_7 (11)
ν_{45}	773.4	0.92	765.4	(758.0)		757.0	δ_2 (27)+ δ_7 (14)+ δ_4 (12)
ν_{46}	698.2	2.94	687.4	688.7	3.623	688.1	δ_6 (44)+ R_8 (11)
ν_{47}	589.7	0.45	585.3	(578.0)		579.1	R'_{18} (17)+ β_9 (15)+ δ_1 (12)+ δ_6 (12)
ν_{48}	568.9	0.73	562.7	(557.0)		557.7	δ_6 (20)+ δ_3 (16)+ δ_4 (11)+ δ_7 (11)
ν_{49}	557.3	0.61	551.5	(546.0)		546.3	β_{10} (39)+ R'_{17} (13)
ν_{50}	529.1	2.61	520.6	(518.0)		517.2	δ_1 (27)+ r'_{13} (18)+ β_{10} (12)
ν_{51}	504.9	0.39	503.0	(495.0)		493.7	δ_7 (30)+ δ_1 (22)+ δ_3 (13)
ν_{52}	392.0	0.47	388.1	(384.0)		383.8	δ_4 (45)
ν_{53}	327.6	0.72	315.2	(321.0)		321.2	r'_{13} (47)+ δ_3 (18)
ν_{54}	303.8	0.00	300.8	(298.0)		297.8	β'_1 (38)+ δ_1 (16)
ν_{55}	214.8	0.81	211.8	(210.0)		210.4	β'_1 (34)+ δ_4 (11)
A''							
ν_{56}	3081.0	15.52	2939.1	2930.8	30.458	2930.6	r'_{11} (100)
ν_{57}	3069.6	19.95	2918.1	(2930.0)		2927.7	r'_9 (100)
ν_{58}	1501.8	7.02	1460.3	(1469.0)		1468.7	$\delta_s(2)$ (94)
ν_{59}	1486.6	7.30	1468.5	(1456.0)		1456.2	$\delta_s(1)$ (92)
ν_{60}	1061.8	3.94	1045.3	1038.5	2.938	1042.7	$\rho(1)$ (50)+ $\delta_a(2)$ (18)+ $\rho(2)$ (10)
ν_{61}	1060.3	0.83	1023.2	(1038.0)		1035.9	δ_9 (52)+ $\delta_a(1)$ (18)
ν_{62}	992.4	0.04	978.0	(973.0)		974.4	γ_7 (30)+ γ_6 (28)+ γ_8 (14) + τ_5 (10)
ν_{63}	979.8	0.00	972.9	(960.0)		959.1	γ_4 (40)+ γ'_3 (39)
ν_{64}	955.5	1.21	958.6	(937.0)		936.5	γ_8 (30)+ γ_5 (26)+ γ_7 (15)+ γ_6 (15)
ν_{65}	903.0	6.90	895.6	885.3	4.505	885.3	$\rho(2)$ (53)+ γ_2 (30)
ν_{66}	881.1	21.29	875.1	864.2	29.969	863.0	γ_5 (15)+ γ_8 (15)+ $\rho(2)$ (12)+ γ_2 (11)
ν_{67}	871.8	4.43	861.9	855.0		853.3	γ_2 (25)+ γ_9 (17)+ $\rho(2)$ (16)
ν_{68}	823.7	19.41	810.7	806.4	24.190	808.5	γ'_3 (27)+ γ_2 (17)+ γ_4 (14)+ τ_2 (10)
ν_{69}	806.9	2.02	807.7	(791.0)		792.6	τ_2 (30)+ γ_9 (15)+ γ_4 (14)+ τ_5 (13)
ν_{70}	757.0	40.94	746.9	742.7	47.598	741.4	γ_7 (24)+ γ_6 (22)+ γ_5 (19)+ γ_8 (16)
ν_{71}	727.3	10.01	718.0	708.7	16.159	708.0	τ_5 (38)+ γ_9 (30)
ν_{72}	616.6	3.42	606.0	603.2	3.525	603.9	τ_5 (19)+ τ_2 (16)+ γ_9 (10)
ν_{73}	583.7	0.05	576.7	(572.0)		573.8	γ'_1 (18)+ γ_{10} (17)+ τ_8 (14)
ν_{74}	532.0	0.20	522.6	(521.0)		521.0	τ_7 (26)+ τ_5 (14)+ γ'_1 (12)+ γ_{10} (11)
ν_{75}	490.3	4.75	484.6	(480.0)		482.8	$\rho(2)$ (24)+ τ_1 (18)+ τ_9 (16)+ τ_6 (14)
ν_{76}	419.3	1.43	403.9	(411.0)		411.1	τ_6 (46)+ τ_3 (12)
ν_{77}	351.3	0.78	327.6	(344.0)		344.6	τ_{ring} (39)+ τ_7 (14)
ν_{78}	325.4	0.86	318.0	(319.0)		318.0	τ_{ring} (37)+ τ_6 (16)+ γ'_1 (10)
ν_{79}	229.3	1.71	222.2	(224.0)		223.8	τ_1 (23)+ τ_9 (15)+ τ_6 (12)+ τ_4 (12)
ν_{80}	187.3	3.77	170.6	(183.0)		182.9	τ_1 (33)+ $\rho(2)$ (12)+ $\rho(2)$ (11)
ν_{81}	177.8	0.36	168.1	(174.0)		174.8	τ_4 (14)+ τ_7 (14)+ γ'_1 (11)+ γ_{10} (11)
ν_{82}	78.1	0.03	61.8	(76.0)		76.2	τ_{ring} (36)+ τ_3 (16)+ τ_8 (11)+ τ_7 (11)
ν_{83}	66.8	0.52	51.8	(65.0)		64.7	τ_{ring} (37)+ τ_3 (18)
ν_{84}	-16.1	0.00	-76.1	(15.0)		nan	τ_{ring} (40)+ τ_3 (12)+ γ_{10} (11)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $2,4-DMP$ and do not have any other significance. RMS error is 2.3804 for the fitting of experimental frequencies.

Table 5.4(c): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6 - 311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $3,9 - DMP$.

Sym	B3LYP/6-311G^{**}			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3203.4	17.48	3063.6	3085.7	19.159	3085.8	r_5 (95)
ν_2	3197.7	26.27	3061.2	3062.5	13.063	3062.5	r_8 (98)
ν_3	3182.7	5.00	3048.0	3029.1	10.757	3030.6	r_1 (50)+ r_6 (48)
ν_4	3176.6	12.81	3026.0	(3029.0)		3027.5	r_1 (47)+ r_6 (46)
ν_5	3170.5	38.13	3039.4	2978.9	10.668	2978.9	r_7 (95)
ν_6	3163.8	2.47	3032.2	(2978.0)		2978.1	r_3 (79)+ r_2 (20)
ν_7	3153.2	20.31	3012.6	2956.3	5.660	2957.0	r_4 (49)+ r_2 (43)
ν_8	3150.2	6.45	3004.5	(2956.0)		2955.2	r_4 (47)+ r_2 (36)+ r_3 (14)
ν_9	3106.2	18.06	2960.1	2933.5	51.838	2936.0	r'_{12} (76)+ r'_{11} (22)
ν_{10}	3102.2	16.61	2954.3	(2933.0)		2935.7	r'_{10} (76)+ r'_9 (23)
ν_{11}	3020.5	36.57	2974.6	2875.0	19.377	2867.0	r'_{11} (64)+ r'_{12} (18) + r'_9 (14)
ν_{12}	3019.0	46.34	2908.1	(2875.0)		2866.8	r'_9 (62)+ r'_{10} (19) + r'_{11} (14)
ν_{13}	1664.1	0.33	1624.1	(1632.0)		1632.8	R_{10} (43)+ β_3 (10)
ν_{14}	1659.2	17.17	1621.2	1620.8	24.167	1623.6	R_4 (19)+ R_2 (11)
ν_{15}	1648.8	6.94	1610.1	1614.2		1614.6	R_{13} (17)+ R_{15} (17)
ν_{16}	1605.2	0.48	1567.4	(1574.0)		1574.9	R_6 (12)+ R_{14} (12)
ν_{17}	1560.4	0.99	1525.0	(1530.0)		1528.9	R_3 (14)+R_{14} (12)
ν_{18}	1539.7	20.01	1505.6	1508.8	20.030	1507.9	β_7 (11)
ν_{19}	1505.0	1.76	1461.3	(1476.0)		1476.1	$\delta_s(2)$ (74)
ν_{20}	1496.3	19.19	1469.8	1460.6	34.618	1460.8	$\delta_s(1)$ (61)
ν_{21}	1481.6	6.57	1451.6	(1437.0)		1439.7	β'_6 (16)
ν_{22}	1459.8	5.28	1427.6	(1431.0)		1427.9	β_8 (17)+ β_5 (11)
ν_{23}	1444.9	1.23	1419.3	(1417.0)		1412.0	R_1 (16)+ $\delta_s(1)$ (13)
ν_{24}	1418.2	6.18	1390.0	1388.3	12.410	1390.8	$\rho(1)$ (24)+ R_9 (17)+ β_3 (10)
ν_{25}	1414.3	0.78	1408.2	(1387.0)		1387.1	δ_8 (87)
ν_{26}	1412.4	0.17	1380.5	(1385.0)		1384.1	$\rho(1)$ (63)
ν_{27}	1381.2	1.16	1346.0	(1349.0)		1349.5	R_6 (20)+ R_2 (16)+ R_4 (15)
ν_{28}	1355.2	1.38	1326.9	1327.6	0.870	1329.3	R_8 (25)+ R_{13} (13)+ R_{15} (11)+ R_{16} (10)
ν_{29}	1325.1	1.92	1302.4	1296.3	1.088	1296.6	β_1 (12)+ β_9 (12)+ R_{11} (11)+ β_2 (10)
ν_{30}	1310.7	0.07	1287.0	(1260.0)		1268.3	δ_2 (18)+ β_5 (14)+ β_8 (11)
ν_{31}	1269.3	1.66	1249.4	(1244.0)		1241.4	β_3 (16)+ R_{16} (13)+ β_8 (13)
ν_{32}	1243.9	1.80	1223.3	1215.2	0.653	1215.9	R_1 (15)
ν_{33}	1230.9	0.95	1210.9	(1207.0)		1206.6	β_3 (23)+ R_5 (18)
ν_{34}	1209.2	2.25	1183.8	1185.0	0.653	1184.9	R'_{17} (18)+ R_7 (14)+ r'_{13} (13)
ν_{35}	1191.0	1.51	1170.5	1166.5	1.306	1167.0	β_7 (35)
ν_{36}	1174.7	2.93	1159.2	1150.0	1.524	1146.2	β'_6 (21)+ β_5 (13)+ β_2 (13)+ β_1 (12)
ν_{37}	1138.3	0.19	1121.6	(1116.0)		1117.2	β'_6 (12)
ν_{38}	1087.5	0.14	1065.6	(1066.0)		1065.3	$\delta_a(2)$ (18)+ δ_5 (16)+ R'_{18} (12)
ν_{39}	1062.4	6.33	1048.6	1040.4	9.797	1040.8	R_{14} (42)+ δ_5 (12)
ν_{40}	1056.8	3.71	1043.4	(1036.0)		1034.7	β_9 (30)+ δ_5 (15)
ν_{41}	1015.9	8.23	1001.9	999.6	3.701	999.4	$\delta_a(2)$ (29)+ δ_5 (14)+ R'_{18} (12)
ν_{42}	1001.4	1.00	988.7	(982.0)		982.2	$\delta_a(1)$ (39)+ δ_9 (13)+ R_3 (11)
ν_{43}	909.8	2.25	898.4	(892.0)		892.4	δ_1 (14)+ δ_5 (12)
ν_{44}	842.9	0.02	832.5	(826.0)		826.9	β_9 (16)+ δ_2 (13)

Table 5.4(c): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-311G^{**}$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $3,9-DMP$.

Sym	B3LYP/6-311G**			Observed		Force field	
No	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{45}	764.9	0.69	755.4	(750.0)		750.3	δ_7 (23)+ R_9 (12)+ δ_2 (11)
ν_{46}	721.0	0.23	713.8	(707.0)		706.9	β_{10} (31)+ δ_6 (17)
ν_{47}	642.1	3.84	636.4	629.1	2.394	629.2	δ_6 (43)+ β_{10} (21)
ν_{48}	607.7	1.64	605.2	(596.0)		594.8	δ_2 (21)+ R'_{18} (11)+ β_{10} (10)
ν_{49}	545.2	0.59	543.1	(534.0)		533.9	δ_1 (25)+ δ_7 (24)+ β_4 (23)
ν_{50}	505.0	0.57	499.8	(495.0)		494.1	δ_4 (31)
ν_{51}	437.7	1.32	433.0	(429.0)		429.2	δ_3 (40)+ r'_{14} (19)+ δ_4 (13)
ν_{52}	398.2	0.23	392.2	(390.0)		390.2	δ_4 (23)+ β_{10} (15)+ R_7 (13)
ν_{53}	340.3	0.49	340.7	(333.0)		333.1	r'_{14} (39)+ δ_1 (20)+ δ_3 (11)
ν_{54}	287.3	0.62	281.3	(281.0)		281.0	β_4 (62)+ δ_7 (10)
ν_{55}	191.9	0.51	191.1	(188.0)		187.9	r'_{14} (32)+ δ_1 (10)
A''							
ν_{56}	3067.5	21.10	2916.8	2908.2	7.838	2914.1	r'_9 (99)
ν_{57}	3064.7	20.18	2921.9	(2908.0)		2914.0	r'_{11} (99)
ν_{58}	1486.2	6.30	1466.8	1453.5		1453.2	$\delta_s(1)$ (92)
ν_{59}	1486.0	7.97	1449.1	(1453.0)		1452.9	$\delta_s(2)$ (92)
ν_{60}	1062.6	0.68	1037.4	(1042.0)		1042.7	$\rho(1)$ (53)+ $\delta_a(2)$ (19)
ν_{61}	1060.7	3.98	1043.2	(1039.0)		1039.4	δ_9 (49)+ $\delta_a(1)$ (17)+ $\rho(2)$ (10)
ν_{62}	989.6	0.00	977.4	(970.0)		970.6	γ'_6 (34)+ γ_7 (34)
ν_{63}	969.4	0.92	963.8	948.7	0.870	948.7	γ'_2 (44)+ γ_1 (43)
ν_{64}	954.0	0.94	954.4	(935.0)		934.5	γ_5 (28)+ γ_8 (28)+ γ_7 (18)+ γ'_6 (16)
ν_{65}	901.8	17.60	882.9	879.1	33.094	879.1	γ_3 (53)+ $\rho(2)$ (16)
ν_{66}	882.5	7.59	887.7	871.7		871.4	$\rho(2)$ (53)+ γ_3 (20)
ν_{67}	873.2	0.13	875.0	(856.0)		855.8	γ_8 (26)+ γ_5 (25)+ τ_5 (14)+ τ_2 (13)
ν_{68}	818.8	13.29	806.4	801.8	16.982	801.7	γ'_2 (39)+ γ_1 (33)
ν_{69}	794.4	2.94	786.5	(779.0)		780.4	τ_2 (33)+ τ_5 (22)+ γ_9 (13)+ γ_7 (10)
ν_{70}	768.0	48.25	760.6	753.9	62.487	753.4	γ'_6 (27)+ γ_5 (15)+ γ_8 (15)+ γ_7 (13)
ν_{71}	738.1	8.66	724.8	723.6	8.055	724.1	γ_9 (41)+ τ_5 (28)
ν_{72}	611.9	2.23	601.9	602.1	4.572	600.5	τ_5 (23)+ τ_2 (15)+ γ_9 (14)+ $\rho(2)$ (12)
ν_{73}	586.2	6.66	579.7	573.6	6.749	573.6	γ_4 (22)+ τ_4 (12)+ $\rho(2)$ (11)+ γ_{10} (10)
ν_{74}	521.9	3.37	510.0	(511.0)		511.7	τ_1 (19)+ τ_3 (17)+ τ_8 (16)+ τ_7 (15)+ $\rho(2)$ (11)
ν_{75}	444.4	2.62	436.6	(435.0)		435.9	τ_1 (21)+ γ_{10} (20)+ τ_6 (20)+ τ_8 (11)
ν_{76}	423.1	1.10	414.6	(414.0)		413.9	τ_6 (39)+ τ_9 (12)
ν_{77}	357.2	1.70	349.2	(350.0)		350.0	$\rho(2)$ (21)+ γ_4 (18)+ τ_1 (11)
ν_{78}	245.9	0.38	236.4	(241.0)		240.7	τ_6 (26)+ γ_{10} (22)+ τ_9 (14)
ν_{79}	220.1	0.25	175.2	(215.0)		214.9	τ_{ring} (60)
ν_{80}	193.0	0.01	159.8	(189.0)		189.2	τ_{ring} (30)+ τ_1 (13)+ τ_3 (12)
ν_{81}	135.5	2.60	129.4	(132.0)		132.0	τ_7 (20)+ γ_4 (16)+ τ_9 (13)+ τ_8 (10)+ τ_2 (10)
ν_{82}	96.4	0.18	79.9	(94.0)		94.2	τ_4 (26)+ τ_7 (15)+ τ_3 (13)+ τ_9 (13)
ν_{83}	79.2	0.26	-90.1	(77.0)		77.0	τ_{ring} (69)
ν_{84}	62.2	0.42	44.4	(61.0)		60.7	τ_3 (25)+ τ_4 (12)+ τ_1 (11)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $3,9-DMP$ and do not have any other significance. RMS error is 2.2038 for the fitting of experimental frequencies.

Table 5.5(a): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PEDs of $1,9-DMP$.

Sym	B3LYP/6-31G^*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3230.3	29.723	3092.1	3089.1	14.454	3088.9	r_5 (63) + r_1 (36)
ν_2	3218.2	29.562	3085.1	3069.7	31.830	3070.0	r_1 (50) + r_5 (27) + r_8 (21)
ν_3	3213.0	0.968	3080.4	(3069.0)		3068.9	r_8 (77) + r_1 (12)
ν_4	3204.8	14.918	3052.1	3035.3	11.215	3035.3	r_4 (99)
ν_5	3199.2	16.626	3066.3	2979.6	14.454	2979.7	r_2 (43) + r_7 (43)
ν_6	3195.2	39.278	3046.2	(2979.0)		2979.5	r_2 (43) + r_7 (43)
ν_7	3184.4	2.290	3051.6	2955.2	8.293	2955.2	r_6 (83) + r_7 (12)
ν_8	3178.4	11.562	3050.0	(2955.0)		2954.9	r_3 (82) + r_2 (12)
ν_9	3127.0	17.148	2990.1	2933.5	34.121	2936.7	r'_{12} (77) + r'_{11} (21)
ν_{10}	3125.8	21.105	2983.7	(2933.0)		2936.1	r'_{10} (76) + r'_9 (20)
ν_{11}	3040.3	31.839	2904.4	2875.3	14.533	2864.3	r'_{11} (65) + r'_{12} (18) + r'_9 (13)
ν_{12}	3038.5	34.593	2909.2	(2875.0)		2863.9	r'_9 (66) + r'_{10} (17) + r'_{11} (13)
ν_{13}	1676.3	8.892	1638.9	1626.5	9.952	1624.8	R_{13} (16) + R_{16} (12) + R_{15} (11)
ν_{14}	1668.0	1.370	1625.0	1619.0		1620.1	R_{10} (32) + R_{15} (11)
ν_{15}	1659.4	6.687	1620.1	1604.6	7.819	1606.8	R_4 (28) + R_1 (12) + R_2 (10)
ν_{16}	1629.5	1.478	1591.5	1584.5		1582.9	R_2 (16) + R_3 (11)
ν_{17}	1584.8	3.469	1551.8	(1536.2)		1538.3	R_{14} (20)
ν_{18}	1541.7	11.020	1510.4	1495.4	3.791	1495.3	R_9 (14)
ν_{19}	1533.7	11.699	1481.9	(1471.2)		1473.3	$\delta_s(1)$ (47) + $\delta_s(2)$ (13)
ν_{20}	1521.8	3.263	1486.0	(1469.0)		1465.5	$\delta_s(1)$ (27) + $\delta_s(2)$ (13) + r'_{14} (11)
ν_{21}	1504.4	12.089	1472.8	1456.0	25.433	1456.4	$\delta_s(2)$ (42)
ν_{22}	1491.3	0.408	1461.6	(1446.0)		1445.0	β_5 (17) + R_{10} (12)
ν_{23}	1457.2	9.055	1431.2	1412.4	6.713	1413.7	β_8 (14) + R_{11} (11)
ν_{24}	1445.4	1.807	1424.3	1389.5	5.213	1391.1	δ_8 (34) + $\rho(1)$ (32)
ν_{25}	1443.8	1.683	1425.0	(1389.0)		1387.9	δ_8 (44) + $\rho(1)$ (44)
ν_{26}	1423.4	0.315	1396.9	(1378.0)		1377.8	R_9 (17) + $\rho(1)$ (10)
ν_{27}	1390.0	0.122	1358.0	(1347.0)		1347.9	R_6 (19) + R_2 (15) + R_4 (14)
ν_{28}	1379.7	0.654	1351.1	(1336.0)		1339.2	R_8 (24) + R_{13} (12)
ν_{29}	1330.7	1.473	1308.9	1296.1	1.263	1295.3	R_7 (18) + β_9 (14) + R_{11} (11)
ν_{30}	1307.8	1.231	1291.3	1273.2	0.868	1274.5	δ_2 (19) + β_5 (14) + β_1 (14) + β_8 (13)
ν_{31}	1284.9	2.543	1265.9	1249.5	3.712	1248.3	R_{16} (12) + β_8 (11) + β_3 (10)
ν_{32}	1266.7	3.597	1250.0	(1228.0)		1228.1	β_3 (28) + R'_{17} (16) + R_5 (11)
ν_{33}	1249.7	2.711	1227.5	1213.0	0.789	1213.9	R_1 (20) + R_{11} (19)
ν_{34}	1213.3	0.241	1197.0	(1179.0)		1179.6	$r'14$ (28) + β'_6 (11)
ν_{35}	1202.2	0.447	1192.2	(1168.0)		1168.3	β_7 (29) + β'_6 (20) + β_8 (11)
ν_{36}	1181.4	1.242	1166.6	1152.7	0.631	1151.5	R_{15} (14) + β_7 (13) + β'_6 (11) + δ_2 (10)
ν_{37}	1121.7	3.163	1107.7	1089.9	2.290	1089.4	R_3 (33) + β_1 (15) + R_2 (11)
ν_{38}	1099.2	0.091	1085.7	(1068.0)		1067.8	$\delta_a(2)$ (12) + R'_{18} (10)
ν_{39}	1086.7	0.285	1067.3	(1061.0)		1061.6	δ_5 (43)
ν_{40}	1068.0	6.035	1050.1	1036.4	7.108	1036.1	R_{14} (42)
ν_{41}	1027.1	0.609	1001.8	(998.0)		998.4	$\delta_a(2)$ (17) + $\delta_a(1)$ (16) + β_9 (16)
ν_{42}	1022.3	4.103	998.6	995.3	2.843	993.7	$\delta_a(1)$ (25) + $\delta_a(2)$ (17) + δ_5 (12)
ν_{43}	894.0	1.905	882.2	(874.0)		872.4	δ_5 (17) + R'_{17} (13) + δ_4 (11)
ν_{44}	869.6	0.239	859.9	(851.0)		850.5	β_9 (33) + R_6 (10)

Table 5.5(a): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $1,9-DMP$.

Sym	B3LYP/6-31G*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{45}	780.9	0.115	770.4	(763.0)		763.3	δ_7 (27) + δ_5 (12) + R_9 (12)
ν_{46}	711.6	3.574	702.2	698.5	3.633	697.1	δ_6 (23) + δ_1 (15) + δ_2 (13)
ν_{47}	635.5	0.490	628.9	(623.0)		623.8	δ_6 (35) + δ_1 (21) + δ_2 (15)
ν_{48}	573.8	0.429	568.8	(563.0)		560.5	δ_7 (25) + δ_1 (21) + β'_4 (21)
ν_{49}	553.1	6.038	547.2	539.5	1.816	540.4	β_{10} (37) + R'_{17} (11) + δ_3 (11)
ν_{50}	514.5	1.761	506.6	(503.0)		502.4	δ_4 (23) + β_{10} (17) + δ_7 (11)
ν_{51}	447.6	0.824	443.1	(438.0)		437.1	δ_4 (28) + β_2 (25) + δ_3 (16)
ν_{52}	426.5	0.230	422.4	(417.0)		416.6	δ_3 (35) + β_{10} (12) + δ_4 (10)
ν_{53}	335.4	0.479	326.8	(327.0)		327.6	β_2 (27) + β'_4 (18)
ν_{54}	284.0	0.198	278.2	(277.0)		277.3	β'_4 (47) + δ_7 (18)
ν_{55}	223.2	0.372	220.3	(217.0)		217.6	δ_1 (24) + β_2 (21)
A''							
ν_{56}	3090.6	21.375	2922.9	2905.0	3.554	2913.6	r'_9 (89) + r'_{11} (11)
ν_{57}	3087.6	18.954	2946.7	(2905.0)		2913.4	r'_{11} (89) + r'_9 (11)
ν_{58}	1517.6	4.201	1466.2	(1461.0)		1460.8	$\delta_s(1)$ (90)
ν_{59}	1514.6	8.336	1474.1	(1458.0)		1457.8	$\delta_s(2)$ (90)
ν_{60}	1079.7	1.658	1054.2	(1043.0)		1044.3	$\rho(1)$ (26) + δ_9 (25)
ν_{61}	1077.1	2.322	1048.4	(1041.0)		1043.7	δ_9 (27) + $\rho(1)$ (27)
ν_{62}	982.9	0.000	975.8	(971.0)		966.4	γ'_6 (32) + γ_7 (29) + γ_8 (17)
ν_{63}	962.9	0.948	962.7	(954.0)		954.0	$\rho(2)$ (50) + γ_1 (24)
ν_{64}	942.8	0.699	945.8	(935.0)		933.4	γ_8 (38) + γ'_6 (29) + γ_5 (15)
ν_{65}	902.3	8.634	898.5	(884.0)		882.7	γ_1 (33) + $\rho(2)$ (23) + γ_3 (22)
ν_{66}	892.5	5.600	893.4	871.4	17.692	871.8	γ_3 (60) + γ_1 (12)
ν_{67}	876.2	0.041	868.2	(856.0)		855.4	γ_5 (33) + γ_7 (13) + γ_8 (13) + τ_5 (13) + τ_2 (11)
ν_{68}	819.6	5.433	809.2	803.5	9.952	802.6	γ_9 (23) + τ_2 (21) + τ_5 (13) +$\rho(2)$ (12)
ν_{69}	772.6	38.966	764.4	748.3	105.602	754.8	γ_7 (23) + γ'_6 (21) + γ_5 (21) + γ_8 (14)
ν_{70}	765.2	30.851	760.2	(746.0)		747.8	$\rho(2)$ (33) +τ_5 (21) + $\rho(2)$ (13) + τ_2 (11)
ν_{71}	745.3	0.224	737.5	(729.0)		730.8	γ_9 (40) + τ_5 (25)
ν_{72}	611.3	0.000	602.3	(598.0)		597.9	τ_5 (25) + τ_2 (17) + γ'_4 (12)
ν_{73}	585.8	1.030	576.5	(567.0)		562.5	τ_8 (19),γ_2 (12) + τ_9 (11) + τ_3 (10)
ν_{74}	540.9	0.210	531.4	(528.0)		526.9	τ_1 (28) + γ_9 (14)
ν_{75}	486.0	0.056	477.0	(473.0)		473.8	τ_7 (24) + γ_2 (17) + γ_{10} (13) + τ_3 (11)
ν_{76}	423.8	2.196	413.8	(412.0)		412.0	τ_6 (54) + γ'_4 (10)
ν_{77}	332.5	0.486	323.5	(322.0)		322.6	γ_2 (17) + γ'_4 (16) + τ_8 (16) + τ_1 (13) + τ_7 (10)
ν_{78}	249.7	0.342	240.2	(240.0)		240.4	γ_{10} (28) + τ_6 (23) + τ_9 (11)
ν_{79}	219.0	0.004	185.9	(207.0)		207.1	τ_{ring} (65)
ν_{80}	197.2	0.007	138.0	(188.0)		187.5	τ_1 (26) + τ_{ring} (17) + τ_{ring} (15)
ν_{81}	189.5	1.125	169.8	(180.0)		180.1	τ_{ring} (69) + γ_2 (11)
ν_{82}	142.8	1.688	135.7	(137.0)		136.9	γ'_4 (19) + τ_9 (16) + τ_8 (14) + τ_7 (13)
ν_{83}	95.2	0.259	90.7	(91.0)		91.3	τ_3 (40) + τ_7 (22) + τ_8 (10)
ν_{84}	60.7	0.025	58.7	(57.0)		57.0	τ_4 (34) + τ_3 (13) + γ_{10} (12) + τ_1 (11)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $1,9-DMP$ and do not have any other significance. RMS error is 2.7233 cm^{-1} for the fitting of experimental frequencies.

Table 5.5(b): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMP$.

Sym	B3LYP/6-31G^*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3335.7	5.028	3182.1	3155.1	2.350	3155.1	r_5 (99)
ν_2	3206.6	29.258	3075.8	3076.5	2.644	3075.2	r_7 (70) + r_6 (24)
ν_3	3196.6	40.682	3050.9	3057.2	41.917	3057.8	r_4 (47) + r_3 (23) + r_6 (22)
ν_4	3188.2	14.459	3056.1	(3057.0)		3056.7	r_6 (52) + r_4 (17) + r_7 (17) + r_3 (10)
ν_5	3179.0	7.684	3030.3	3038.0	17.237	3039.3	r_8 (50) + r_3 (32)
ν_6	3176.0	7.570	3033.7	(3038.0)		3036.3	r_8 (38) + r_3 (32) + r_4 (25)
ν_7	3173.3	8.308	3017.8	3017.1	6.072	3018.0	r_2 (50) + r_1 (48)
ν_8	3171.2	27.353	3024.4	(3017.0)		3016.2	r_1 (50) + r_2 (48)
ν_9	3125.7	16.627	2981.9	2976.7	20.273	2976.5	r'_{10} (86) + r'_9 (13)
ν_{10}	3121.5	22.597	2979.8	(2976.0)		2976.1	r'_{12} (89)
ν_{11}	3045.3	22.030	2890.6	2882.3	18.902	2883.5	r'_9 (87) + r'_{10} (12)
ν_{12}	3041.3	45.565	2930.3	(2882.0)		2881.0	r'_{11} (90)
ν_{13}	1685.5	0.908	1647.3	(1636.0)		1635.2	R_{10} (41)
ν_{14}	1677.1	20.827	1635.4	1621.4	28.206	1622.7	R_4 (19) + R_5 (13) + R_2 (12) +δ_1 (11)
ν_{15}	1665.5	6.941	1627.8	(1609.1)		1610.0	R_{15} (20) + R_{13} (16) + R_{16} (11) + δ_7 (10)
ν_{16}	1620.3	2.093	1584.0	(1573.0)		1571.4	R_{14} (17)
ν_{17}	1580.4	1.524	1549.8	(1532.0)		1532.3	R_3 (13) + R_{14} (13)
ν_{18}	1547.2	14.780	1498.5	(1498.0)		1495.3	R_9 (17)
ν_{19}	1543.8	5.145	1495.7	1470.9	40.742	1471.4	$\delta_s(2)$ (68)
ν_{20}	1515.9	9.749	1476.5	1457.4		1459.2	$\delta_s(1)$ (45)
ν_{21}	1502.4	12.860	1466.8	(1456.0)		1454.2	$\delta_s(1)$ (20) + β_5 (13)
ν_{22}	1473.5	1.954	1454.3	1431.8	1.567	1430.4	β_7 (14) + β_6 (11)
ν_{23}	1450.7	0.111	1405.3	(1402.0)		1400.1	R_5 (14) + r'_{14} (12) + β_2 (11)
ν_{24}	1445.8	0.632	1411.9	(1390.0)		1389.7	R_2 (12) + β_2 (10)
ν_{25}	1440.7	0.616	1407.7	1384.4	2.644	1384.4	$\rho(1)$ (70)
ν_{26}	1440.0	0.305	1404.0	(1380.0)		1380.1	δ_8 (81)
ν_{27}	1379.4	0.648	1354.4	(1335.0)		1333.2	R_8 (20) + R_{13} (14) + R_{15} (14) + R_{16} (12)
ν_{28}	1373.9	4.981	1344.8	1324.7	1.371	1322.7	R_6 (19) + R_2 (12)
ν_{29}	1334.4	1.922	1313.0	1300.0	1.469	1299.5	R_7 (13) + β_5 (12) + β_9 (11)
ν_{30}	1310.9	1.519	1276.2	1270.6	0.976	1271.7	r'_{14} (27) + R_7 (16)
ν_{31}	1286.3	0.732	1269.8	(1250.0)		1250.5	β_8 (11)
ν_{32}	1255.2	3.485	1230.3	1217.4	2.546	1217.6	β_6 (13) + β_5 (12)
ν_{33}	1239.3	0.104	1221.4	(1203.0)		1203.9	R_9 (21) + R_{12} (18) + R_{16} (10)
ν_{34}	1222.7	1.195	1198.2	(1184.0)		1184.2	β_2 (26) + β'_3 (12) + R'_{18} (11) + r'_{14} (11)
ν_{35}	1202.9	2.464	1191.1	1170.6	2.056	1170.2	β_6 (22) + β_7 (10)
ν_{36}	1189.5	1.094	1186.8	1148.6	0.391	1149.4	β_4 (24) + β'_3 (20)
ν_{37}	1156.0	0.316	1144.3	(1126.0)		1126.8	β_7 (20) + R_{15} (11) + δ_5 (11)
ν_{38}	1086.8	3.888	1070.1	1053.2	3.525	1053.6	R_{14} (47) + R_{15} (11)
ν_{39}	1068.7	0.805	1025.2	(1036.0)		1031.6	$\delta_a(2)$ (39) + $\rho(1)$ (12)
ν_{40}	1052.2	3.620	1031.9	(1020.0)		1020.1	$\delta_a(1)$ (37) + δ_9 (12)
ν_{41}	1010.9	3.449	998.9	996.4	4.896	994.6	β_9 (31) + δ_5 (24)
ν_{42}	989.3	1.954	972.3	968.8	0.587	967.5	R'_{18} (22) + R'_{17} (17) + δ_5 (12)
ν_{43}	987.6	0.510	963.6	944.9	0.489	951.1	δ_1 (12) + $\delta_a(2)$ (12) + R_6 (11) + R_{11} (10)

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Table 5.5(b): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $2,4-DMP$.

Sym	B3LYP/6-31G*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{44}	859.9	1.554	853.5	(841.0)		842.7	δ_5 (18) + R_8 (11) + δ_7 (11) + δ_3 (10)
ν_{45}	773.2	1.029	768.6	(758.0)		757.4	δ_2 (27) + δ_7 (14) + δ_4 (12)
ν_{46}	669.4	3.068	691.3	688.7	3.623	688.2	δ_6 (45) + R_8 (11)
ν_{47}	590.6	0.293	585.0	(578.0)		578.7	R'_{18} (16) + β_9 (14) + δ_1 (12) + δ_6 (12)
ν_{48}	569.7	0.816	562.5	(557.0)		557.8	δ_6 (19) + δ_3 (15) + δ_7 (12) +
ν_{49}	558.3	0.775	547.7	(546.0)		546.3	β_{10} (40) + R'_{17} (13)
ν_{50}	530.0	2.734	522.1	(518.0)		517.3	δ_1 (27) + r'_{13} (19) + β_{10} (10)
ν_{51}	505.1	0.335	501.6	(495.0)		493.8	δ_7 (30) + δ_1 (23) + δ_3 (13)
ν_{52}	391.8	0.454	388.5	(384.0)		383.7	δ_4 (45)
ν_{53}	328.6	0.632	319.6	(321.0)		321.2	r'_{13} (46) + δ_3 (19)
ν_{54}	304.3	0.009	307.3	(298.0)		297.7	β'_1 (36) + δ_1 (16)
ν_{55}	215.3	0.687	218.9	(210.0)		210.4	β'_1 (35) + δ_4 (11)
A''							
ν_{56}	3102.9	16.738	2958.9	2930.8	30.458	2931.7	r'_{11} (100)
ν_{57}	3092.4	20.430	2941.7	(2930.0)		2929.0	r'_9 (100)
ν_{58}	1530.0	5.686	1407.1	(1469.0)		1468.6	$\delta_s(2)$ (94)
ν_{59}	1513.8	5.931	1511.6	(1456.0)		1456.2	$\delta_s(1)$ (92)
ν_{60}	1076.0	3.310	1053.9	1038.5	2.938	1044.5	$\rho(1)$ (51) + $\delta_a(2)$ (19) + $\rho(2)$ (11)
ν_{61}	1074.3	3.063	1029.9	(1038.0)		1035.9	δ_9 (53) + $\delta_a(1)$ (18)
ν_{62}	986.1	0.027	987.2	(973.0)		971.2	γ_6 (26) + γ_7 (25) + γ_8 (19)
ν_{63}	972.7	0.016	975.0	(960.0)		956.6	γ'_3 (46) + γ_4 (28)
ν_{64}	945.7	2.141	953.9	(937.0)		934.5	γ_8 (41) + γ_6 (27) + γ_5 (14)
ν_{65}	903.7	8.070	895.3	885.3	4.505	883.7	γ_2 (43) + $\rho(2)$ (39)
ν_{66}	885.6	16.731	875.3	864.2	29.969	863.3	$\rho(2)$ (22) + γ_5 (16)
ν_{67}	876.0	4.954	867.1	(855.0)		855.1	$\rho(2)$ (21) + γ_2 (20) + γ_5 (13) + γ_9 (12)
ν_{68}	828.0	19.735	824.5	806.4	24.190	811.9	γ_4 (26) + γ'_3 (25) + γ_2 (13)
ν_{69}	809.2	0.656	821.4	(791.0)		795.5	τ_2 (33) + τ_5 (19) + γ_9 (11) + γ_7 (10)
ν_{70}	761.7	29.636	756.4	742.7	47.598	744.6	γ_5 (26) + γ_7 (21) + γ_6 (19) + γ_8 (12)
ν_{71}	726.6	4.632	738.2	708.7	16.159	708.4	τ_5 (36) + γ_9 (32)
ν_{72}	617.0	1.768	618.0	603.2	3.525	602.5	τ_2 (17) + τ_5 (14) + γ_9 (13)
ν_{73}	588.2	0.167	586.5	(572.0)		570.8	γ'_1 (17) + γ_{10} (16) + τ_8 (13) + γ_9 (11)
ν_{74}	533.3	0.166	528.2	(521.0)		521.0	τ_7 (25) + γ'_1 (13) + γ_{10} (12) + τ_5 (11)
ν_{75}	494.3	2.642	489.6	(480.0)		483.2	$\rho(2)$ (25) + τ_1 (17) + τ_9 (15) + τ_6 (14)
ν_{76}	422.5	0.540	409.4	(411.0)		411.1	τ_6 (44) + τ_3 (12)
ν_{77}	358.7	0.999	341.3	(344.0)		344.6	τ_{ring} (43) + τ_7 (13)
ν_{78}	331.4	0.460	337.1	(319.0)		317.4	τ_{ring} (31) + τ_6 (16) + γ'_1 (12) + τ_8 (11)
ν_{79}	233.1	0.910	233.4	(224.0)		224.9	τ_1 (22) + τ_9 (15) + τ_6 (12) + τ_4 (12)
ν_{80}	189.5	2.366	187.5	(183.0)		182.6	τ_1 (34) + $\rho(2)$ (10)
ν_{81}	180.0	0.345	177.3	(174.0)		174.9	γ'_1 (15) + τ_7 (14) + τ_4 (13)
ν_{82}	79.4	0.007	64.4	(76.0)		76.5	τ_{ring} (32) + τ_3 (17) + τ_8 (13) + τ_7 (11)
ν_{83}	67.7	0.418	55.3	(65.0)		64.5	τ_{ring} (40) + τ_3 (16)
ν_{84}	-11.6	0.001	-95.5	(15.0)		nan	τ_{ring} (41) + τ_3 (12) + γ_{10} (11)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $2,4-DMP$ and do not have any other significance. RMS error is 2.4226 cm^{-1} for the fitting of experimental frequencies.

Table 5.5(c): Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $3, 9 - DMP$.

Sym	B3LYP/6-31G^*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
A'							
ν_1	3223.3	21.701	3077.0	3085.7	19.159	3085.7	r_5 (96)
ν_2	3217.4	32.672	3081.7	3062.5	13.063	3062.5	r_8 (92)
ν_3	3202.4	7.123	3058.7	3029.1	10.757	3029.4	r_1 (49) + r_7 (44)
ν_4	3196.4	12.566	3045.9	(3029.0)		3028.7	r_1 (47) + r_7 (46)
ν_5	3190.8	43.623	3059.5	2978.9	10.668	2978.9	r_6 (93)
ν_6	3184.2	2.660	3041.5	(2978.0)		2978.1	r_3 (77) + r_2 (19)
ν_7	3173.5	21.030	3026.2	2956.3	5.660	2957.0	r_4 (49) + r_2 (43)
ν_8	3170.2	7.174	3026.9	(2956.0)		2955.2	r_4 (48) + r_2 (36) + r_3 (14)
ν_9	3127.7	17.218	2982.7	2933.5	51.838	2936.5	r'_{12} (75) + r'_{11} (22)
ν_{10}	3124.3	15.728	2976.8	(2933.0)		2936.2	r'_{10} (75) + r'_9 (24)
ν_{11}	3039.6	37.050	2991.6	2875.0	19.377	2865.5	r'_{11} (65) + r'_{12} (19) + r'_9 (12)
ν_{12}	3038.0	46.760	2980.2	(2875.0)		2865.1	r'_9 (64) + r'_{10} (20) + r'_{11} (12)
ν_{13}	1680.4	0.288	1642.0	(1632.0)		1632.1	R_{10} (43) + β_3 (10)
ν_{14}	1675.4	15.146	1635.6	1620.8	24.167	1623.5	R_4 (18)
ν_{15}	1666.0	6.173	1625.3	(1614.2)		1615.2	R_{15} (17) + R_{13} (16)
ν_{16}	1620.2	0.454	1580.9	(1574.0)		1574.2	R_6 (12) + R_{14} (12)
ν_{17}	1578.3	0.623	1538.8	(1530.0)		1531.3	R_3 (16) + R_{14} (13)
ν_{18}	1556.4	17.345	1521.6	1508.8	20.030	1509.1	β_7 (10)
ν_{19}	1531.6	2.139	1469.4	(1476.0)		1475.9	$\delta_s(2)$ (77)
ν_{20}	1522.8	15.292	1479.8	1460.6	34.618	1460.8	$\delta_s(1)$ (63)
ν_{21}	1496.4	5.066	1466.9	(1437.0)		1440.8	β'_6 (17)
ν_{22}	1477.1	4.294	1444.9	(1431.0)		1427.8	β_8 (18) + β_5 (11)
ν_{23}	1461.0	1.702	1430.6	(1417.0)		1411.4	R_1 (17) + $\delta_s(1)$ (13)
ν_{24}	1442.1	1.179	1431.7	1388.3	12.410	1391.8	R_9 (20) + $\rho(1)$ (14) + β_3 (12)
ν_{25}	1441.7	2.979	1431.0	(1387.0)		1387.0	δ_8 (86)
ν_{26}	1432.3	2.922	1403.8	(1385.0)		1384.5	$\rho(1)$ (72)
ν_{27}	1398.0	1.220	1363.8	(1349.0)		1350.7	R_6 (20) + R_2 (17) + R_4 (15)
ν_{28}	1373.2	1.350	1345.5	1327.6	0.870	1330.1	R_8 (25) + R_{13} (12) + R_{16} (11) + R_{15} (10)
ν_{29}	1337.5	1.189	1315.1	1296.3	1.088	1297.6	β_9 (14) + β_1 (12) + R_{11} (12)
ν_{30}	1318.5	0.032	1297.4	(1260.0)		1266.2	δ_2 (19) + β_5 (15) + β_8 (11)
ν_{31}	1282.5	1.930	1264.0	(1244.0)		1241.4	β_3 (15) + R_{16} (14) + β_8 (13)
ν_{32}	1258.2	1.388	1234.8	1215.2	0.653	1216.3	R_1 (18) + R_{11} (13)
ν_{33}	1244.7	0.986	1226.3	(1207.0)		1205.8	β_3 (28) + R_5 (16)
ν_{34}	1220.5	2.387	1196.5	1185.0	0.653	1186.0	R'_{17} (19) + R_7 (13) + r'_{13} (13)
ν_{35}	1201.8	1.052	1185.5	1166.5	1.306	1166.2	β_7 (37) + β'_6 (11)
ν_{36}	1185.2	2.603	1170.4	1150.0	1.524	1146.5	β'_6 (20) + β_2 (16) + β_1 (14) + β_5 (12)
ν_{37}	1146.2	0.079	1129.3	(1116.0)		1116.8	β'_6 (12)
ν_{38}	1097.0	0.180	1078.0	(1066.0)		1065.2	δ_5 (19) + $\delta_a(2)$ (16) + R'_{18} (14)
ν_{39}	1071.5	4.170	1058.4	1040.4	9.797	1040.5	R_{14} (41) + δ_5 (14)
ν_{40}	1061.7	5.500	1047.9	(1036.0)		1034.6	β_9 (29) + δ_5 (13)
ν_{41}	1025.1	6.228	1012.0	999.6	3.701	999.4	$\delta_a(2)$ (31) + δ_5 (12) + $\rho(1)$ (10) + R'_{18} (10)
ν_{42}	1012.4	1.024	996.5	(982.0)		981.6	$\delta_a(1)$ (38) + δ_9 (12) + R_3 (11)
ν_{43}	913.0	1.800	901.3	(892.0)		891.6	δ_1 (14) + δ_5 (12)
ν_{44}	845.2	0.028	835.5	(826.0)		826.5	β_9 (16) + δ_2 (13)

Table 5.5(c): (Continued)Calculated harmonic, anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) at $B3LYP/6-31G^*$, observed frequencies (in cm^{-1}) and intensities (in km/mol), fitted frequencies (in cm^{-1}) and PED of $3,9-DMP$.

Sym	B3LYP/6-31G^*			Observed		Force field	
Mode	Harm.	Int.	Anharm.	Freq.	Int.	Fitted	PED
ν_{45}	766.2	0.983	754.0	(750.0)		749.6	δ_7 (23) + R_9 (12) + δ_2 (10)
ν_{46}	722.3	0.245	714.3	(707.0)		706.9	β_{10} (33) + δ_6 (16)
ν_{47}	641.7	3.798	635.5	629.1	2.394	629.5	δ_6 (44) + β_{10} (19)
ν_{48}	608.1	1.718	602.9	(596.0)		595.6	δ_2 (21) + R'_{18} (11) + β_{10} (10)
ν_{49}	544.5	0.605	543.1	(534.0)		533.4	δ_1 (25) + δ_7 (25) + β_4 (23)
ν_{50}	505.6	0.560	499.1	(495.0)		494.0	δ_4 (31)
ν_{51}	437.1	1.295	433.1	(429.0)		429.1	δ_3 (40) + r'_{14} (18) + δ_4 (13)
ν_{52}	399.0	0.203	395.8	(390.0)		389.8	δ_4 (23) + β_{10} (14) + R_7 (13)
ν_{53}	340.6	0.475	343.6	(333.0)		332.9	r'_{14} (39) + δ_1 (19) + δ_3 (10)
ν_{54}	288.6	0.501	286.8	(281.0)		281.1	β_4 (62) + δ_7 (10)
ν_{55}	192.6	0.444	195.1	(188.0)		188.2	r'_{14} (33)
A''							
ν_{56}	3089.5	21.865	2925.4	2908.2	7.838	2915.3	r'_{11} (98)
ν_{57}	3087.0	20.419	2927.8	(2908.0)		2915.1	r'_9 (98)
ν_{58}	1513.5	4.711	1525.2	(1453.5)		1453.3	$\delta_s(1)$ (92)
ν_{59}	1513.4	7.105	1529.0	(1453.0)		1452.9	$\delta_s(2)$ (93)
ν_{60}	1078.4	1.352	1055.6	(1042.0)		1043.3	$\rho(1)$ (53) + $\delta_a(2)$ (19)
ν_{61}	1074.9	4.802	1048.4	(1039.0)		1040.8	δ_9 (50) + $\delta_a(1)$ (17) + $\rho(2)$ (10)
ν_{62}	981.8	0.002	972.8	(970.0)		969.6	γ_7 (33) + γ'_6 (30) + γ_8 (19)
ν_{63}	962.4	0.972	960.1	948.7	0.879	946.3	γ'_2 (55) + γ_1 (30)
ν_{64}	943.6	1.650	947.0	(935.0)		933.5	γ_8 (37) + γ'_6 (30) + γ_5 (16)
ν_{65}	904.9	15.499	895.1	879.1	33.094	879.2	$\rho(2)$ (36) + γ_3 (31)
ν_{66}	883.3	7.322	880.6	(871.7)		870.7	γ_3 (45) + $\rho(2)$ (34)
ν_{67}	876.4	0.009	874.3	(856.0)		856.8	γ_5 (32) + γ_8 (14) + τ_5 (14) + τ_2 (12) + γ_7 (12)
ν_{68}	822.3	11.194	814.1	801.8	16.982	805.5	γ_1 (43) + γ'_2 (29)
ν_{69}	796.7	4.090	787.1	(779.0)		780.0	τ_2 (30) + τ_5 (23) + γ_7 (15) + γ_9 (14)
ν_{70}	772.0	35.830	766.8	753.9	62.487	754.5	γ'_6 (25) + γ_5 (24) + γ_8 (11) + γ_7 (10)
ν_{70}	738.0	5.947	735.5	723.6	8.055	725.5	γ_9 (44) + τ_5 (26)
ν_{72}	611.5	0.719	603.3	602.1	4.572	600.2	τ_5 (23) + τ_2 (15) + γ_9 (13) + $\rho(2)$ (12)
ν_{73}	591.3	4.534	584.5	573.6	6.749	570.3	γ_4 (23) + τ_4 (13) + γ_{10} (11) + $\rho(2)$ (10)
ν_{74}	526.8	1.569	517.4	(511.0)		511.2	τ_3 (18) + τ_7 (18) + τ_1 (15) + τ_8 (14) + $\rho(2)$ (11)
ν_{75}	448.1	1.043	442.0	(435.0)		435.5	τ_6 (23) + τ_1 (21),γ_{10} (18) + τ_8 (13)
ν_{76}	425.8	0.523	419.6	(414.0)		413.8	τ_6 (38) + τ_9 (11) + γ_4 (10)
ν_{77}	359.3	1.246	355.7	(350.0)		349.2	$\rho(2)$ (23) + γ_4 (16) + τ_1 (13)
ν_{78}	249.1	0.255	241.9	(241.0)		241.1	τ_6 (24) + γ_{10} (23) + τ_9 (15)
ν_{79}	226.0	0.246	185.3	(215.0)		214.8	τ_{ring} (62)
ν_{80}	197.1	0.007	173.3	(189.0)		189.5	τ_{ring} (26) + τ_1 (16) + τ_3 (13)
ν_{81}	137.6	1.599	138.8	(132.0)		132.3	τ_7 (19) + γ_4 (15) + τ_9 (13) + τ_2 (11)
ν_{82}	98.5	0.104	92.9	(94.0)		94.3	τ_4 (26) + τ_9 (15) + τ_7 (13) + τ_3 (12)
ν_{83}	79.6	0.243	-44.6	(77.0)		77.0	τ_{ring} (72)
ν_{84}	63.8	0.323	62.6	(61.0)		60.9	τ_3 (25) + τ_4 (13) + τ_1 (12)

Since the fitting algorithm required all the experimental frequencies, the numbers in parenthesis are introduced as good guesses for $3,9-DMP$ and do not have any other significance. RMS error is 2.5541 cm^{-1} for the fitting of experimental frequencies.

2866.0, 2884.9, and 2867.0 cm^{-1} in the three DMPs. This band is of low intensity in 1,9-DMP and of moderate intensity in the other two isomers. From tables it is clear that the anharmonic frequencies of the antisymmetric/symmetric methyl C-H vibrations are overestimated /underestimated in the DFT calculations by about 20 and 30 cm^{-1} for 6-31G* and 6-311G** basis sets, respectively. It is also found that the absolute intensities of the C-H stretching bands do not match well with the calculated band intensities since the bands are not well resolved.

5.4.2 Spectral region 1700 – 2800 cm^{-1}: Non-fundamental bands

A limited number of bands is observed in this region which do not correspond to any calculated fundamentals (see Table 5.6). Initially, non-fundamental bands are tentatively assigned using calculated anharmonic frequencies obtained at the B3LYP/6-311G** level since the calculated frequencies at the B3LYP/6-31G* level of theory deviate from the frequencies at the B3LYP/6-311G** level by more than 100 cm^{-1} in some instances (see Table 5.3). The assignment is then confirmed by force field fitted frequencies. There are many possibilities for the assignment of the observed non-fundamental bands with the calculated ones. However, we have assigned these bands by correlating with the fundamental bands that are intense.

The band observed at 1915.5 cm^{-1} in 1,9-DMP, 1912.5 cm^{-1} in 2,4-DMP and 1913.8 cm^{-1} in 3,9-DMP can be correlated with the calculated anharmonic band at 1922.4 cm^{-1} in 1,9-DMP, 1952.9 cm^{-1} in 2,4-DMP, and 1931.5 cm^{-1} in 3,9-DMP, respectively. Their respective scaled force field fitted frequencies are 1908.0, 1916.9, and 1919.9 cm^{-1}. This band is assigned to a combination of ($v_{66} + v_{40}$) for 1,9-DMP, ($v_{66} + v_{38}$) for 2,4-DMP and ($v_{65} + v_{39}$) for 3,9-DMP. The next band observed at 1944.8, 1943.1, and 1942.9 cm^{-1} for 1,9-, 2,4- and 3,9-DMP,

respectively, is assigned as the first overtone of ν_{40}, ν_{41} and ν_{39} in 1,9-, 2,4- and 3,9-DMP, respectively.

Table 5.6: Comparison of the observed, anharmonic and force field fitted non-fundamental frequencies (in cm^{-1}).

Compound	Observed		Anharmonic		Fitted	Assignment	
	Freq.	Int.	6-311G**	6-31G*	6-311G**	Overtone	Combination
1,9-DMP	1915.5	2.37	1922.4	1943.7	1908.0		$\nu_{66} + \nu_{40}$
	1944.8	1.18	2078.8	2099.4	2073.0	$2\nu_{40}$	
	2745.5	1.18	2751.0	2817.3	2781.2	$2\nu_{24}$	
2,4-DMP	1912.5	2.05	1952.9	1965.7	1916.9		$\nu_{66} + \nu_{38}$
	1943.1	1.66	1989.0	1997.3	1990.2	$2\nu_{41}$	
	2744.4	1.56	2896.6	2930.0	2908.8	$2\nu_{21}$	
3,9-DMP	1913.8	3.91	1931.5	2159.2	1919.9		$\nu_{65} + \nu_{39}$
	1942.9	2.61	2096.0	2115.3	2081.6	$2\nu_{39}$	
	2743.5	2.39	2774.7	2836.4	2781.6	$2\nu_{24}$	

In the 5th column, ν_i is the frequency of the i-th fundamental vibration. For description see Tables 5.4 and 5.5. All intensities are in km mol^{-1}.

DFT calculated non-fundamental anharmonic band at 2078.8, 1989.0, and 2096.0 cm^{-1} is correlated with the observed ones. This band can also be correlated with the force field fitted frequencies at 2073.0 cm^{-1} in 1,9-DMP, 1990.2 cm^{-1} in 2,4-DMP, and 2081.6 cm^{-1} in 3,9-DMP. Another band found at 2745.5 cm^{-1} in 1,9-DMP, 2744.4 cm^{-1} in 2,4-DMP, and 2743.5 cm^{-1} in 3,9-DMP corresponds to the calculated anharmonic band at 2751.0 cm^{-1} in 1,9-DMP, 2896.6 cm^{-1} in 2,4-DMP, and 2774.7 cm^{-1} in 3,9-DMP which is also a first overtone of ν_{24} for 1,9-

DMP, ν_{21} for 2,4-DMP, and ν_{24} for 3,9-DMP, respectively. Their respective force field fitted frequency is 2781.2 cm^{-1} in 1,9-DMP, 2908.8 cm^{-1} in 2,4-DMP and 2781.6 cm^{-1} in 3,9-DMP. The deviation between observed non-fundamental frequencies and force field fitted frequencies calculated with 6-311G** basis set is found to be 63 cm^{-1} in the worse case. On the otherhand calculated anharmonic frequencies differ by 65 cm^{-1} from the experimental frequencies (see Table 5.3). Therefore, it is clear that for the assignment of non-fundamental bands either scaled force fields or anharmonic calculation can be used.
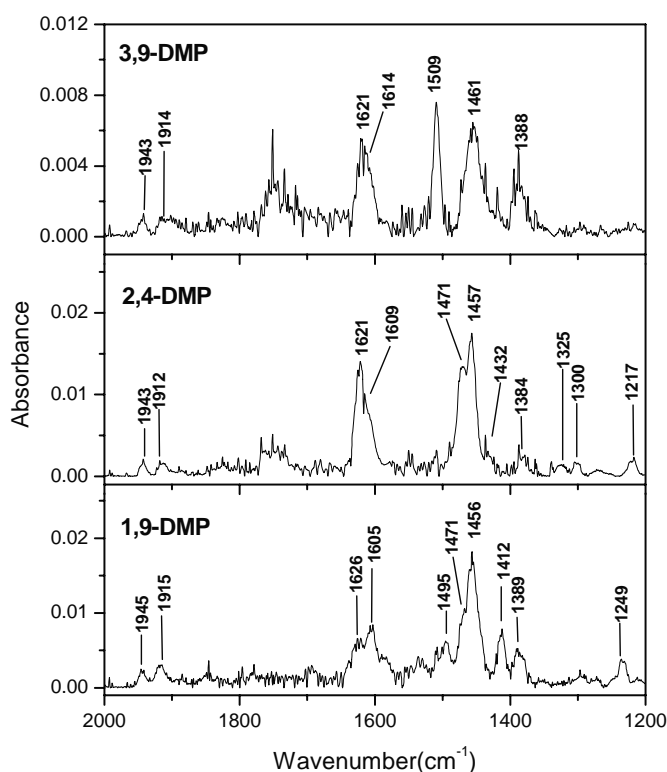
Figure 5.3. Expanded gas phase IR spectra of 1,9-, 2,4- and 3,9 - DMPs from 1200 to 2000 cm^{-1} at 0.5 cm^{-1} resolution.

5.4.3 Spectral region 1200 – 1700 cm^{-1}

Several bands have been identified in this region and they belong to A′ irreducible representation. Assignment in the 1400 - 1700 cm^{-1} region is difficult because of the presence

of H_2O bands. However, we could assign a few bands in this region after subtracting the H_2O spectrum. Bands observed at 1626.5 and 1604.6 cm^{-1} in 1,9-DMP; 1621.4 and 1609.1 cm^{-1} in 2,4-DMP; 1620.8 and 1614.2 cm^{-1} in 3,9-DMP are assigned to aromatic C-C stretching vibrations. Their respective force field fitted frequencies are 1626.9 and 1604.9 cm^{-1} in 1,9-DMP; 1624.0 and 1609.9 cm^{-1} in 2,4-DMP; 1623.6 and 1614.6 cm^{-1} in 3,9-DMP. These bands have low intensity in 1,9-DMP and moderate intensities in 2,4- and 3,9-DMP although they are not well resolved.

Another low intensity band found at 1495.4 cm^{-1} in 1,9-DMP is correlated with the force field fitted frequency at 1495.3 cm^{-1} whereas in 3,9-DMP, another moderate intensity band seen at 1508.8 cm^{-1} corresponds to the force field fitted frequencies at 1507.9 cm^{-1}. This band is assigned to aromatic C-C stretching vibration (R) in 1,9-DMP and aromatic C-H in-plane bending (β) vibrations in 3,9-DMP. A pair of bands seen at 1471.2 and 1456.0 cm^{-1} in 1,9-DMP; 1470.9 and 1457.4 cm^{-1} in 2,4-DMP; 1460.6 and 1453.5 cm^{-1} in 3,9-DMP have been assigned to methyl C-H asymmetric deformation vibrations (δ_s) by comparing with the force field fitted frequencies at 1473.9 and 1455.7 cm^{-1} in 1,9-DMP; 1471.5 and 1460.2 cm^{-1} in 2,4-DMP; 1460.8 and 1453.2 cm^{-1} in 3,9-DMP, respectively. We could not measure individual band intensity in this region since bands are not well separated in the recorded spectra (see Figure 5.3). However, the total intensity of the observed bands is comparable with the sum of the calculated individual band intensity. In 2,4-DMP calculated anharmonic frequency corresponds to observed band at 1470.9 cm^{-1} is underestimated by 60 cm^{-1} with 6-311G** basis set whereas it is overestimated by 25 cm^{-1} with 6-31G* basis set (see Tables 5.4b and 5.5b). A low intensity band observed at 1412.4 cm^{-1} in 1,9-DMP and at 1384.4 cm^{-1} in 2,4-DMP has been assigned to aromatic C-H in-plane bending vibration (β) by comparing with

the scaled force field fitted frequencies at 1413.5 cm^{-1} in 1,9-DMP and 1429.6 cm^{-1} in 2,4-DMP, respectively. This band is not observed in 3,9-DMP, perhaps, it has been masked by the strong band at 1460.6 cm^{-1}.

The next low intensity band observed at 1389.5, 1384.4, and 1388.3 cm^{-1} for 1,9-DMP, 2,4-DMP and 3,9-DMP, respectively, corresponds to the force field fitted frequencies at 1390.6, 1384.4, and 1390.8 cm^{-1} for 1,9-, 2,4-, and 3,9-DMP. This band is unique for different isomers of DMP and is assigned to a mixture of in-plane aromatic ring deformation (δ) and out-of-plane methyl rocking vibration (ρ) in 1,9-DMP, out-of-plane methyl rocking vibration (ρ) in 2,4-DMP and a mixture of out-of-plane methyl rocking (ρ) and aromatic C-C stretching vibrations (R) in 3,9-DMP.

Another low intensity band observed at 1296.1cm^{-1} in 1,9-DMP; 1300.0 cm^{-1} in 2,4-DMP; 1296.0 cm^{-1} in 3,9-DMP is correlated with the force field fitted frequencies at 1295.2 cm^{-1} in 1,9-DMP, 1298.6 cm^{-1} in 2,4-DMP, and 1296.6 cm^{-1} in 3,9-DMP. This band is assigned to aromatic C-C stretching (R) vibration in 1,9- and 2,4-DMP and aromatic C-H in-plane bending (β) vibration in 3,9-DMP. A low intensity band found at 1213.0, 1217.4, and 1215.2 cm^{-1} for 1,9-, 2,4-, and 3,9-DMP, respectively, is assigned to aromatic C-C stretching vibration (R) in 1,9- and 3,9-DMP and aromatic C-H in-plane bending vibration (β) in 2,4-DMP by comparing with the force field fitted frequency at 1213.4, 1218.2, and 1215.9 cm^{-1} for 1,9-, 2,4-, and 3,9-DMP, respectively. The calculated anharmonic frequencies deviates by about 15 and 10 cm^{-1} with the 6-31G* and 6-311G** basis sets, respectively (see Tables 5.4a and 5.5a). On the other hand, the force field fitted frequencies match well within 2 cm^{-1} with the observed frequencies in this region.

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5.4.4 Spectral region 500 – 1200 cm⁻¹

Bands observed in this region belong to both the A′ and A″ irreducible representations. The band observed at 1185.0 cm⁻¹ in 3,9-DMP is assigned to a mixture of aromatic-methyl C-C stretching (R′) and aromatic C-C stretching (R) vibrations by comparing with the force field fitted frequency at 1184.9 cm⁻¹ and DFT predicted anharmonic frequency at 1183.8 cm⁻¹. This band is of low intensity and is not observed in the rest of the isomers of DMP.
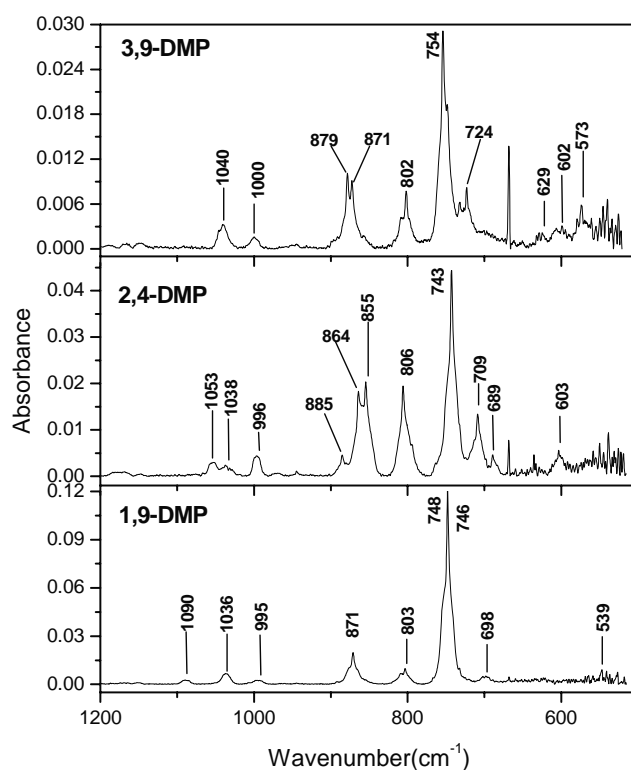
Figure 5.4. Expanded gas phase IR spectra of 1,9-, 2,4- and 3,9 - DMPs from 500 to 1200 cm⁻¹ at 0.5 cm⁻¹ resolution.

A low intensity band observed at 1170.6 cm⁻¹ in 2,4-DMP and 1166.5 cm⁻¹ in 3,9-DMP corresponds to aromatic C-H in-plane bending vibration (β) by comparing with the scaled force fitted frequency at 1169.8 cm⁻¹ in 2,4-DMP and 1167.0 cm⁻¹ in 1,9-DMP, respectively.

The next band observed at 1152.7 cm^{-1} in 1,9-DMP at 1148.6 cm^{-1} in 2,4-DMP, and at 1150.0 cm^{-1} in 3,9-DMP is of low intensity and corresponds to the force field fitted frequencies at 1151.7 cm^{-1} in 1,9-DMP, 1150.3 cm^{-1} in 2,4-DMP and 1146.2 cm^{-1} in 3,9-DMP, respectively. It is assigned to the aromatic C-C stretching vibration (R) in 1,9-DMP, the aromatic C-H in-plane bending vibrations (β) in 2,4-DMP and a mixture of aromatic methyl C-C stretching (R$'$) and aromatic C-H in-plane-bending vibration (β) in 3,9-DMP. Another weak band observed at 1036.4 cm^{-1} in 1,9-DMP, 1053.2 cm^{-1} in 2,4-DMP and 1040.4 cm^{-1} in 3,9-DMP is correlated with the scaled force fitted frequency at 1036.5 cm^{-1} in 1,9-DMP, 1053.9 cm^{-1} in 2,4-DMP and 1040.8 cm^{-1} in 3,9-DMP, respectively. This band is assigned as an aromatic C-C stretching vibration in 1,9- and 2,4-DMP and a mixture of aromatic C-C stretching (R) and aromatic ring deformation vibrations (δ) in 3,9-DMP.

The next one set of low intensity band observed at 995.3, 996.4 and 999.6 cm^{-1} for 1,9-, 2,4- and 3,9-DMP, respectively, is assigned to methyl C-H symmetric deformation vibration(δ_a) for 1,9- and 3,9-DMP whereas in 2,4-DMP it is assigned to an aromatic C-H in-plane bending vibration (β). The respective scaled force field fitted frequency is 993.6, 995.1 and 999.4 cm^{-1} in 1,9-, 2,4- and 3,9-DMP. This band belongs to A$'$ irreducible representation.

A band of low intensity observed at 885.3 cm^{-1} in 2,4-DMP is assigned to a mixture of methyl rocking (ρ) and aromatic C-H out-of-plane (γ) vibration by comparing with the scaled force field fitted frequency at 885.3 cm^{-1}. A moderately intense band observed at 871.4 cm^{-1} in 1,9-DMP is assigned to aromatic C-H in-plane bending vibration (β). On the other hand, in 2,4- and 3,9-DMP this band appears as a doublet, at 864.2 and 855.0 cm^{-1} and 879.1 and 871.7 cm^{-1}, respectively, due to a mixture of local coordinate vibrations of aromatic C-H out-of-plane (γ) and methyl rocking (ρ). A band observed at 803.5 cm^{-1} in 1,9-DMP, 806.4 cm^{-1} in

2,4-DMP and 801.8 cm^{-1} in 3,9-DMP corresponds to the force field fitted frequencies at 801.9 cm^{-1} in 1,9-DMP, 808.5 cm^{-1} in 2,4-DMP and 801.7 cm^{-1} for 3,9-DMP. This band is of moderate intensity and is assigned to the aromatic C-H out-of-plane bending vibration in 1,9-DMP and a mixture of local coordinate vibrations of aromatic-methyl C-C stretching (R) and aromatic C-H out-plane-bending (γ) in 2,4- and 3,9-DMP. A highly intense band observed at 748.3/746.0 cm^{-1} in 1,9-DMP, 742.7 cm^{-1} in 2,4-DMP and 753.9 cm^{-1} in 3,9-DMP corresponds to the force field fitted band at 749.0/746.7 cm^{-1} in 1,9-DMP, 741.4 cm^{-1} in 2,4-DMP and 753.4 cm^{-1} in 3,9-DMP, respectively, which is assigned to the aromatic C-H out-of-plane bending vibration (γ). A band observed at 708.7 cm^{-1} in 2,4-DMP and at 723.6 cm^{-1} in 3,9-DMP is of low intensity and match well with the force field fitted frequency at 708.0 cm^{-1} in 2,4-DMP and 724.1 cm^{-1} in 3,9-DMP, respectively. This band is assigned to a mixture of local coordinate vibrations of torsion around C-C bond (τ) and an aromatic C-H out-of-plane bending (γ).

Next a low intensity band observed at 698.5 cm^{-1} in 1,9-DMP, 688.7 cm^{-1} in 2,4-DMP, and 629.1 cm^{-1} in 3,9-DMP is correlated with the force field fitted frequency at 697.8 cm^{-1} in 1,9-DMP, 688.1 cm^{-1} in 2,4-DMP, and 629.2 cm^{-1} in 3,9-DMP, respectively. This band is assigned to in-plane aromatic ring deformation vibration (δ). A band observed in the lower frequency region such as 603.2 cm^{-1} in 2,4-DMP and 602.1 cm^{-1} in 3,9-DMP is assigned to a mixture of torsion around C-C bond (τ) and aromatic C-H out-of-plane bending (γ) vibration. In this region the fundamental anharmonic frequencies calculated with 6-311G** basis set deviate by about 10 cm^{-1} from the observed ones whereas force field fitted frequencies match within 3 cm^{-1}.

Table 5.7: Comparison of observed aromatic C-H out-of-plane bending, methyl C-H symmetric[a] and asymmetric[b] stretching and aromatic C-H stretching vibrations in DMPs.

Mode of vibration	1,9-DMP	2,4-DMP	3,9-DMP
Aromatic C-H out-of-plane	748.3 (1.000)	742.7 (1.000)	754.0 (1.000)
Methyl C-H stretching	2875.3[a] (0.277)	2882.3[a] (0.397)	2875.0[a] (0.310)
	2905.0[b] (0.067)	2930.8[b] (0.639)	2908.2[b] (0.125)
	2933.5[b] (0.652)	2976.7[b] (0.425)	2933.5[b] (0.829)
Aromatic C-H stretching	3069.7 (0.608)	3057.2 (0.880)	3085.7 (0.307)

[a, b]*methyl C-H symmetric and antisymmetric stretching vibrations, respectively. The band positions are given in cm^{-1} and the intensities in $km\ mol^{-1}$.*

In Table 5.7, I have listed four characteristic bands of DMPs which may help identification of DMPs in a mixture. The aromatic C-H out-of-plane bending vibration (γ) is a highly intense band in the DMPs and is easy to identify around 750 cm^{-1}. The DMPs are clearly distinguishable from this band. A moderately intense band observed in 2885 - 2870 cm^{-1} region is assigned to methyl C-H symmetric stretching vibration in DMPs. Another set of methyl C-H antisymmetric stretching bands observed in the spectral range of (2930 – 2980) cm^{-1} and (2900 – 2930) cm^{-1}, respectively can also help to identify a particular DMP in a mixture. With respect to this vibration, 2,4-DMP isomer is clearly distinguishable from the other two isomers. DMPs are clearly distinguishable with respect to intense aromatic C-H stretching band observed at 3069.7 cm^{-1} in 2,4-DMP, at 3057.2 cm^{-1} in 2,6-DMP, and at 3085.7 cm^{-1} in 2,7-DMP.

5.5 Conclusion

I have reported the gas phase vibrational spectra of 1,9-DMP, 2,4-DMP, and 3,9-DMP at 0.5 cm^{-1} resolution and assigned the spectra using scaled force field frequencies and their PEDs at the B3LYP/6-31G* and B3LYP/6-311G** levels of theory. The anharmonic frequencies, even calculated with an extended basis set, are less accurate for the assignment of the aromatic C-H and methyl C-H stretching fundamental vibrations. But the error in fitting is within 3 cm^{-1} between the observed fundamental vibrations and the scaled force field fitted frequencies emphasizing the need for such calculations in the assignment of the vibrational spectra. I have shown that it is possible to distinguish different isomers of DMPs with the help of the observed intense bands.

5.6 References

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Chapter-6

Is there Intramolecular Hydrogen Bonding in Diols?

An FT-IR and DFT investigation

6.1 Introduction

In the introduction chapter, I have discussed that diols exist in a mixture of conformers with various possibility of intermolecular and intramolecular interaction between two hydroxyl groups. Electron density topological analysis has not shown a bond critical point (BCP) and atomic bond path corresponding to intramolecular hydrogen bonding (IHB) in 1,2 EG.[1a, b] Further, this has been corroborated by X-ray and neutron diffraction studies in the liquid phase[2], NMR spectroscopic study in solution[3], and X-ray study in crystalline form.[4] From the small red-shift in the O–H stretching frequency in the observed mid-IR and their overtone spectrum of 1,2-EG in the gas phase, several author concluded that *gauche* conformers are stabilized by the weak IHB.

An interesting question which arises is that of the extent to which the intramolecular hydrogen bond is found between vicinal hydroxyl groups in 1,2-EG in the gas phase. Infrared red-shifts for the O–H stretching vibration, ranging from a few tens of wavenumbers to many hundred wavenumbers, are frequently used by spectroscopists as an evidence for hydrogen bonding.[5] Combination of theoretical and FT-IR spectroscopic studies of 1,2-EG and 1,4-BD in the gas phase is very limited. A few reports are available in the literature on IR spectroscopic studies of 1,2-EG and 1,4-BD in the gas phase.[6-9] However, experimentally most of these studies are silent about intensity changes which are expected to be there due to intramolecular interaction or IHB formation.

Therefore, my goal of this work is (1) to record the IR spectra of 1,2-EG and 1,4-BD at lowest possible concentrations in the gas phase where intermolecular interaction is minimum/does not exist, (2) to calculate the equilibrium population of each conformers of 1,2-EG and 1,4-BD at experimental temperatures, (3) to identify the conformers of 1,2-EG and

1,4-BD with the help of the simulated population weighted spectrum and the observed spectrum at a particular temperature, and (4) to answer whether intramolecular hydrogen bond (IHB) exist in diols or not by looking at the red-shifts and intensities of the O–H stretching bands in the observed and calculated spectra of 1,2-EG and 1,4-BD. This study is a valuable complement to the computational work which is carried out by Klein for the series of diols.[10]

6.2 Experimental section

The sample 1,2-ethylene glycol ($HOCH_2CH_2OH$, LR grade, Ranbaxy) and 1,4-butanediol ($HOCH_2CH_2CH_2CH_2OH$, 98%, Merck) were used for this study. Details of the experimental set-up have been described in section 2.3.1 of chapter 2. The sample was placed in a ~2 ml bulb mounted on gas cell and degassed by several freeze-pump-thaw cycles, and subsequently pumped on the vacuum line for an hour to remove dissolved gases. The vacuum was then closed and the sample vapor was allowed to equilibrate throughout the vacuum line and gas cell at 303 K and 313 K for 1,2-EG and 1,4-BD, respectively. The sample vapor was then diluted with 100 mmHg Ar (buffer gas) in order to minimize intermolecular interaction. All spectra were recorded with spectral resolution of 0.5 cm^{-1} and averaged over 2048 scans. The spectra were recorded at three different temperatures with the increments of 10 degree Celsius in each stage from the starting temperature to check for existence of intermolecular interaction.

6.3 Computational methods

EG is a typical rotor molecule that can exist in one of the $3^3=27$ conformation. Some of the structures are degenerate due to symmetry, and the number of unique conformations is 10. The 10 conformers are shown in Figure 6.1. In case of 1,4-BD, there are five intramolecular

rotational degrees of freedom with three of them characterizing the backbone structure (OCCC, CCCC and CCCO) and the remaining two are related to the orientation of the two OH groups (HOCC).
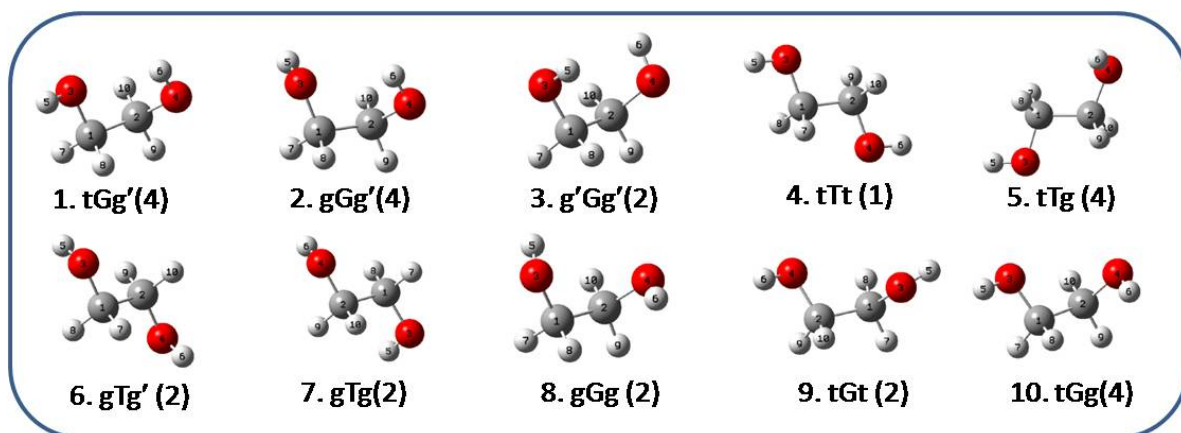
Figure 6.1. The 10 unique conformers of 1,2-EG. The structural degeneracy of each conformer is indicated in parentheses.

The existence of three-fold axis around each of the five dihedral angles can result in a total $3^5 =$ 243 conformation that complicates the structural studies of 1,4-BD. However, symmetry considerations reduce this number to 70 unique conformations. Out of these, 10 conformers were chosen based on the backbone family as shown in Figure 6.2. The conformers are defined according to the following rule: assuming three possible minima per torsion, i.e., *trans* ($180^o \pm 30^o$), +*gauche* ($60^o \pm 30^o$), and –*gauche* ($-60^o \pm 30^o$) abbreviated by t or T, g or G and g′ or G′. Capital letters refer to the backbone structure while the lower case letters refer to the OH orientation and superscript 'prime' indicates the sense of internal rotation corresponding to the negative dihedral angle.

Geometry optimization and frequency calculations on 10 conformers of 1,2-EG and 1,4-BD were carried out at the B3LYP/6-311++G** level of theory. We have carried out

frequency calculations on 10 conformers of 1,2-EG and 1,4-BD to ensure that we were dealing with the true minima and not the transition states or saddle points. In case of the g′Gg′ conformer, however, one imaginary frequency at 75.1 cm^{-1} indicated the presence of a first-order transition point and not a true minimum. This has been pointed by earlier as well.[10] Graphical examination of the DFT calculated vibrational frequencies using Gauss View 3.0, showed that the single imaginary frequency corresponded to a wagging mode vibration for the pendant OH groups. It has been found that geometry optimization of conformer tGt led to another conformer g′Gg′. Therefore conformer tGt is not a true minimum at this level of theory and, thus, we don't consider for the population analysis. All computations were carried out using the Gaussian 03 set of programs.[11]
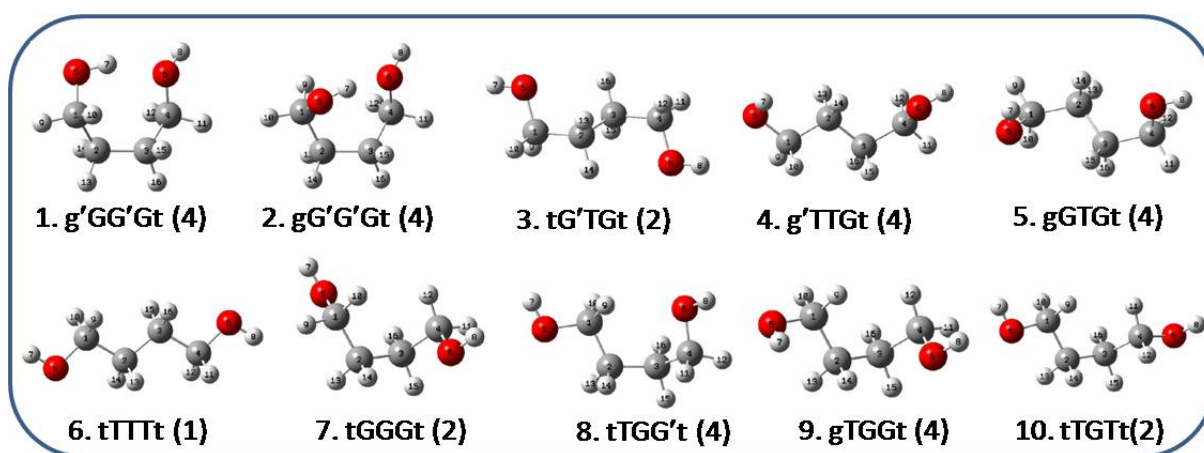
Figure 6.2. Geometries of the most populated conformers of each of the backbone families of 1,4-BDO. The structural degeneracy of each conformer is indicated in parentheses.

I have performed a statistical thermodynamic population analysis with 9 and 10 conformers of 1,2-EG and 1,4-BD, respectively, at experimental temperatures. The purpose of the theoretical population analysis is to predict which conformers contribute to the vibrational

spectra at that temperature. Standard statistical mechanical relationships were used to calculate

the free energies and thus the relative populations of the 9 and 10 conformers of 1,2-EG and

1,4-BD, respectively, in a manner similar to that performed by Cramer and Howard.[8,12] In brief,

the electronic energy values obtained after geometry optimization were corrected with the

zero-point vibrational energy giving total energy at 0 K ($E_o = E_{elc} + ZPE$). Translational,

rotational and vibrational thermal energies were added to this value in order to obtain the

enthalpy ($H = E + RT$, where $E = E_o + E_{vib} + E_{rot} + E_{trans}$) at 298 K for 1,2-EG and 1,4-BD,

respectively. From this quantity and that calculated for the entropy, the Gibbs energy ($G = H -$

TS) was determined. The relative weight of each conformer in the gas phase was obtained

from Boltzmann distribution based on the Gibbs energy.

6.4 Results and discussion

6.4.1 Gas phase infrared spectra of 1,2-EG and 1,4-BD

Figure 6.3 shows the experimental IR absorption spectra of 1,2-EG and 1,4-BD at three

different temperatures. Frequencies, FWHM and band areas of the O–H stretching vibrations

for 1,2-EG and 1,4-BD as a function of temperature are listed in Table 6.1. We note that in the

gas phase both the in/free O–H and the out/bound O–H stretching frequencies can be seen at

experimental temperatures (in and out abbreviation used for two OH groups in 1,2-EG whereas

in 1,4-BD it is free and bound). The frequencies of both of these bands are entirely

independent of temperature since the red-shift (Δv in cm^{-1}) in O–H stretching frequency is

constant as the temperature is increased (see Figure 6.3 and Table 6.1). This implies that there

is no intermolecular interaction. If intermolecular interaction is there the interacted O–H

stretching frequency as well as intensity expected to be changed as function of temperature because this interaction is a concentration dependent phenomenon.
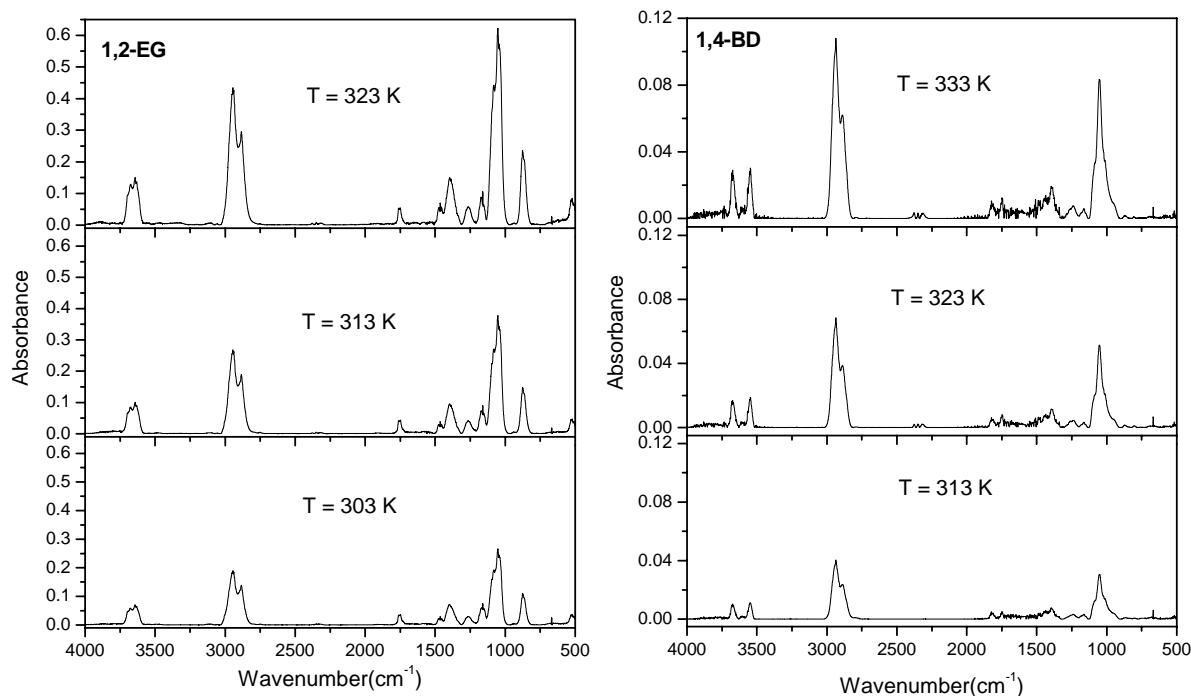
Figure 6.3. Gas phase IR spectra of 1,2-EG and 1,4-BD at three different temperatures (T's). Samples was loaded at the lowest possible temperature, 303 or 313 K for 1,2-EG or 1,4-BD, respectively. Total pressure in the gas cell containing the buffer gas (Ar) and the sample was maintained at 100 mmHg.

Furthermore, it has been found that the ratio of integrated band area (R) of O–H$_{in/bound}$ to the O–H$_{out/free}$ at higher temperatures of 323 K and 333 K for 1,2-EG and 1,4-BD, respectively, is slightly smaller than those at lower temperatures 303 K and 313 K. This clearly implies that the conformational equilibrium between bound (hydrogen bonded) and free (non-hydrogen bonded) forms is shifted towards free forms by a small extent at higher temperature. Out of these three sets of spectra, we have chosen one set of spectrum measured at 303 K in 1,2-EG

and 313 K in 1,4-BD for the identification of conformers in the gas phase by comparing with

the simulated spectrum and for further discussions.

Table 6.1: Frequency (ν, cm^{-1}), FWHM ($\nu_{1/2}$, cm^{-1}), integrated band area (S) and ratio of integrated band area (R = $S_{in/bound}/S_{out/free}$) of O–H absorption bands for 1,2-EG and 1,4-BD observed at three different temperatures.

System	T/K	O–H$_{out/free}$			O–H$_{in/bound}$			R
		ν	$\nu_{1/2}$	S	ν	$\nu_{1/2}$	S	
	303	3682.8	42.3	1.947	3637.5	41.6	2.582	1.326
1,2-EG	313	3682.2	45.3	3.036	3637.3	41.3	3.551	1.169
	323	3681.1	41.2	3.873	3637.7	40.3	4.959	1.280
	313	3672.5	27.2	0.272	3606.5	8.6	8.6 x 10^{-3}	0.031
					3548.4	24.0	0.288	1.058
1,4-BD*	323	3672.5	27.7	0.471	3606.1	11.3	2.2 x 10^{-2}	0.046
					3548.7	25.0	0.475	1.008
	333	3672.5	28.6	0.859	3605.9	15.9	4.9x10^{-2}	0.057
					3549.2	26.6	0.799	0.930

In 1,2-EG, two O–H stretching vibration is defined as O–H$_{in}$ and O–H$_{out}$ whereas in 1,4-BD it is defined as O–H$_{bound}$ and O–H$_{free}$, respectively.

*In 1,4-BD, bands observed at 3606 and 3549 cm^{-1} for bound O–H group which correspond to two hydrogen bonded conformers (see text for details).

6.4.2 Population analysis

The calculated zero point vibrational energy (ZPVE) corrected energies, ΔE_o and relative

free energies, ΔG, of the 9 conformers of 1,2-EG and 10 conformers of 1,4-BD are presented

in Tables 6.2 and 6.3, respectively. Each conformer has a contribution to its free energy of *–RT*

lnω, where ω is the structural degeneracy of conformers listed in Figures 6.1 and 6.2 for 1,2-

EG and 1,4-BD, respectively. The fractional gas-phase equilibrium population *F(M)* of a

conformer M is calculated according to the Boltzmann distribution

$$F(M) = \frac{\exp(-\Delta G_M^0 / RT)}{\sum_i \exp(-\Delta G_i^0 / RT)} ------ (6.1)$$

where *i* spans all the 10 conformers. I have used the *ΔG*^{0} values from Tables 6.2 – 6.3. In

tables, $A(\%) \equiv 100 \times F(M)$.

Calculated % population of chosen conformers of 1,2-EG and 1,4-BD are listed in Table

6.2 and 6.3, respectively. From Table 6.2 it is clear that conformer tGg′ in 1,2-EG is most

populated one followed by gGg′ and g′Gg′ conformers at experimental temperature 303 K. Out

of three, the conformers tGg′ and gGg′ unlikely to have IHB. The experimental spectra of 1,2-

EG match well with the simulated spectra (see discussion in next section). It implies that the

calculated % populations at a particular temperature agree well with the experimental

populations. On the other hand, in 1,4-BD one hydrogen bonded and three non-hydrogen

bonded conformers are most populated at experimental temperature 313 K (see Table 6.3). The

gas phase equilibrium population calculated to be 26.8 and 8.0 % for the hydrogen bonded

conformer g′GG′Gt and gG′G′Gt, respectively and for the non-hydrogen bonded conformers

tG′TGt, g′TTGt and gGTGt it is 17.8, 17.7 and 14.6%, respectively. The discrepancy between

simulated and observed spectra at 313 K has been found in 1,4-BD (see next section) which

clearly indicate that calculated % population of conformers must be different from the

experimental one. Therefore, I have varied the calculated A(%) to find the experimental A(%)

which is designated by "fitted A" as shown in Table 6.3. Now experimental population found

to be 17.8, 4.0, 21.8, 20.7, 17.6, and 6.8 % for g′GG′Gt, gG′G′Gt, tG′TGt, g′TTGt, gGTGt, and tTTTt, respectively. It implies that in spite of IHB, the hydrogen bonded conformers are less stable than some of the non-hydrogen bonded conformers due to steric hindrance.

Table 6.2: Symmetry point groups, relative energies (in kJ mol^{-1}) and equilibrium gas phase populations of the conformers of 1,2-EG at 298 and 303 K at the B3LYP/6-311++G level.**

Conformers of 1,2-EG	Sym (ω)	ΔE_o	ΔG at 298 K	A (%) at 298 K	ΔG at 303 K	A (%) at 303 K	[a]A (%) at 298 K
tGg′	C_1 (4)	0.00	0.00	65.8	0.00	65.2	57.7
gGg′	C_1 (4)	2.34	2.83	20.9	2.84	21.1	25.7
g′Gg′	C_2 (2)	3.27	5.52	7.0	5.55	7.1	10.4
tTt	C_{2h}(1)	8.98	10.31	1.0	10.37	1.1	0.5
tTg	C_1 (4)	10.37	8.02	2.6	8.02	2.7	2.2
gTg′	C_i (2)	10.73	11.19	0.7	11.22	0.7	0.9
gTg	C_2 (2)	11.79	14.00	0.2	14.03	0.2	0.3
gGg	C_2 (2)	10.71	11.12	0.7	11.15	0.7	0.8
tGt[b]	C_2 (2)	---	---	---	---	---	0.8
tGg	C_1 (4)	13.74	10.61	0.9	11.61	0.9	0.8

All energies are relative to the most stable conformer tGg′. Each symmetry point group is associated with the conformational degeneracy (ω) given in the parentheses. Gibbs energies at 298 and 303 K account for the degeneracy by adding an –RT ln(ω) term.

[a]Reported % populations of conformers were obtained using energy calculated at the CCSD (T)/aug-cc-pVTZ level of theory at 298 K.[8]

[b] Not a stationary point at this level of theory.

Table 6.3: Symmetry point groups, relative energies (in kJ mol^{-1}) and equilibrium gas phase populations of the conformers of 1,4-BD at 298 and 313 K at the B3LYP/6-311++G** level.

Conformers of 1,4-BD	Sym (ω)	ΔE_o	ΔG at 298K	A(%) at 298K	ΔG at 313K	A (%) at 313K	*A(%) at 298K	A(%) Fitted	$\Delta G_{Expt.}$ at 313 K
g′GG′Gt	C_1 (4)	0.00	0.00	27.3	0.00	26.7	30.21	17.8	0.53
gG′G′Gt	C_1 (4)	3.78	3.14	7.7	3.14	8.0	17.06	4.0	4.41
tG′TGt	C_i (2)	5.62	0.97	18.5	1.05	17.8	14.51	21.8	0.00
g′TTGt	C_1 (4)	7.28	1.07	17.7	1.07	17.7	15.55	20.7	0.13
gGTGt	C_1 (4)	7.33	1.58	14.4	1.58	14.5	7.04	17.6	0.56
tTTTt	C_{2h}(1)	7.39	4.92	3.7	5.09	3.7	3.54	6.8	3.03
tGGGt	C_2 (2)	9.15	6.90	1.7	6.98	1.8	4.38	1.8	6.49
tGGG′t	C_1 (4)	10.79	4.18	5.0	4.18	5.3	3.45	5.4	3.63
gTGGt	C_1 (4)	11.51	5.75	2.7	5.75	2.9	3.32	2.9	5.24
tTGTt	C_2 (2)	12.00	7.90	1.1	7.99	1.2	0.94	1.2	7.54

All energies are relative to the most stable conformer g′GG′Gt. Each symmetry point group is associated with the conformational degeneracy (ω) given in the parentheses. Gibbs energies at 298 and 313 K account for the degeneracy by adding an –RT ln(ω) term.

*Reported % populations of conformers were obtained using energy calculated at the MP2/6-311G** level of theory at 298 K.[13] For the fitted A(%) value see text.

$\Delta G_{Expt.}$ at 313 K for the chosen 10 conformers were calculated using fitted % population value and equation 6.1.

6.4.3 Identification of conformers

The comparison between the experimental and simulated spectra allows us to verify the presence of the most stable conformers in the gas phase. In order to interpret the experimental

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spectra, we considered 9 conformers out of 27 in 1,2-EG and 10 conformers out of 243

conformers in 1,4-BD. Then we assumed that population of each conformer corresponds to its

weight at the experimental temperature. The calculated intensities of the spectra of each

conformer were weighted by its population as described in Tables 6.2 – 6.3. The calculated

frequencies and their intensities of O–H stretching region of 1,2-EG and 1,4-BD are listed in

Table 6.4 and 6.5, respectively.
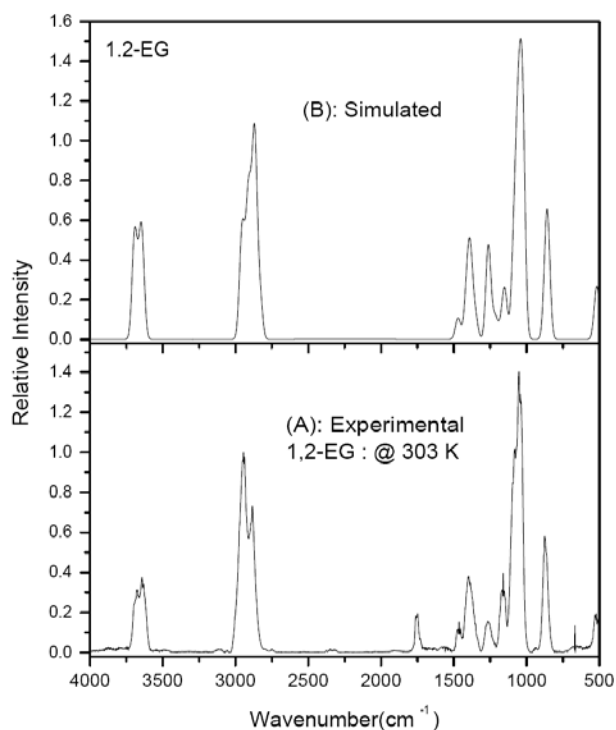
***Figure 6.4. Experimental IR absorption spectrum of 1,2-EG in the gas phase at 303 K (A) and
stimulated spectrum of a mixture of stable conformers tGg′, gGg′ and g′Gg′ (B). The calculated
intensities in the individual spectra of conformers were weighted by the population of the
respective conformer as described in Table 6.2. The frequencies of the calculated spectra were
scaled by two scaling factors: 0.9578 for O–H and methyl C–H stretching frequencies and
0.9824 for frequencies below 1600 cm^{-1}. The simulated spectrum (B) was obtained using
Gaussian functions centered at the scaled frequencies and with a band width at half-height of
35 cm^{-1}.***
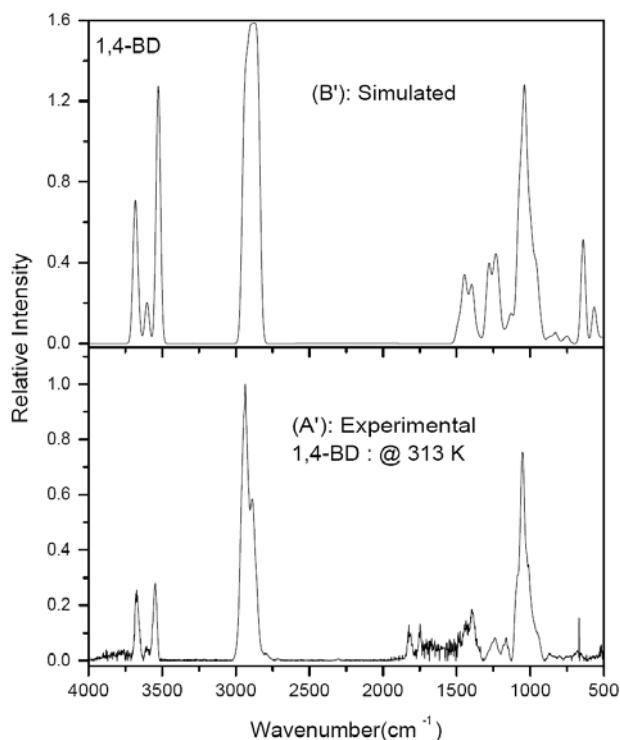
Figure 6.5. Experimental IR absorption spectrum of 1,4-BD in the gas phase at 313 K (A′), stimulated spectrum of a mixture of conformers g′GG′Gt, gG′G′Gt, tG′TGt, g′TTGt, gGTGt, tTTTt, tGGGt, tTGG′t, and gTGGt (B′). The calculated intensities in the individual spectra of conformers were weighted by the population of the respective conformer as described in Table 6.3. The frequencies of the calculated spectra were scaled by two scaling factors: 0.9578 for O–H and methyl C–H stretching frequencies and 0.9824 for frequencies below 1600 cm^{-1}. The simulated spectrum (B′) was obtained using Gaussian functions centered at the scaled frequencies and with a band width at half-height of 35 cm^{-1}.

The experimental and simulated spectra of 1,2-EG and 1,4-BD are presented in Figures 6.4 and 6.5, respectively. The stimulated spectrum (at 303 K) of 1,2-EG, a mixture of most stable conformers: tGg′, gGg′ and g′Gg′ with a contribution of 65.2, 21.1 and 7.1 %, respectively, is shown in Figure 4 (B, upper frame). The simulated spectrum (at 313 K) of 1,4-

BD derived from a mixture of conformers: g′GG′Gt, gG′G′Gt, tG′TGt, g′TTGt, gGTGt, tTTTt, tGGGt, tTGG′t, and gTGGt with weightages of 26.8, 8.0, 17.8, 17.7, 14.6, 3.8, 1.8, 5.4, and 2.9 %, respectively, is shown in Figure 6.4 (B′, upper frame). The conformer, tTGTt was not considered for the simulation of calculated spectrum of 1,4-BD since % population is very low compared to other conformers.

In the O−H stretching region, the gas phase IR spectra of the 1,2-EG exhibit two distinct bands, whereas 1,4-BD exhibits three bands. The higher frequency band appears at 3682.8 and 3672.5 cm^{-1} in 1,2-EG and 1,4-BD, respectively. This band corresponds to the stretching vibration of the out/free O−H group. This absorption band has a contribution of all the conformers which are used for the simulation of the calculated spectra. The second O−H stretching band observed at 3637.5 cm^{-1} in 1,2-EG is assigned to the O−H$_{in}$ stretching vibration. Only two conformers of 1,2-EG (tGg′ and gGg′) are contributed to this band. In 1,4-BD two bands are observed in this region at 3548.4 and 3606.5 cm^{-1}. The appearance of two hydrogen bonded O−H stretching bands provide evidence for the existence of two differently hydrogen bonded conformers, namely gG′G′Gt and g′GG′Gt, respectively. One low intense band observed at 1754.7 and 1820.4 cm^{-1} for 1,2-EG and 1,4-BD, respectively, in the experimental spectrum which is not corresponding to any calculated frequency. Therefore, this band is assigned as a non-fundamental band such overtone or combination band. Detail of the bands assignments have not done in this work since we are interested only to address the question whether IHB exist in vicinal diols or not.

The experimental spectra of 1,2-EG match well with the simulated spectra. It implies that the calculated % populations at particular temperature agree well with experiment. From Figure 6.4 and Table 6.2, it is clear that, in case of 1,2-EG most stable conformers, tGg′, gGg′

and g′Gg′ that the *gauche* conformers are present in the gas phase. On the other hand, in 1,4-BD comparison of the experimental spectrum with the simulated spectra reveals that although frequencies match well, the relative intensities of the bound O–H band observed at 3548.4 and 3606.5 cm^{-1} do not agree well with the simulated spectra (see Figure 6.5). The discrepancy between the observed and calculated relative intensities in 1,4-BD suggests that lowest energy conformers, g′GG′Gt and gG′G′Gt do not exist with 26.8 and 8.0 % population in the equilibrium mixture, respectively, rather it is less than that of the calculated population. We then varied the % population of a few conformers having ΔE_o value below 8 kJ mol^{-1} to simulate the spectrum of 1,4-BD in a way to reproduce the experimental spectrum.
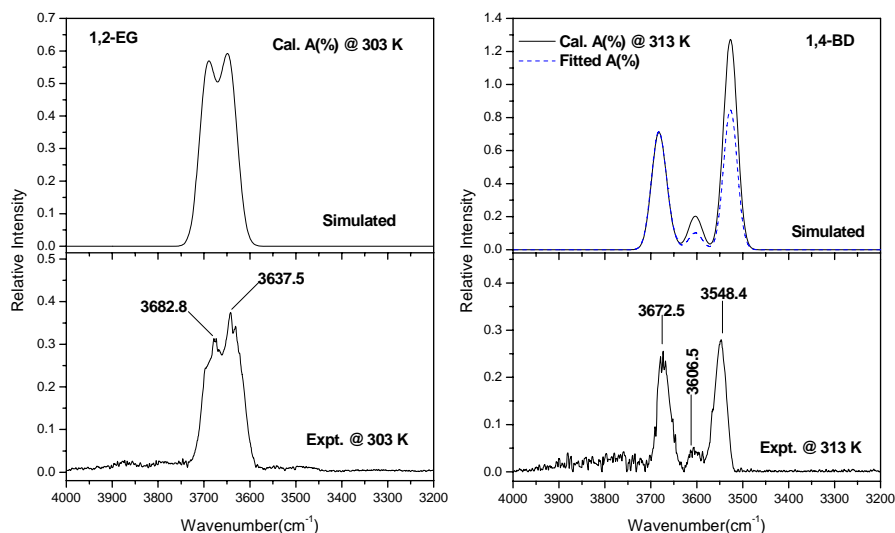
Figure 6.6. Enlarged view of the O–H stretching regions of observed and simulated spectra of 1,2-EG and 1,4-BD. In 1,4-BD, simulated spectra obtained with the calculated and fitted population is shown by solid line (–) and dash line (-----), respectively. See text for the details.

The fitted % population values found by trial and error are 17.8, 4.0, 21.8, 20.7, 17.6, and 6.8 for g′GG′Gt, gG′G′Gt, tG′TGt, g′TTGt, gGTGt, and tTTTt, respectively, as reported in Table

6.3 whereas % population of the rest of the conformers were not changed. The experimental and simulated spectrum in the O–H stretching region of 1,2-EG and 1,4-BD are shown in Figure 6.6.

6.4.4 Estimation of the hydrogen bond energy

The peak frequency shift, $\Delta\nu = (\nu_{out/free} - \nu_{in/bound})$ is commonly used to evaluate the strength of the hydrogen bond and a correlation between this and the enthalpy of the hydrogen bond formation has been reported by several groups. The HB formation enthalpy can be estimated using the empirical equations proposed by Iogansen[14]

$$\Delta H^I = -0.3312(\Delta\nu - 40)^{1/2} - - - - - - - -(6.2)$$

with ΔH^I in kcal mol^{-1} and $\Delta\nu$ in cm^{-1}. This equation is valid only when $\Delta\nu \geq 40$ cm^{-1}. This empirical relation has found a minimum of 40 cm^{-1} for a hydrogen bond induced red shift.

The red-shift in O–H stretching vibration of 1,2-EG found to be 45.3 cm^{-1} which is slightly higher than previously reported[7] value, 33.0 cm^{-1} whereas calculated red-shifts are found to be 47 and 30 cm^{-1} for tGg′ and gGg′ conformers, respectively (see Table 6.4). In calculation, some of the conformers showed very small red-shift of ~2 cm^{-1} in such cases coupled vibrations have been observed between O–H$_{in}$ and O–H$_{out}$ groups (see Table 6.4). In 1,4-BD the red-shift of two bands relative to the O–H$_{free}$ stretching band observed at 3672.5 cm^{-1} are 124.1 and 66.0 cm^{-1} for the g′GG′Gt and gG′G′Gt, respectively. The estimated HB formation enthalpy of the 1,2-EG and 1,4-BD are listed in Tables 6.4 and 6.5, respectively. In 1,2-EG, it is difficult to get HB enthalpy for the individual conformer involved in

intramolecular interaction between two hydroxyl groups from experimental spectrum because bands are not well separated for different conformers.

Table 6.4: Calculated (B3LYP/6-311++G**) O–H stretching frequencies and their intensities (in km mol^{-1}), observed (at 303 K) O–H stretching frequencies (in cm^{-1}) and their band areas (in cm^{-1}), red shifts (in cm^{-1}) between "in" and "out" O–H stretching frequencies, and hydrogen-bond enthalpy in 1,2-EG.

Conformers of 1,2-EG	O–H$_{in}$		O–H$_{out}$		shift	-ΔH^I	Rel. Int.
	Freq.	Int.	Freq.	Int.	cm^{-1}	kcal mol^{-1}	
tGg′	3647.8	42.43	3694.8	44.65	47.0	0.8	0.95
gGg′	3634.6	44.77	3664.0	28.99	29.4		1.54
g′Gg′	3682.2	15.68	3684.0	56.85			
tTt	3692.8	0.00	3693.2	80.16			
tTg	3672.4	26.85	3690.8	38.17			
gTg′	3670.5	58.31	3671.9	0.00			
gTg	3667.3	27.26	3668.1	24.12			
gGg	3664.5	42.40	3665.4	12.02			
tGt	3682.2	15.61	3684.0	56.76			
tGg	3665.7	21.19	3686.0	35.03			
Observed	3637.5	2.228*	3682.8	1.680*	45.3	0.7	1.3
Reported[a]	3644.0		3677.0		33.3		
Reported[b]	3607.0		3642.8		35.6		
Reported[c]	3624.1		3663.2		39.1		

DFT calculated frequencies are scaled by a factor 0.9578. [a] Data taken at 47 ^oC from ref[7]; Data taken from [b]solution phase[15] and [c]matrix-isolation IR spectroscopic study.[16]

*Observed band area weighted by sum of the % population corresponds to conformer **tGg′ and gGg′**.

Table 6.5: Calculated (B3LYP/6-311++G**) O–H stretching frequencies and their intensities (in km mol⁻¹), observed (at 313 K) O–H stretching frequencies (in cm⁻¹) and their band areas (in cm⁻¹), red shifts (in cm⁻¹) between "free" and "bound" O–H stretching frequencies, and hydrogen-bond enthalpy in 1,4-BD.

Conformers of 1,4-BDO	O–H$_{bound}$		O–H$_{free}$		Shift	-ΔH^I	Rel. Int.
	Freq.	Int.	Freq.	Int.	cm⁻¹	kcal mol⁻¹	
g′GG′Gt	3526.7	304.68	3678.0	41.22	151.3	3.5	7.4
gG′G′Gt	3603.1	125.31	3686.0	39.70	82.9	2.1	1.5
tG′TGt	3685.9	64.38	3686.0	0.00			
gGTGt	3662.8	23.05	3686.4	33.66			
g′TTGt	3666.8	22.85	3685.6	35.51			
tTGG′t	3681.7	31.51	3685.4	28.77			
tTTTt	3681.6	62.47	3681.7	0.000			
tGGGt	3685.9	37.38	3686.0	26.13			
gTGGt	3665.3	23.26	3685.5	35.59			
tTGTt	3682.3	40.10	3682.5	22.31			
Observed	3548.4	0.288	3672.5	0.048*	124.1	3.0	6.0
	3606.5	8.6x10⁻³		0.011*	66.0	1.7	0. 8
Reported^a					110.0	2.7	
Reported^b	3474.1		3634.3		160.2	3.6	

DFT calculated frequencies in the O-H stretching region are scaled by a factor 0.9578. [a]Red-shift value taken from ref[6]; [b]Data taken from IR spectroscopic study in CCl₄.[17]

*Band observed at 3672.5 cm⁻¹ in the experimental spectrum corresponds to the free O-H group and its band area has contribution from all the conformers chosen for the calculations. Therefore, observed band area for the hydrogen bonded conformers is obtained by weighted their % population of the total band area at 3672.5 cm⁻¹.

On the other hand, in 1,4-BD, we could calculate the HB enthalpy for two intramolecularly hydrogen bonded conformers since bands are well separated in the experimental spectrum. The HB enthalpy value is more in 1,4-BD compared to that in 1,2-EG as seen in Tables 6.4 and 6.5, respectively. In 1,4-BD, a seven member ring results from the formation of the IHB and energy of formation is maximum whereas in 1,2-EG IHB formation leads to a five member ring whose strain energies nearly cancels out the HB stabilization energy. Another contribution to the enhanced stabilization of the 1,4-BD lies in the possibility of closer approach of the two hydroxyl groups to each other, which is, in turn, reflected in the large O–H stretching frequency shift. From these data we conclude that the intramolecular interaction or intramolecular hydrogen bonding is a major stabilizing factor in the lowest energy conformers for 1,4-BD.

6.4.5 Nature of hydrogen bond in diols

In general, forming of IHB increases the O–H equilibrium distance and thus the magnitude of the electrical transition dipole moment of the O–H stretching mode, which is the reason for the intensity enhancement. In Table 6.6, the values calculated for structural characteristics related with the hydrogen-bonding manifestations for the lowest energy conformers of 1,2-EG and 1,4-BD are displayed.

In 1,4-BD, the formation of an intramolecular hydrogen-bonded conformation involves the distortion of the carbon chain to a gauche arrangement which helps to bring two hydroxyl groups closer to each other. The O–H bond length and H-bonding parameters listed in Table 6.6 clearly show that the calculated shortest HB donor-acceptor distance (H···O), (1.9 – 2.0 Å) found in 1,4-BD is within the criteria defined for the existence of an intramolecular hydrogen

bond proposed by Desiraju and Steiner.[18] However, the deviation of $O_A \cdots H-O_D$ angle from the most favorable geometry (180°) turns this bond into a weak one. In 1,2-EG, the calculated $O_A \cdots H$ bond distance and $O_A \cdots H-O_D$ bond angle lie around 2.4 Å and 106 – 110°, respectively, which is below the criteria of IHB. Furthermore, the $O_A \cdots H$ distance is less than the sum of *van der Walls* radii of O and H (2.6 Å), it is more than the sum of 'hydrogen bond radii' (2.0 Å), appropriate for OH (0.7 Å) and O (1.3 Å), as proposed by Raghavendra et al. in 2006.[19]

Table 6.6: Calculated (B3LYP/6-311++G**) hydrogen bond parameters of lowest energy conformers in 1,2-EG and 1,4-BD.

Compound	Conformer	Hydrogen bonding parameters[a]		
		$O_A \cdots H$ /Å	O_D-H /Å	$\angle O_A \cdots H-O_D$
1,2-EG	tGg′	2.395	0.964	106.4
	gGg′	2.397	0.965	109.6
	tTt		0.961	
1,4-BDO	g′GG′Gt	1.874	0.970	155.9
	gG′G′Gt	2.063	0.967	141.6
	tTTTt		0.961	

[a] O_D = donor oxygen: atom number 4 in 1,2-EG (see Figure 1) and 6 in 1,4-BD (see Figure 2); O_A = acceptor oxygen: atom number 3 in 1,2-EG (see Figure 1) and 5 in 1,4-BD (see Figure 2). One of the non-hydrogen bonded conformers, tTt in 1,2-EG and tTTTt in 1,4-BD listed in the table for the comparison of O_D-H distance with hydrogen bonded conformers.

In 1,2-EG, the small red-shift is found to be 45.3 cm^{-1} (see Table 4). This small red-shift could be due to intramolecular interactions between two hydroxyl groups. It has been predicted by several authors. However, the QCISD/6-311++G** and the B3LYP/6-311G** charge densities of the tGg′ and gGg′ conformers of 1,2-EG do not present any bond path connecting

H_6 and O_3 (see Figure 6.1) as suggested by Mandado et al.[20] This confirms the conclusion obtained by Klein with several DFT levels of calculation that IHB is absent in this compound.[10]

The findings that the crystal structure for 1,2-EG preserves the *gauche* configuration in the crystalline state and a small red-shift of the bound O–H stretching frequencies without changing intensity for intramolecular hydrogen bonding raise its an important question: What is the driving force that maintains the gauche configuration in 1,2-EG in the gas phase if it is not primarily the O–H···O interaction as frequently assumed in the literature? As it has been pointed out by numbers of authors, hyper-conjugative effects such as n_o (O_A-LP electrons) $\Rightarrow$ σ[C-H]* and σ[C-H] $\Rightarrow$ σ[O-H]* are energetically more significant than $n_o \Rightarrow \sigma$[O_D-H]* interaction.[4, 10, 22, 23] This hyper-conjugation effect is likely to be present in molecules containing neighboring C–H and O–H moieties, particularly if the C–H and O–H bonds are in *trans* or in nearly trans configurations which is found in tGg′ and gGg′ conformers of 1,2-EG. The dihedral angle (H_6-O_4-C_2-H_9, see Figure 6.1) is calculated to be -173.6° and 165.9° in tGg′ and gGg′, respectively.

The frequency change occurs as a result of the O···H–O interaction, obscuring hyper-conjugative effects on both $\nu_{out/free}$ and $\nu_{in/bound}$.[21] Using hyper-conjugation method, Howard et al. reported experimental $\Delta\nu$ red-shifts for the two most stable conformers of 1,2-EG (tGg′ and gGg′) of 285 and 173 cm^{-1}, respectively, in the fifth overtone vapor-phase spectra ($\Delta\nu_{OH}$=5).[8] These authors also pointed out that the red-shift within a conformer is not necessarily a measure of hydrogen bonding since the stretching frequency for the 'free' *gauche* O–H in the gGg′ is red-shifted by 208 cm^{-1} at $\Delta\nu_{OH}$=5 compared to the 'free' *trans* O–H group in the tGg′

conformer. Rotation of an open-chain 1,2-diol trans O–H group to either the g+ and g⁻(also known as g and g′) configuration with or without the possibility of interaction with the second O–H group, results in a '*gauche*' red-shift of up to 30 - 40 cm^{-1} for the O–H fundamental. This red-shift is paralleled by an increase in the σ*[O-H] occupancy. Even larger *trans* $\Rightarrow$ *gauche* effect found in strained cyclic diols and it gives red-shift of 50 cm^{-1}. This non-hydrogen bond related red-shifts result from O–H bond weakening due to σ $\Rightarrow$ σ* interactions involving C-C and C-H bond rather than that from interactions with the oxygen lone-pair electrons.[5] As Klein pointed out that increasing the σ* antibonding orbital occupancy in vicinal diols weakens the O–H bond, reducing the stretching force constant and producing a red-shift associated with bond lengthening.[22]

The analysis of the natural bond orbitals demonstrates the HB acceptor oxygen LP electrons to be of the highest energy and lowest energy occupancy for the LP in 1,4-BD with delocalization into the O–H$_D$ antibonding orbital.[14, 22] Reduction in occupancy for the oxygen LP associated with the increase in occupancy for the O–H antibonding orbital is consistent with the energy stabilization. Increasing stability of the interaction between LP and the O–H antibond is associated with increased delocalization and increased occupancy of the O–H antibond. The percentage of s-character of the interacting LP electrons increases markedly in line with the $n_o \Rightarrow$ σ* delocalization. Based on these results, the IHB in 1,4-BD with seven member ring is the most stable.

In 1,2-EG, the intensity between O–H$_{in}$ and O–H$_{out}$ is enhanced by a factor of 1.3 for a mixture of conformers (see Table 6.4) in the observed spectrum (see Figure 6.6). From the Table 6.4 we note that the most stable hydrogen bonded conformers of 1,2-EG, tGg′ has not

shown the intensity enhancement in the O–H$_{in}$ with respect to O–H$_{out}$ stretching vibrations. Although, the second most populated conformer has shown the intensity enhancement by a factor of 1.5 however red-shift value is very small, ~30 cm^{-1} which is below the criteria of ≥40 cm^{-1} in order to have hydrogen bond (see equation 6.2). It clearly indicates that intramolecular hydrogen bond interaction does not exist. On the other hand in 1,4-BD, experimentally, we found that there is a red-shift more than 65 cm^{-1} as well as significant intensity enhancement have been observed between O–H$_{bound}$ and O–H$_{free}$ stretching vibration in the intramolecularly hydrogen bonded conformers (see Figure 6.6) which is consistent with the calculations (see Table 6.5).

6.5 Conclusions

In this work, I have collected the gas phase IR spectra of 1,2-EG and 1,4-BD at three different temperatures. The conformers of 1,2-EG and 1,4-BD have been investigated by means of DFT calculation and experimental methods. The infrared spectra of 1,2-EG and 1,4-BD in the gas phase are found to show a good agreement with a population weighted calculated spectrum. Comparison between the observed and calculated spectra of diols reveals the existence of more than one conformers weighted by the Boltzmann factor in the gas phase. The small red-shift in O–H band position and no significant intensity enhancement compared to the 'out' O–H peak do not support the idea of an intramolecular hydrogen bonding in 1, 2-EG. On the other hand, in 1,4-BD, there is a 124.1 cm^{-1} shift in the O–H stretching frequency and intensity enhancement by a factor of 6.0 (Expt.) for the 'bonded' O–H compared to the 'free' O–H which strongly support the existence of an intramolecular hydrogen bonding in the compound.

6.7 References

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Chapter-7

Concluding remarks and future directions

7.1 Concluding remarks

This work has broadly fulfilled the following objectives: First, it has provided an experimental verification of low concentration (up-to ppm level) IR spectroscopic measurement which is essential for the detection of atmospherically and astronomically important PAHs. The low concentration measurement is essential even for the detection of intramolecular hydrogen bonded conformers in a mixture in the gas phase.

Second, this work has established the potential of the FT-IR spectroscopic technique combined with scaled force field calculations for the identification of different PAHs. We have shown a better agreement between experiment and theory can be achieved by scaling the force fields rather than the frequencies which is a common practice. For assigning the fundamental vibration in aromatic molecules particularly in the aromatic and methyl C-H stretching bands scaled force field methods is absolutely necessary for unambiguous assignment. However, clear identification of Fermi resonances in large molecules such as PAHs is still difficult. It will require selective isotope substitution and careful analysis of the spectra of the substituted compounds.

Third, combined experimental and theoretical IR spectroscopic study on diols evidences that intramolecular hydrogen bonding does not exist in small diols, like 1,2-EG.

7.2 Future direction: Photochemistry of PAHs and time-resolved FT-IR spectroscopy

In section 7.1, I have discussed about potential of the FT-IR spectroscopic technique for the identification of neutral PAHs in the gas phase. There is another potential application of this technique is the investigation of photochemical reactions of PAHs which is important in

the area of atmospheric photochemistry. IR spectroscopy may be used to identify reaction intermediates in a time resolved manner.
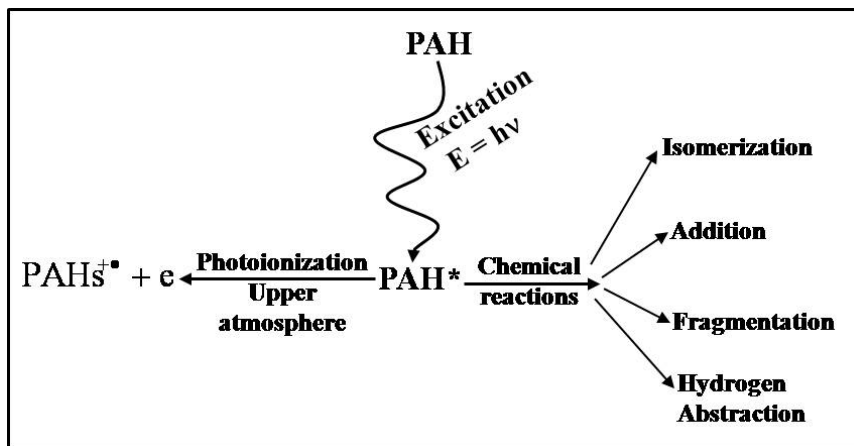
Figure 7.2. Photoionization and some photochemical reactions of PAHs.

Since PAHs cause health hazard it is necessary to destroy them or find some ways to remove them from the atmosphere. There are three effective ways by which PAHs can be removed from the atmosphere: (1) photochemical transformation, (2) photoinduced oxidation (in presence of OH-radicals, NO_3 or O_3) and (3) biological transformation. PAHs can be converted into less toxic materials by any of the above processes.

PAHs have strong UV absorption at ~ 266 nm which is present in the solar radiation and many of them are readily photo-oxidized. A few photochemical along with photoionization processes are shown in Figure 7.1. The photochemical degradation and photoinduced oxidation occur mostly in the gas phase in the upper atmosphere and in the aquatic environment. PAHs are expected to be photoionized at low intensity of incident light whereas at higher intensity photodestruction channel opens up. Subsequently, suitable techniques are needed for the identification of products generated in the photoionization or photodestruction

of PAHs. The step-scan time-resolved FT-IR spectroscopy is one of the suitable methods to obtain spectral and kinetic information on such chemical reactions. In the near future it will be desirable to couple an UV laser with a step-scan FT-IR spectrometer to study the photochemical reactions of PAHs and to characterize the short lived radical or radical-cation of PAHs in the gas phase in laboratory. The time resolved FT-IR spectroscopy of the PAHs followed by their photochemical degradation under UV irradiation may lead us develop possible scavenging schemes for their removal.

Appendix

Symbolic Force constant matrix, unscaled and scaled Force constants in terms of nonredundant local coordinates

TABLE I1: A symbolic Force constant matrix of 2,4-DMQ

```
-----------------------------------------
  Symbolic F matrix  nf= 1235ndim 63
 =========================================
           1     2     3     4     5     6     7     8     9    10    11

 -----------------------------------------------

     1      1    62    63    65    68    72    77    83    90    98   107
     2     62     2    64    66    69    73    78    84    91    99   108
     3     63    64     3    67    70    74    79    85    92   100   109
     4     65    66    67     4    71    75    80    86    93   101   110
     5     68    69    70    71     5    76    81    87    94   102   111
     6     72    73    74    75    76     6    82    88    95   103   112
     7     77    78    79    80    81    82     7    89    96   104   113
     8     83    84    85    86    87    88    89     8    97   105   114
     9     90    91    92    93    94    95    96    97     9   106   115
    10     98    99   100   101   102   103   104   105   106    10   116
    11    107   108   109   110   111   112   113   114   115   116    11
    12    117   118   119   120   121   122   123   124   125   126   127
    13    128   129   130   131   132   133   134   135   136   137   138
    14    140   141   142   143   144   145   146   147   148   149   150
    15    153   154   155   156   157   158   159   160   161   162   163
    16    167   168   169   170   171   172   173   174   175   176   177
    17    182   183   184   185   186   187   188   189   190   191   192
    18    198   199   200   201   202   203   204   205   206   207   208
    19    215   216   217   218   219   220   221   222   223   224   225
    20    215   216   217   218   219   220   221   222   223   224   225
    21    234   235   236   237   238   239   240   241   242   243   244
    22    253   254   255   256   257   258   259   260   261   262   263
    23    253   254   255   256   257   258   259   260   261   262   263
    24    275   276   277   278   279   280   281   282   283   284   285
    25    296   297   298   299   300   301   302   303   304   305   306
    26    318   319   320   321   322   323   324   325   326   327   328
    27    341   342   343   344   345   346   347   348   349   350   351
    28    365   366   367   368   369   370   371   372   373   374   375
    29    390   391   392   393   394   395   396   397   398   399   400
    30    416   417   418   419   420   421   422   423   424   425   426
    31    443   444   445   446   447   448   449   450   451   452   453
    32    471   472   473   474   475   476   477   478   479   480   481
    33    500   501   502   503   504   505   506   507   508   509   510
    34    530   531   532   533   534   535   536   537   538   539   540
    35    561   562   563   564   565   566   567   568   569   570   571
    36    593   594   595   596   597   598   599   600   601   602   603
```

```
37   626   627   628   629   630   631   632   633   634   635   636
38   660   661   662   663   664   665   666   667   668   669   670
39   695   696   697   698   699   700   701   702   703   704   705
40   733   734   735   736   737   738   739   740   741   742   743
41   772   773   774   775   776   777   778   779   780   781   782
42     0     0     0     0     0     0     0     0     0     0     0
43   814   815   816   817   818   819   820   821   822   823   824
44   853   854   855   856   857   858   859   860   861   862   863
45   896   897   898   899   900   901   902   903   904   905   906
46   939   940   941   942   943   944   945   946   947   948   949
47     0     0     0     0     0     0     0     0     0     0     0
48     0     0     0     0     0     0     0     0     0     0     0
49     0     0     0     0     0     0     0     0     0     0     0
50     0     0     0     0     0     0     0     0     0     0     0
51     0     0     0     0     0     0     0     0     0     0     0
52     0     0     0     0     0     0     0     0     0     0     0
53     0     0     0     0     0     0     0     0     0     0     0
54     0     0     0     0     0     0     0     0     0     0     0
55     0     0     0     0     0     0     0     0     0     0     0
56     0     0     0     0     0     0     0     0     0     0     0
57     0     0     0     0     0     0     0     0     0     0     0
58     0     0     0     0     0     0     0     0     0     0     0
59     0     0     0     0     0     0     0     0     0     0     0
60     0     0     0     0     0     0     0     0     0     0     0
61     0     0     0     0     0     0     0     0     0     0     0
62     0     0     0     0     0     0     0     0     0     0     0
63     0     0     0     0     0     0     0     0     0     0     0

=================================================
      12    13    14    15    16    17    18    19    20    21    22


-------------------------------------------------


12    12   139   151   164   178   193   209   226   226   245   264
13   139    13   152   165   179   194   210   227   227   246   265
14   151   152    14   166   180   195   211   228   228   247   266
15   164   165   166    15   181   196   212   229   229   248   267
16   178   179   180   181    16   197   213   230   230   249   268
17   193   194   195   196   197    17   214   231   231   250   269
18   209   210   211   212   213   214    18   232   232   251   270
19   226   227   228   229   230   231   232    19   233   252   271
20   226   227   228   229   230   231   232   233    19   252   272
21   245   246   247   248   249   250   251   252   252    20   273
22   264   265   266   267   268   269   270   271   272   273    21
23   264   265   266   267   268   269   270   272   271   273   274
24   286   287   288   289   290   291   292   293   293   294   295
25   307   308   309   310   311   312   313   314   314   315   316
26   329   330   331   332   333   334   335   336   336   337   338
27   352   353   354   355   356   357   358   359   359   360   361
28   376   377   378   379   380   381   382   383   383   384   385
29   401   402   403   404   405   406   407   408   408   409   410
30   427   428   429   430   431   432   433   434   434   435   436
31   454   455   456   457   458   459   460   461   461   462   463
32   482   483   484   485   486   487   488   489   489   490   491
33   511   512   513   514   515   516   517   518   518   519   520
```

34	541	542	543	544	545	546	547	548	548	549	550
35	572	573	574	575	576	577	578	579	579	580	581
36	604	605	606	607	608	609	610	611	611	612	613
37	637	638	639	640	641	642	643	644	644	645	646
38	671	672	673	674	675	676	677	678	678	679	680
39	706	707	708	709	710	711	712	713	714	715	716
40	744	745	746	747	748	749	750	751	752	753	754
41	783	784	785	786	787	788	789	790	790	791	792
42	0	0	0	0	0	0	0	810	-810	0	811
43	825	826	827	828	829	830	831	832	832	833	834
44	864	865	866	867	868	869	870	871	872	873	874
45	907	908	909	910	911	912	913	914	915	916	917
46	950	951	952	953	954	955	956	957	957	958	959
47	0	0	0	0	0	0	0	981	-981	0	982
48	0	0	0	0	0	0	0	988	-988	0	989
49	0	0	0	0	0	0	0	996	-996	0	997
50	0	0	0	0	0	0	0	1005	-1005	0	1006
51	0	0	0	0	0	0	0	1015	-1015	0	1016
52	0	0	0	0	0	0	0	1026	-1026	0	1027
53	0	0	0	0	0	0	0	1038	-1038	0	1039
54	0	0	0	0	0	0	0	1051	-1051	0	1052
55	0	0	0	0	0	0	0	1065	-1065	0	1066
56	0	0	0	0	0	0	0	1080	-1080	0	1081
57	0	0	0	0	0	0	0	1096	-1096	0	1097
58	0	0	0	0	0	0	0	1113	-1113	0	1114
59	0	0	0	0	0	0	0	1131	-1131	0	1132
60	0	0	0	0	0	0	0	1150	-1150	0	1151
61	0	0	0	0	0	0	0	1170	-1170	0	1171
62	0	0	0	0	0	0	0	1191	-1191	0	1192
63	0	0	0	0	0	0	0	1213	-1213	0	1214

===

| | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |

23	21	295	316	338	361	385	410	436	463	491	520
24	295	22	317	339	362	386	411	437	464	492	521
25	316	317	23	340	363	387	412	438	465	493	522
26	338	339	340	24	364	388	413	439	466	494	523
27	361	362	363	364	25	389	414	440	467	495	524
28	385	386	387	388	389	26	415	441	468	496	525
29	410	411	412	413	414	415	27	442	469	497	526
30	436	437	438	439	440	441	442	28	470	498	527
31	463	464	465	466	467	468	469	470	29	499	528
32	491	492	493	494	495	496	497	498	499	30	529
33	520	521	522	523	524	525	526	527	528	529	31
34	550	551	552	553	554	555	556	557	558	559	560
35	581	582	583	584	585	586	587	588	589	590	591
36	613	614	615	616	617	618	619	620	621	622	623
37	646	647	648	649	650	651	652	653	654	655	656
38	680	681	682	683	684	685	686	687	688	689	690
39	717	718	719	720	721	722	723	724	725	726	727
40	755	756	757	758	759	760	761	762	763	764	765
41	792	793	794	795	796	797	798	799	800	801	802

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42    -811      0      0      0      0      0      0      0      0      0      0
43     834    835    836    837    838    839    840    841    842    843    844
44     875    876    877    878    879    880    881    882    883    884    885
45     918    919    920    921    922    923    924    925    926    927    928
46     959    960    961    962    963    964    965    966    967    968    969
47    -982      0      0      0      0      0      0      0      0      0      0
48    -989      0      0      0      0      0      0      0      0      0      0
49    -997      0      0      0      0      0      0      0      0      0      0
50   -1006      0      0      0      0      0      0      0      0      0      0
51   -1016      0      0      0      0      0      0      0      0      0      0
52   -1027      0      0      0      0      0      0      0      0      0      0
53   -1039      0      0      0      0      0      0      0      0      0      0
54   -1052      0      0      0      0      0      0      0      0      0      0
55   -1066      0      0      0      0      0      0      0      0      0      0
56   -1081      0      0      0      0      0      0      0      0      0      0
57   -1097      0      0      0      0      0      0      0      0      0      0
58   -1114      0      0      0      0      0      0      0      0      0      0
59   -1132      0      0      0      0      0      0      0      0      0      0
60   -1151      0      0      0      0      0      0      0      0      0      0
61   -1171      0      0      0      0      0      0      0      0      0      0
62   -1192      0      0      0      0      0      0      0      0      0      0
63   -1214      0      0      0      0      0      0      0      0      0      0

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        34     35     36     37     38     39     40     41     42     43     44

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34      32    592    624    657    691    728    766    803      0    845    886
35     592     33    625    658    692    729    767    804      0    846    887
36     624    625     34    659    693    730    768    805      0    847    888
37     657    658    659     35    694    731    769    806      0    848    889
38     691    692    693    694     36    732    770    807      0    849    890
39     728    729    730    731    732     37    771    808    812    850    891
40     766    767    768    769    770    771     38    809    813    851    892
41     803    804    805    806    807    808    809     39      0    852    893
42       0      0      0      0      0    812    813      0     40      0    894
43     845    846    847    848    849    850    851    852      0     41    895
44     886    887    888    889    890    891    892    893    894    895     42
45     929    930    931    932    933    892    934    935    936    937    938
46     970    971    972    973    974    975    976    977      0    978    979
47       0      0      0      0      0    983    984      0    985      0    986
48       0      0      0      0      0    990    991      0    992      0    993
49       0      0      0      0      0    998    999      0   1000      0   1001
50       0      0      0      0      0   1007   1008      0   1009      0   1010
51       0      0      0      0      0   1017   1018      0   1019      0   1020
52       0      0      0      0      0   1028   1029      0   1030      0   1031
53       0      0      0      0      0   1040   1041      0   1042      0   1043
54       0      0      0      0      0   1053   1054      0   1055      0   1056
55       0      0      0      0      0   1067   1068      0   1069      0   1070
56       0      0      0      0      0   1082   1083      0   1084      0   1085
57       0      0      0      0      0   1098   1099      0   1100      0   1101
58       0      0      0      0      0   1115   1116      0   1117      0   1118
59       0      0      0      0      0   1133   1134      0   1135      0   1136
60       0      0      0      0      0   1152   1153      0   1154      0   1155
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 61         0     0     0     0     0  1172  1173     0  1174     0  1175
 62         0     0     0     0     0  1193  1194     0  1195     0  1196
 63         0     0     0     0     0  1215  1216     0  1217     0  1218


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          45    46    47    48    49    50    51    52    53    54    55


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 45        43   980   987   994  1002  1011  1021  1032  1044  1057  1071
 46       980    44     0     0     0     0     0     0     0     0     0
 47       987     0    45   995  1003  1012  1022  1033  1045  1058  1072
 48       994     0   995    46  1004  1013  1023  1034  1046  1059  1073
 49      1002     0  1003  1004    47  1014  1024  1035  1047  1060  1074
 50      1011     0  1012  1013  1014    48  1025  1036  1048  1061  1075
 51      1021     0  1022  1023  1024  1025    49  1037  1049  1062  1076
 52      1032     0  1033  1034  1035  1036  1037    50  1050  1063  1077
 53      1044     0  1045  1046  1047  1048  1049  1050    51  1064  1078
 54      1057     0  1058  1059  1060  1061  1062  1063  1064    52  1079
 55      1071     0  1072  1073  1074  1075  1076  1077  1078  1079    53
 56      1086     0  1087  1088  1089  1090  1091  1092  1093  1094  1095
 57      1102     0  1103  1104  1105  1106  1107  1108  1109  1110  1111
 58      1119     0  1120  1121  1122  1123  1124  1125  1126  1127  1128
 59      1137     0  1138  1139  1140  1141  1142  1143  1144  1145  1146
 60      1156     0  1157  1158  1159  1160  1161  1162  1163  1164  1165
 61      1176     0  1177  1178  1179  1180  1181  1182  1183  1184  1185
 62      1197     0  1198  1199  1200  1201  1202  1203  1204  1205  1206
 63      1219     0  1220  1221  1222  1223  1224  1225  1226  1227  1228


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          56    57    58    59    60    61    62    63


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 56        54  1112  1129  1147  1166  1186  1207  1229
 57      1112    55  1130  1148  1167  1187  1208  1230
 58      1129  1130    56  1149  1168  1188  1209  1231
 59      1147  1148  1149    57  1169  1189  1210  1232
 60      1166  1167  1168  1169    58  1190  1211  1233
 61      1186  1187  1188  1189  1190    59  1212  1234
 62      1207  1208  1209  1210  1211  1212    60  1235
 63      1229  1230  1231  1232  1233  1234  1235    61


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TABLE I2: The complete force field in terms of unscaled and scaled nonredundant local coordinate force constants of 2,4-DMQ

Loc. Force constants according to Symf (unscaled)

1	6.2781	2	7.9180	3	6.1247	4	8.6614	5	6.8128
6	6.0318	7	6.4057	8	7.7489	9	6.5595	10	7.7964
11	6.4571	12	4.7106	13	5.5552	14	4.6790	15	5.6384
16	5.6059	17	5.6068	18	5.6669	19	5.2264	20	5.4524
21	5.2348	22	5.3579	23	0.9949	24	0.5643	25	0.9542
26	0.5694	27	0.5568	28	0.5565	29	0.5272	30	1.5533
31	1.4426	32	1.7053	33	1.5177	34	1.4453	35	1.5539
36	0.5912	37	0.6574	38	0.6739	39	0.5967	40	0.5978
41	0.5954	42	0.6686	43	0.6984	44	0.6125	45	0.6065
46	0.5912	47	0.4569	48	0.5892	49	0.4478	50	0.4619
51	0.4699	52	0.4749	53	0.2660	54	0.2089	55	0.2540
56	0.3188	57	0.2715	58	0.3126	59	0.4172	60	0.0177
61	0.0571	62	0.6588	63	-0.5063	64	0.6956	65	0.2421
66	-0.4048	67	0.9636	68	-0.3319	69	0.2595	70	-0.5256
71	0.6727	72	0.6662	73	-0.3012	74	0.0353	75	-0.3336
76	0.8205	77	0.7051	78	-0.1671	79	0.0098	80	-0.2013
81	0.0829	82	0.6410	83	-0.1587	84	0.1605	85	-0.0866
86	0.0798	87	-0.2227	88	-0.2895	89	0.6653	90	-0.0171
91	-0.0852	92	0.2281	93	-0.0990	94	0.0109	95	0.1252
96	-0.4621	97	0.7390	98	-0.2163	99	0.0697	100	-0.0780
101	0.1828	102	-0.1621	103	-0.3054	104	0.2307	105	-0.4124
106	0.7518	107	0.0606	108	-0.1965	109	0.0231	110	-0.1959
111	0.9327	112	0.6357	113	-0.3351	114	0.2151	115	-0.4550
116	0.6561	117	0.3259	118	0.2930	119	-0.0149	120	-0.0721

121 -0.0503 122 -0.0171 123 -0.0049 124 0.0246 125 -0.0180

126 0.0042 127 -0.0100 128 -0.0095 129 0.0983 130 0.0847

131 -0.0046 132 -0.0166 133 -0.0088 134 0.0036 135 0.0009

136 -0.0022 137 0.0006 138 0.0021 139 0.0029 140 -0.0474

141 -0.0397 142 0.3212 143 0.5043 144 0.0300 145 -0.0753

146 -0.0105 147 0.0102 148 -0.0132 149 0.0144 150 -0.0067

151 0.0027 152 0.0081 153 -0.0862 154 -0.0022 155 0.0272

156 0.0323 157 0.0127 158 -0.0598 159 0.0630 160 0.1092

161 0.0180 162 0.0083 163 -0.0135 164 0.0025 165 0.0021

166 0.0017 167 0.0051 168 0.0006 169 -0.0039 170 -0.0004

171 0.0037 172 -0.0134 173 -0.0046 174 0.1070 175 0.1008

176 -0.0049 177 -0.0169 178 0.0003 179 0.0011 180 0.0005

181 0.0110 182 0.0008 183 -0.0020 184 -0.0035 185 0.0008

186 0.0147 187 -0.0118 188 -0.0164 189 -0.0054 190 0.1006

191 0.1103 192 -0.0089 193 0.0003 194 0.0006 195 0.0014

196 0.0035 197 0.0103 198 -0.0021 199 0.0176 200 0.0098

201 0.0038 202 -0.0240 203 -0.0265 204 -0.0189 205 -0.0041

206 0.0028 207 0.0976 208 0.0675 209 0.0013 210 0.0002

211 0.0012 212 0.0015 213 0.0022 214 0.0100 215 -0.0124

216 0.0098 217 -0.0016 218 0.0191 219 0.0069 220 -0.0024

221 0.0039 222 -0.0030 223 0.0018 224 -0.0005 225 0.0013

226 0.0009 227 0.0055 228 0.0943 229 0.0005 230 0.0002

231 0.0003 232 0.0002 233 0.0516 234 0.0108 235 -0.0035

236 0.0006 237 -0.0229 238 -0.0010 239 0.0041 240 -0.0006

241 0.0009 242 -0.0022 243 0.0014 244 -0.0001 245 0.0017

246 -0.0016 247 0.0421 248 -0.0001 249 0.0002 250 0.0001

251 0.0003 252 0.0342 253 -0.0227 254 -0.0054 255 0.0046

256 0.0054 257 -0.0051 258 -0.0001 259 0.0064 260 -0.0052
261 0.0024 262 0.0045 263 0.0013 264 0.1090 265 -0.0016
266 0.0005 267 0.0099 268 0.0000 269 -0.0001 270 0.0000
271 0.0002 272 0.0000 273 0.0004 274 0.0511 275 -0.0049
276 -0.0012 277 0.0026 278 -0.0014 279 0.0077 280 -0.0045
281 -0.0095 282 0.0022 283 0.0020 284 0.0010 285 0.0007
286 0.0532 287 0.0132 288 0.0012 289 -0.0030 290 0.0005
291 0.0005 292 0.0009 293 0.0004 294 -0.0001 295 0.0402
296 -0.3937 297 0.2570 298 0.0371 299 0.0572 300 0.0086
301 -0.0692 302 -0.0640 303 -0.0214 304 0.0422 305 0.0512
306 0.0011 307 0.0417 308 -0.0320 309 0.0084 310 0.0543
311 -0.0006 312 -0.0006 313 -0.0037 314 0.0002 315 0.0025
316 0.0467 317 -0.0664 318 -0.0108 319 -0.2034 320 0.1600
321 0.0218 322 -0.0217 323 0.0187 324 -0.0096 325 -0.0040
326 0.0057 327 0.0022 328 0.0021 329 0.0173 330 0.0043
331 -0.0028 332 0.0001 333 -0.0008 334 0.0001 335 -0.0007
336 0.0033 337 -0.0048 338 0.0011 339 -0.0084 340 -0.0097
341 -0.0374 342 0.0090 343 -0.2290 344 0.4550 345 0.0345
346 -0.0234 347 0.0078 348 -0.0085 349 0.0057 350 -0.0033
351 0.0139 352 -0.0107 353 0.0103 354 0.0391 355 0.0016
356 0.0000 357 0.0010 358 0.0008 359 0.0422 360 -0.0864
361 -0.0023 362 -0.0005 363 -0.0150 364 0.0000 365 0.0324
366 0.0056 367 -0.0001 368 -0.0185 369 0.0026 370 0.0130
371 0.1833 372 -0.1736 373 -0.0180 374 0.0074 375 -0.0205
376 0.0247 377 0.0003 378 0.0005 379 -0.0238 380 0.0087
381 -0.0082 382 -0.0001 383 0.0003 384 -0.0004 385 0.0028
386 -0.0023 387 -0.0391 388 0.0002 389 0.0013 390 0.0082

391 0.0042 392 −0.0053 393 −0.0011 394 −0.0024 395 −0.0160

396 0.0117 397 0.1778 398 −0.1710 399 −0.0128 400 0.0181

401 −0.0001 402 0.0010 403 0.0002 404 −0.0090 405 −0.0013

406 0.0071 407 −0.0074 408 0.0000 409 0.0001 410 0.0001

411 0.0003 412 0.0000 413 −0.0012 414 −0.0002 415 0.0079

416 0.0022 417 0.0030 418 0.0055 419 −0.0054 420 −0.0156

421 0.0113 422 −0.0197 423 0.0136 424 0.1713 425 −0.1723

426 −0.0085 427 −0.0012 428 −0.0003 429 −0.0006 430 0.0085

431 −0.0070 432 0.0007 433 0.0074 434 −0.0001 435 −0.0001

436 −0.0005 437 0.0001 438 −0.0002 439 −0.0002 440 −0.0012

441 −0.0125 442 0.0096 443 −0.0052 444 −0.0112 445 −0.0108

446 −0.0012 447 0.0350 448 0.0199 449 0.0198 450 −0.0265

451 −0.0016 452 0.1656 453 −0.1422 454 −0.0022 455 0.0004

456 −0.0003 457 0.0001 458 0.0079 459 −0.0090 460 −0.0191

461 0.0003 462 −0.0003 463 0.0001 464 −0.0008 465 0.0046

466 0.0010 467 0.0004 468 −0.0020 469 −0.0121 470 0.0088

471 0.1817 472 0.0471 473 −0.0070 474 −0.2611 475 −0.4031

476 0.0120 477 0.2375 478 0.0972 479 0.0005 480 −0.0825

481 −0.2615 482 −0.1799 483 0.1228 484 −0.1822 485 −0.0199

486 0.0076 487 −0.0074 488 0.0143 489 −0.0099 490 −0.0019

491 −0.0099 492 −0.0028 493 −0.0630 494 0.0014 495 −0.0317

496 0.0184 497 0.0132 498 0.0122 499 −0.0041 500 0.2037

501 0.0342 502 −0.2990 503 0.3485 504 0.5235 505 −0.0434

506 0.1596 507 −0.0459 508 −0.1603 509 −0.0288 510 0.1707

511 −0.2473 512 0.0546 513 0.1093 514 −0.0131 515 0.0073

516 0.0064 517 −0.0171 518 0.0041 519 −0.0042 520 −0.0095

521 0.0019 522 −0.0285 523 −0.0758 524 0.0872 525 −0.0140

526   0.0076   527   -0.0073   528   0.0155   529   -0.0071   530   0.0033

531   0.2797   532   0.0865   533   -0.2976   534   -0.0183   535   -0.0818

536   0.2656   537   0.1049   538   -0.0127   539   -0.0896   540   -0.3169

541   0.0257   542   -0.0949   543   0.2166   544   -0.0466   545   0.0034

546   -0.0071   547   0.0248   548   0.0138   549   -0.0080   550   -0.0079

551   -0.0049   552   -0.0352   553   -0.0495   554   0.0278   555   0.0341

556   0.0117   557   0.0127   558   -0.0122   559   0.2020   560   -0.0034

561   0.3114   562   0.1053   563   -0.0064   564   -0.1094   565   -0.3799

566   -0.0020   567   0.1646   568   0.0540   569   -0.0138   570   -0.0476

571   -0.1684   572   0.0084   573   0.0067   574   -0.0062   575   -0.1393

576   0.1081   577   -0.1089   578   0.1181   579   -0.0018   580   0.0001

581   -0.0031   582   0.0011   583   -0.0814   584   -0.0133   585   -0.0119

586   0.0228   587   0.0035   588   0.0032   589   -0.0121   590   0.3554

591   -0.0199   592   0.4026   593   0.2072   594   -0.0528   595   -0.1904

596   -0.0308   597   0.2733   598   -0.0301   599   0.2450   600   0.0578

601   -0.3666   602   0.0785   603   0.2257   604   -0.0039   605   0.0075

606   0.0086   607   -0.1222   608   0.0522   609   0.0508   610   -0.1095

611   0.0005   612   0.0021   613   0.0011   614   -0.0029   615   -0.0284

616   -0.0082   617   0.0032   618   0.0077   619   0.0744   620   -0.0756

621   0.0129   622   -0.0180   623   0.2823   624   -0.0267   625   -0.0115

626   -0.3593   627   -0.1102   628   0.0218   629   0.1076   630   0.3980

631   -0.0391   632   0.0272   633   -0.2696   634   0.0214   635   0.2658

636   0.0165   637   -0.0169   638   -0.0030   639   0.0122   640   0.0440

641   0.0854   642   -0.0839   643   -0.0236   644   0.0026   645   0.0002

646   0.0095   647   -0.0009   648   0.1262   649   0.0118   650   0.0116

651   0.0521   652   -0.0483   653   -0.0486   654   0.0965   655   -0.3733

656   0.0283   657   -0.4179   658   -0.2510   659   0.0138   660   -0.0008

661   0.0000   662   0.0263   663   0.0194   664   0.0200   665   -
0.0095
666   -0.0009   667   0.0008   668   -0.0040   669   0.0043   670   -
0.0017
671   0.0015   672   0.0064   673   0.3046   674   0.0004   675
0.0001
676   0.0005   677   0.0004   678   -0.0693   679   -0.0539   680
0.0001
681   0.0004   682   0.0020   683   0.0029   684   -0.0063   685
0.0001
686   0.0000   687   -0.0001   688   -0.0003   689   -0.0251   690
0.0166
691   0.0205   692   -0.0017   693   0.0033   694   0.0040   695
0.0010
696   -0.0070   697   -0.0174   698   0.0282   699   0.0091   700   -
0.0036
701   -0.0001   702   0.0001   703   -0.0009   704   0.0019   705   -
0.0003
706   -0.0015   707   0.0033   708   -0.0126   709   0.0005   710
0.0000
711   0.0004   712   0.0001   713   0.0946   714   -0.0513   715   -
0.0480
716   -0.0004   717   -0.0005   718   0.0002   719   -0.0028   720
0.0021
721   0.0713   722   0.0004   723   -0.0001   724   -0.0002   725
0.0005
726   0.0050   727   0.0078   728   -0.0049   729   -0.0021   730
0.0010
731   0.0029   732   0.0010   733   0.0018   734   -0.0121   735   -
0.0302
736   0.0488   737   0.0157   738   -0.0062   739   -0.0002   740
0.0001
741   -0.0016   742   0.0034   743   -0.0006   744   -0.0025   745
0.0057
746   -0.0218   747   0.0008   748   0.0001   749   0.0006   750
0.0001
751   -0.0046   752   0.0796   753   -0.0831   754   -0.0008   755   -
0.0007
756   0.0004   757   -0.0049   758   0.0036   759   0.1235   760
0.0007
761   -0.0001   762   -0.0003   763   0.0008   764   0.0087   765
0.0134
766   -0.0085   767   -0.0036   768   0.0017   769   0.0051   770
0.0017
771   0.0143   772   0.0089   773   -0.0118   774   0.0107   775   -
0.0209
776   -0.0012   777   -0.0016   778   -0.0032   779   0.0021   780   -
0.0030
781   0.0025   782   -0.0027   783   -0.0005   784   0.0029   785   -
0.0431
786   0.0000   787   -0.0002   788   -0.0001   789   -0.0001   790
0.0683
791   -0.1043   792   -0.0002   793   0.0002   794   0.0000   795
0.0036

796   -0.0373   797   -0.0001   798   0.0000   799   0.0000   800   -0.0001

801   0.0029   802   0.0001   803   -0.0066   804   0.0002   805   0.0007

806   0.0010   807   -0.0054   808   0.0047   809   0.0082   810   -0.1082

811   -0.0002   812   0.0013   813   -0.0007   814   0.0269   815   0.0168

816   0.0060   817   -0.0130   818   -0.0071   819   0.0052   820   0.0116

821   0.0050   822   -0.0062   823   0.0020   824   -0.0012   825   0.3320

826   0.0081   827   0.0014   828   0.0011   829   0.0003   830   0.0000

831   0.0005   832   0.0004   833   0.0006   834   -0.0708   835   -0.0711

836   0.0136   837   -0.0038   838   -0.0031   839   0.0082   840   0.0003

841   -0.0005   842   -0.0006   843   -0.0228   844   -0.0335   845   0.0046

846   0.0044   847   0.0031   848   -0.0041   849   0.0004   850   -0.0004

851   -0.0007   852   -0.0001   853   -0.0041   854   0.0150   855   -0.0016

856   -0.0061   857   0.0021   858   0.0063   859   0.0161   860   0.0021

861   -0.0078   862   -0.0032   863   -0.0028   864   -0.0228   865   -0.0038

866   0.0002   867   -0.0063   868   -0.0002   869   0.0000   870   -0.0005

871   -0.0001   872   0.0000   873   0.0005   874   0.0907   875   -0.0512

876   -0.0409   877   0.0376   878   0.0021   879   -0.0023   880   0.0060

881   -0.0001   882   -0.0001   883   0.0010   884   0.0134   885   0.0068

886   0.0199   887   0.0038   888   0.0062   889   -0.0076   890   0.0001

891   -0.0011   892   -0.0006   893   -0.0002   894   -0.0007   895   -0.0070

896   -0.0071   897   0.0259   898   -0.0027   899   -0.0105   900   0.0036

901   0.0109   902   0.0279   903   0.0037   904   -0.0135   905   -0.0056

906   -0.0048   907   -0.0395   908   -0.0065   909   0.0004   910   -0.0108

911   -0.0003   912   0.0000   913   -0.0010   914   0.0000   915   -0.0001

916   0.0009   917   -0.0068   918   0.0752   919   -0.0708   920   0.0652

921   0.0037   922   -0.0039   923   0.0103   924   -0.0003   925   -0.0001

926   0.0017   927   0.0233   928   0.0118   929   0.0344   930   0.0066

931 0.0107 932 -0.0132 933 0.0001 934 -0.0018 935 -0.0004
936 0.0004 937 -0.0121 938 0.0259 939 0.0283 940 -0.0046
941 -0.0061 942 -0.0102 943 0.0003 944 0.0027 945 0.0053
946 0.0028 947 -0.0097 948 -0.0036 949 -0.0020 950 -0.0377
951 0.0033 952 -0.0013 953 -0.0034 954 -0.0002 955 -0.0003
956 0.0000 957 -0.0001 958 -0.0002 959 0.0636 960 -0.1186
961 -0.0416 962 -0.0010 963 0.0002 964 0.0102 965 0.0001
966 -0.0005 967 0.0000 968 0.0068 969 -0.0009 970 0.0119
971 0.0097 972 0.0077 973 -0.0123 974 -0.0003 975 0.0000
976 0.0001 977 0.0001 978 -0.0014 979 0.0070 980 0.0121
981 -0.0002 982 -0.1105 983 -0.0001 984 0.0000 985 -0.0001
986 -0.0088 987 0.0051 988 0.0006 989 -0.0313 990 0.0033
991 -0.0019 992 0.0031 993 -0.0994 994 0.0574 995 -0.0140
996 0.0071 997 0.0067 998 0.0027 999 -0.0016 1000 0.0026
1001 0.0185 1002 -0.0107 1003 -0.0082 1004 -0.1036 1005 -0.0309
1006 0.0007 1007 -0.0927 1008 0.0535 1009 0.0001 1010 0.0045
1011 -0.0026 1012 -0.0010 1013 -0.0190 1014 -0.0364 1015 0.0000
1016 0.0033 1017 -0.0002 1018 0.0001 1019 -0.0001 1020 0.0040
1021 -0.0023 1022 0.0096 1023 0.0071 1024 0.0074 1025 0.0020
1026 -0.0002 1027 0.0003 1028 -0.0003 1029 0.0002 1030 0.0001
1031 -0.0007 1032 0.0004 1033 -0.0002 1034 0.0052 1035 -0.0010
1036 0.0011 1037 -0.0872 1038 0.0001 1039 0.0003 1040 0.0007
1041 -0.0004 1042 -0.0002 1043 -0.0004 1044 0.0002 1045 0.0001
1046 0.0006 1047 0.0032 1048 -0.0016 1049 0.0051 1050 -0.0530
1051 0.0000 1052 0.0000 1053 -0.0009 1054 0.0005 1055 -0.0002
1056 -0.0006 1057 0.0003 1058 0.0000 1059 0.0028 1060 0.0006
1061 0.0037 1062 -0.0221 1063 0.0059 1064 -0.0889 1065 0.0098

1066   0.0091   1067   0.0259   1068   -0.0150   1069   -0.0022   1070
0.0314
1071   -0.0181   1072   0.0007   1073   -0.1379   1074   0.1575   1075   -
0.1290
1076   0.0137   1077   -0.0092   1078   0.0071   1079   -0.0190   1080   -
0.0096
1081   0.0028   1082   -0.0279   1083   0.0161   1084   -0.0002   1085
0.0103
1086   -0.0059   1087   0.0073   1088   -0.0407   1089   -0.0408   1090
0.1376
1091   0.0116   1092   -0.0080   1093   -0.0036   1094   -0.0205   1095   -
0.0323
1096   0.0001   1097   -0.0094   1098   0.0168   1099   -0.0097   1100   -
0.0018
1101   -0.0354   1102   0.0204   1103   0.0006   1104   0.1528   1105   -
0.1565
1106   -0.0456   1107   0.0060   1108   0.0051   1109   0.0052   1110   -
0.0107
1111   -0.0587   1112   -0.0253   1113   0.0009   1114   0.0011   1115
0.0024
1116   -0.0014   1117   -0.0005   1118   0.0039   1119   -0.0022   1120
0.0047
1121   -0.0082   1122   0.0119   1123   -0.0089   1124   0.1472   1125   -
0.1583
1126   0.1552   1127   -0.1544   1128   0.0382   1129   0.0078   1130
0.0021
1131   0.0004   1132   0.0016   1133   -0.0006   1134   0.0003   1135   -
0.0003
1136   0.0037   1137   -0.0021   1138   0.0049   1139   -0.0039   1140
0.0085
1141   -0.0005   1142   0.0442   1143   0.0616   1144   -0.1646   1145
0.1192
1146   0.0056   1147   -0.0123   1148   -0.0175   1149   -0.0732   1150
0.0004
1151   -0.0011   1152   0.0023   1153   -0.0014   1154   -0.0002   1155   -
0.0005
1156   0.0003   1157   -0.0027   1158   -0.0059   1159   -0.0051   1160   -
0.0086
1161   -0.1528   1162   0.1534   1163   0.0202   1164   -0.1267   1165
0.0043
1166   -0.0137   1167   0.0123   1168   -0.0414   1169   -0.0348   1170
0.0015
1171   -0.0013   1172   0.0032   1173   -0.0018   1174   -0.0009   1175
0.0070
1176   -0.0040   1177   0.0044   1178   -0.0386   1179   -0.0217   1180   -
0.0204
1181   -0.0292   1182   -0.0182   1183   -0.0220   1184   -0.0483   1185
0.0088
1186   0.0378   1187   -0.0423   1188   0.0047   1189   -0.0276   1190
0.0565
1191   -0.0143   1192   0.0003   1193   0.0148   1194   -0.0085   1195   -
0.0322
1196   0.0010   1197   -0.0006   1198   -0.0001   1199   -0.0034   1200   -
0.0048

```
1201    0.0294   1202    -0.0002   1203     0.0004   1204     0.0004   1205
0.0001
1206   -0.0089   1207     0.0098   1208    -0.0008   1209    -0.0005   1210    -
0.0008
1211    0.0004   1212    -0.0033   1213     0.0001   1214    -0.0253   1215
0.0005
1216   -0.0003   1217    -0.0001   1218     0.0133   1219    -0.0077   1220    -
0.0063
1221    0.0221   1222    -0.0117   1223    -0.0021   1224     0.0110   1225    -
0.0008
1226   -0.0007   1227    -0.0007   1228    -0.0039   1229     0.0067   1230
0.0045
1231    0.0077   1232     0.0076   1233     0.0005   1234     0.0093   1235
0.0001
```


Fitting with nfit= 1(Pulay's method)

Force constants according to Symf 1235 (scaled)

```
   1    5.8185    2     7.4194    3     5.7031    4     7.8897    5
6.4993
   6    5.8089    7     5.8958    8     7.5018    9     6.2178   10
7.3547
  11    6.1504   12     4.4130   13     4.8871   14     4.6767   15
5.1915
  16    4.8935   17     5.0700   18     5.1815   19     4.6878   20
4.7713
  21    4.6815   22     4.7828   23     0.9307   24     0.5325   25
0.9201
  26    0.5285   27     0.5320   28     0.5139   29     0.4942   30
1.5125
  31    1.3571   32     1.6062   33     1.4390   34     1.3914   35
1.4324
  36    0.5454   37     0.6483   38     0.6645   39     0.5535   40
0.5641
  41    0.5638   42     0.6317   43     0.6599   44     0.5821   45
0.5567
  46    0.5530   47     0.4285   48     0.5140   49     0.4409   50
0.4413
  51    0.4185   52     0.4743   53     0.2486   54     0.1968   55
0.2446
  56    0.3066   57     0.2656   58     0.3025   59     0.3930   60
0.0162
  61    0.0535   62     0.6140   63    -0.4704   64     0.6497   65
0.2224
  66   -0.3740   67     0.8875   68    -0.3120   69     0.2454   70    -
0.4954
  71    0.6271   72     0.6294   73    -0.2861   74     0.0334   75    -
0.3125
  76    0.7865   77     0.6512   78    -0.1552   79     0.0091   80    -
0.1843
  81    0.0777   82     0.6035   83    -0.1504   84     0.1529   85    -
0.0822
```

86 0.0749 87 -0.2141 88 -0.2796 89 0.6280 90 -0.0160
91 -0.0803 92 0.2143 93 -0.0920 94 0.0104 95 0.1196
96 -0.4316 97 0.7079 98 -0.2022 99 0.0655 100 -0.0731
101 0.1694 102 -0.1538 103 -0.2911 104 0.2150 105 -0.3941
106 0.7109 107 0.0570 108 -0.1857 109 0.0218 110 -0.1825
111 0.8891 112 0.6088 113 -0.3137 114 0.2065 115 -0.4323
116 0.6219 117 0.3037 118 0.2745 119 -0.0139 120 -0.0666
121 -0.0475 122 -0.0162 123 -0.0046 124 0.0234 125 -0.0170
126 0.0040 127 -0.0095 128 -0.0086 129 0.0892 130 0.0767
131 -0.0041 132 -0.0152 133 -0.0081 134 0.0033 135 0.0008
136 -0.0020 137 0.0005 138 0.0019 139 0.0027 140 -0.0456
141 -0.0384 142 0.3098 143 0.4812 144 0.0293 145 -0.0739
146 -0.0101 147 0.0101 148 -0.0129 149 0.0140 150 -0.0066
151 0.0026 152 0.0076 153 -0.0796 154 -0.0020 155 0.0252
156 0.0296 157 0.0119 158 -0.0563 159 0.0580 160 0.1031
161 0.0169 162 0.0077 163 -0.0126 164 0.0023 165 0.0019
166 0.0016 167 0.0046 168 0.0005 169 -0.0035 170 -0.0004
171 0.0033 172 -0.0123 173 -0.0042 174 0.0984 175 0.0917
176 -0.0044 177 -0.0154 178 0.0003 179 0.0010 180 0.0005
181 0.0099 182 0.0008 183 -0.0018 184 -0.0032 185 0.0007
186 0.0137 187 -0.0110 188 -0.0149 189 -0.0051 190 0.0931
191 0.1019 192 -0.0083 193 0.0002 194 0.0005 195 0.0013
196 0.0032 197 0.0092 198 -0.0019 199 0.0163 200 0.0090
201 0.0034 202 -0.0224 203 -0.0249 204 -0.0173 205 -0.0038
206 0.0026 207 0.0906 208 0.0630 209 0.0012 210 0.0002
211 0.0011 212 0.0014 213 0.0020 214 0.0091 215 -0.0113
216 0.0090 217 -0.0015 218 0.0173 219 0.0064 220 -0.0022

221 0.0035 222 -0.0028 223 0.0016 224 -0.0004 225 0.0012
226 0.0009 227 0.0049 228 0.0893 229 0.0005 230 0.0001
231 0.0003 232 0.0002 233 0.0463 234 0.0097 235 -0.0032
236 0.0005 237 -0.0204 238 -0.0009 239 0.0038 240 -0.0005
241 0.0008 242 -0.0020 243 0.0013 244 -0.0001 245 0.0016
246 -0.0014 247 0.0394 248 -0.0001 249 0.0002 250 0.0001
251 0.0002 252 0.0303 253 -0.0207 254 -0.0050 255 0.0042
256 0.0049 257 -0.0047 258 -0.0001 259 0.0058 260 -0.0048
261 0.0022 262 0.0041 263 0.0012 264 0.0998 265 -0.0015
266 0.0004 267 0.0090 268 0.0000 269 -0.0001 270 0.0000
271 0.0001 272 0.0000 273 0.0004 274 0.0457 275 -0.0044
276 -0.0011 277 0.0024 278 -0.0012 279 0.0071 280 -0.0042
281 -0.0086 282 0.0021 283 0.0018 284 0.0009 285 0.0006
286 0.0486 287 0.0117 288 0.0011 289 -0.0027 290 0.0004
291 0.0004 292 0.0008 293 0.0004 294 -0.0001 295 0.0359
296 -0.3666 297 0.2406 298 0.0346 299 0.0528 300 0.0082
301 -0.0657 302 -0.0594 303 -0.0204 304 0.0397 305 0.0481
306 0.0010 307 0.0391 308 -0.0290 309 0.0081 310 0.0504
311 -0.0005 312 -0.0005 313 -0.0034 314 0.0002 315 0.0022
316 0.0428 317 -0.0607 318 -0.0101 319 -0.1913 320 0.1500
321 0.0202 322 -0.0206 323 0.0178 324 -0.0089 325 -0.0038
326 0.0054 327 0.0021 328 0.0020 329 0.0163 330 0.0039
331 -0.0027 332 0.0001 333 -0.0008 334 0.0001 335 -0.0006
336 0.0031 337 -0.0043 338 0.0011 339 -0.0077 340 -0.0091
341 -0.0354 342 0.0085 343 -0.2170 344 0.4264 345 0.0331
346 -0.0225 347 0.0074 348 -0.0082 349 0.0055 350 -0.0031
351 0.0133 352 -0.0102 353 0.0095 354 0.0384 355 0.0015

356   0.0000   357   0.0009   358   0.0007   359   0.0392   360   −0.0794
361   −0.0021   362   −0.0005   363   −0.0143   364   0.0000   365   0.0301
366   0.0052   367   0.0000   368   −0.0170   369   0.0024   370   0.0123
371   0.1694   372   −0.1646   373   −0.0169   374   0.0069   375   −0.0193
376   0.0230   377   0.0002   378   0.0005   379   −0.0220   380   0.0078
381   −0.0075   382   −0.0001   383   0.0002   384   −0.0003   385   0.0026
386   −0.0021   387   −0.0364   388   0.0002   389   0.0012   390   0.0077
391   0.0040   392   −0.0050   393   −0.0010   394   −0.0023   395   −0.0154
396   0.0110   397   0.1710   398   −0.1627   399   −0.0121   400   0.0172
401   −0.0001   402   0.0009   403   0.0002   404   −0.0085   405   −0.0012
406   0.0066   407   −0.0069   408   0.0000   409   0.0001   410   0.0001
411   0.0003   412   0.0000   413   −0.0012   414   −0.0002   415   0.0074
416   0.0021   417   0.0028   418   0.0051   419   −0.0049   420   −0.0146
421   0.0107   422   −0.0182   423   0.0129   424   0.1602   425   −0.1608
426   −0.0079   427   −0.0011   428   −0.0002   429   −0.0005   430   0.0078
431   −0.0063   432   0.0007   433   0.0068   434   −0.0001   435   −0.0001
436   −0.0005   437   0.0001   438   −0.0001   439   −0.0002   440   −0.0011
441   −0.0116   442   0.0090   443   −0.0049   444   −0.0105   445   −0.0101
446   −0.0011   447   0.0331   448   0.0189   449   0.0184   450   −0.0253
451   −0.0015   452   0.1558   453   −0.1343   454   −0.0020   455   0.0004
456   −0.0003   457   0.0001   458   0.0072   459   −0.0083   460   −0.0176
461   0.0003   462   −0.0003   463   0.0001   464   −0.0007   465   0.0043
466   0.0010   467   0.0004   468   −0.0019   469   −0.0115   470   0.0082
471   0.1726   472   0.0450   473   −0.0067   474   −0.2459   475   −0.3885
476   0.0116   477   0.2248   478   0.0943   479   0.0005   480   −0.0791
481   −0.2519   482   −0.1718   483   0.1136   484   −0.1797   485   −0.0188
486   0.0070   487   −0.0069   488   0.0135   489   −0.0093   490   −0.0018

491 -0.0092 492 -0.0026 493 -0.0601 494 0.0013 495 -0.0307
496 0.0175 497 0.0127 498 0.0115 499 -0.0039 500 0.1902
501 0.0321 502 -0.2798 503 0.3226 504 0.4960 505 -0.0413
506 0.1485 507 -0.0438 508 -0.1513 509 -0.0271 510 0.1616
511 -0.2322 512 0.0497 513 0.1060 514 -0.0122 515 0.0067
516 0.0059 517 -0.0159 518 0.0038 519 -0.0038 520 -0.0087
521 0.0017 522 -0.0268 523 -0.0714 524 0.0831 525 -0.0131
526 0.0072 527 -0.0068 528 0.0146 529 -0.0068 530 0.0031
531 0.2628 532 0.0810 533 -0.2756 534 -0.0173 535 -0.0779
536 0.2473 537 0.1002 538 -0.0120 539 -0.0845 540 -0.3002
541 0.0242 542 -0.0864 543 0.2102 544 -0.0434 545 0.0030
546 -0.0065 547 0.0231 548 0.0126 549 -0.0073 550 -0.0073
551 -0.0045 552 -0.0331 553 -0.0467 554 0.0264 555 0.0319
556 0.0111 557 0.0119 558 -0.0115 559 0.1934 560 -0.0032
561 0.2919 562 0.0992 563 -0.0060 564 -0.1017 565 -0.3613
566 -0.0019 567 0.1537 568 0.0517 569 -0.0131 570 -0.0450
571 -0.1600 572 0.0079 573 0.0061 574 -0.0060 575 -0.1301
576 0.0983 577 -0.1008 578 0.1100 579 -0.0016 580 0.0001
581 -0.0029 582 0.0010 583 -0.0767 584 -0.0126 585 -0.0113
586 0.0214 587 0.0034 588 0.0030 589 -0.0114 590 0.3415
591 -0.0188 592 0.3804 593 0.1957 594 -0.0501 595 -0.1803
596 -0.0288 597 0.2619 598 -0.0289 599 0.2307 600 0.0558
601 -0.3502 602 0.0748 603 0.2161 604 -0.0037 605 0.0069
606 0.0085 607 -0.1150 608 0.0478 609 0.0474 610 -0.1028
611 0.0005 612 0.0020 613 0.0010 614 -0.0027 615 -0.0270
616 -0.0078 617 0.0031 618 0.0073 619 0.0714 620 -0.0713
621 0.0123 622 -0.0174 623 0.2686 624 -0.0255 625 -0.0110

626 -0.3321 627 -0.1024 628 0.0202 629 0.0986 630 0.3732
631 -0.0368 632 0.0251 633 -0.2547 634 0.0200 635 0.2478
636 0.0155 637 -0.0157 638 -0.0027 639 0.0117 640 0.0405
641 0.0766 642 -0.0766 643 -0.0217 644 0.0024 645 0.0002
646 0.0086 647 -0.0009 648 0.1172 649 0.0110 650 0.0110
651 0.0482 652 -0.0454 653 -0.0449 654 0.0897 655 -0.3537
656 0.0263 657 -0.3894 658 -0.2347 659 0.0130 660 -0.0007
661 0.0000 662 0.0244 663 0.0178 664 0.0188 665 -0.0089
666 -0.0008 667 0.0008 668 -0.0038 669 0.0040 670 -0.0016
671 0.0014 672 0.0058 673 0.2925 674 0.0004 675 0.0001
676 0.0005 677 0.0004 678 -0.0630 679 -0.0484 680 0.0001
681 0.0004 682 0.0019 683 0.0027 684 -0.0060 685 0.0001
686 0.0000 687 -0.0001 688 -0.0002 689 -0.0238 690 0.0154
691 0.0191 692 -0.0016 693 0.0031 694 0.0037 695 0.0010
696 -0.0067 697 -0.0167 698 0.0267 699 0.0088 700 -0.0035
701 -0.0001 702 0.0001 703 -0.0009 704 0.0019 705 -0.0003
706 -0.0014 707 0.0031 708 -0.0125 709 0.0005 710 0.0000
711 0.0004 712 0.0000 713 0.0890 714 -0.0483 715 -0.0446
716 -0.0004 717 -0.0004 718 0.0002 719 -0.0027 720 0.0020
721 0.0695 722 0.0004 723 -0.0001 724 -0.0002 725 0.0004
726 0.0049 727 0.0075 728 -0.0047 729 -0.0020 730 0.0010
731 0.0028 732 0.0010 733 0.0017 734 -0.0117 735 -0.0289
736 0.0463 737 0.0153 738 -0.0061 739 -0.0002 740 0.0001
741 -0.0015 742 0.0032 743 -0.0005 744 -0.0024 745 0.0053
746 -0.0217 747 0.0008 748 0.0001 749 0.0006 750 0.0001
751 -0.0044 752 0.0749 753 -0.0772 754 -0.0007 755 -0.0007
756 0.0004 757 -0.0047 758 0.0035 759 0.1204 760 0.0007

761   -0.0001   762   -0.0003   763   0.0008   764   0.0086   765
0.0129
766   -0.0082   767   -0.0035   768   0.0017   769   0.0049   770
0.0017
771   0.0141   772   0.0083   773   -0.0110   774   0.0100   775   -
0.0192
776   -0.0011   777   -0.0015   778   -0.0030   779   0.0020   780   -
0.0028
781   0.0023   782   -0.0025   783   -0.0005   784   0.0026   785   -
0.0415
786   0.0000   787   -0.0001   788   -0.0001   789   -0.0001   790
0.0623
791   -0.0940   792   -0.0002   793   0.0002   794   0.0000   795
0.0033
796   -0.0353   797   -0.0001   798   0.0000   799   0.0000   800   -
0.0001
801   0.0028   802   0.0001   803   -0.0062   804   0.0002   805
0.0007
806   0.0009   807   -0.0050   808   0.0045   809   0.0078   810   -
0.0996
811   -0.0001   812   0.0012   813   -0.0007   814   0.0252   815
0.0158
816   0.0056   817   -0.0121   818   -0.0067   819   0.0049   820
0.0108
821   0.0048   822   -0.0059   823   0.0018   824   -0.0012   825
0.3128
826   0.0074   827   0.0013   828   0.0010   829   0.0003   830
0.0000
831   0.0004   832   0.0003   833   0.0005   834   -0.0651   835   -
0.0654
836   0.0128   837   -0.0035   838   -0.0029   839   0.0077   840
0.0003
841   -0.0004   842   -0.0006   843   -0.0219   844   -0.0317   845
0.0043
846   0.0042   847   0.0030   848   -0.0038   849   0.0004   850   -
0.0004
851   -0.0007   852   -0.0001   853   -0.0038   854   0.0141   855   -
0.0015
856   -0.0056   857   0.0020   858   0.0060   859   0.0150   860
0.0020
861   -0.0074   862   -0.0030   863   -0.0026   864   -0.0215   865   -
0.0034
866   0.0002   867   -0.0058   868   -0.0001   869   0.0000   870   -
0.0005
871   -0.0001   872   0.0000   873   0.0005   874   0.0834   875   -
0.0471
876   -0.0376   877   0.0354   878   0.0020   879   -0.0022   880
0.0056
881   -0.0001   882   0.0000   883   0.0009   884   0.0129   885
0.0064
886   0.0187   887   0.0036   888   0.0059   889   -0.0071   890
0.0000
891   -0.0011   892   -0.0005   893   -0.0002   894   -0.0007   895   -
0.0066

191

896   -0.0066   897   0.0244   898   -0.0025   899   -0.0098   900
0.0034
901   0.0104   902   0.0260   903   0.0035   904   -0.0128   905   -
0.0053
906   -0.0046   907   -0.0372   908   -0.0060   909   0.0003   910   -
0.0101
911   -0.0002   912   0.0000   913   -0.0009   914   0.0000   915   -
0.0001
916   0.0008   917   -0.0062   918   0.0691   919   -0.0651   920
0.0613
921   0.0035   922   -0.0037   923   0.0097   924   -0.0002   925   -
0.0001
926   0.0016   927   0.0223   928   0.0111   929   0.0325   930
0.0062
931   0.0102   932   -0.0124   933   0.0001   934   -0.0017   935   -
0.0004
936   0.0004   937   -0.0115   938   0.0244   939   0.0265   940   -
0.0044
941   -0.0057   942   -0.0095   943   0.0003   944   0.0026   945
0.0050
946   0.0027   947   -0.0092   948   -0.0034   949   -0.0019   950   -
0.0356
951   0.0030   952   -0.0013   953   -0.0032   954   -0.0002   955   -
0.0003
956   0.0000   957   0.0000   958   -0.0002   959   0.0587   960   -
0.1093
961   -0.0393   962   -0.0009   963   0.0002   964   0.0096   965
0.0001
966   -0.0005   967   0.0000   968   0.0066   969   -0.0008   970
0.0113
971   0.0092   972   0.0074   973   -0.0115   974   -0.0003   975
0.0000
976   0.0001   977   0.0001   978   -0.0013   979   0.0066   980
0.0114
981   -0.0002   982   -0.1001   983   -0.0001   984   0.0000   985   -
0.0001
986   -0.0082   987   0.0048   988   0.0006   989   -0.0286   990
0.0031
991   -0.0018   992   0.0029   993   -0.0935   994   0.0540   995   -
0.0130
996   0.0065   997   0.0061   998   0.0026   999   -0.0015   1000
0.0024
1001   0.0174   1002   -0.0101   1003   -0.0076   1004   -0.0971   1005   -
0.0274
1006   0.0006   1007   -0.0860   1008   0.0497   1009   0.0000   1010
0.0041
1011   -0.0023   1012   -0.0009   1013   -0.0172   1014   -0.0329   1015
0.0000
1016   0.0031   1017   -0.0002   1018   0.0001   1019   -0.0001   1020
0.0038
1021   -0.0022   1022   0.0091   1023   0.0068   1024   0.0071   1025
0.0019
1026   -0.0002   1027   0.0003   1028   -0.0003   1029   0.0001   1030
0.0001

1031 −0.0007 1032   0.0004 1033 −0.0002 1034   0.0049 1035   −
0.0009
1036   0.0010 1037 −0.0845 1038   0.0001 1039   0.0003 1040
0.0007
1041 −0.0004 1042 −0.0002 1043 −0.0003 1044   0.0002 1045
0.0001
1046   0.0005 1047   0.0029 1048 −0.0014 1049   0.0048 1050   −
0.0489
1051   0.0000 1052   0.0000 1053 −0.0009 1054   0.0005 1055   −
0.0002
1056 −0.0006 1057   0.0003 1058   0.0000 1059   0.0027 1060
0.0006
1061   0.0034 1062 −0.0219 1063   0.0057 1064 −0.0839 1065
0.0090
1066   0.0083 1067   0.0249 1068 −0.0144 1069 −0.0021 1070
0.0295
1071 −0.0170 1072   0.0007 1073 −0.1289 1074   0.1474 1075   −
0.1165
1076   0.0131 1077 −0.0087 1078   0.0064 1079 −0.0183 1080   −
0.0088
1081   0.0026 1082 −0.0269 1083   0.0155 1084 −0.0001 1085
0.0097
1086 −0.0056 1087   0.0068 1088 −0.0382 1089 −0.0383 1090
0.1248
1091   0.0112 1092 −0.0076 1093 −0.0033 1094 −0.0199 1095   −
0.0304
1096   0.0001 1097 −0.0087 1098   0.0164 1099 −0.0095 1100   −
0.0017
1101 −0.0338 1102   0.0195 1103   0.0006 1104   0.1451 1105   −
0.1488
1106 −0.0418 1107   0.0059 1108   0.0048 1109   0.0048 1110   −
0.0105
1111 −0.0557 1112 −0.0241 1113   0.0008 1114   0.0011 1115
0.0023
1116 −0.0013 1117 −0.0005 1118   0.0037 1119 −0.0021 1120
0.0044
1121 −0.0078 1122   0.0113 1123 −0.0082 1124   0.1432 1125   −
0.1517
1126   0.1436 1127 −0.1513 1128   0.0362 1129   0.0074 1130
0.0021
1131   0.0003 1132   0.0015 1133 −0.0006 1134   0.0003 1135   −
0.0003
1136   0.0035 1137 −0.0020 1138   0.0046 1139 −0.0038 1140
0.0082
1141 −0.0005 1142   0.0434 1143   0.0596 1144 −0.1536 1145
0.1178
1146   0.0053 1147 −0.0118 1148 −0.0170 1149 −0.0710 1150
0.0004
1151 −0.0010 1152   0.0023 1153 −0.0013 1154 −0.0002 1155   −
0.0005
1156   0.0003 1157 −0.0025 1158 −0.0056 1159 −0.0049 1160   −
0.0079
1161 −0.1491 1162   0.1475 1163   0.0188 1164 −0.1245 1165
0.0041

1166   -0.0131   1167   0.0119   1168   -0.0400   1169   -0.0339   1170
0.0014
1171   -0.0012   1172   0.0031   1173   -0.0018   1174   -0.0008   1175
0.0066
1176   -0.0038   1177   0.0040   1178   -0.0362   1179   -0.0204   1180   -
0.0185
1181   -0.0281   1182   -0.0173   1183   -0.0201   1184   -0.0469   1185
0.0083
1186   0.0356   1187   -0.0403   1188   0.0045   1189   -0.0265   1190
0.0540
1191   -0.0130   1192   0.0003   1193   0.0141   1194   -0.0081   1195   -
0.0299
1196   0.0009   1197   -0.0005   1198   -0.0001   1199   -0.0032   1200   -
0.0044
1201   0.0263   1202   -0.0002   1203   0.0003   1204   0.0004   1205
0.0001
1206   -0.0083   1207   0.0091   1208   -0.0007   1209   -0.0004   1210   -
0.0007
1211   0.0004   1212   -0.0031   1213   0.0001   1214   -0.0232   1215
0.0005
1216   -0.0003   1217   -0.0001   1218   0.0125   1219   -0.0072   1220   -
0.0058
1221   0.0207   1222   -0.0110   1223   -0.0019   1224   0.0106   1225   -
0.0007
1226   -0.0006   1227   -0.0007   1228   -0.0036   1229   0.0063   1230
0.0043
1231   0.0074   1232   0.0073   1233   0.0005   1234   0.0087   1235
0.0001

List of Publications

1. Infrared spectra of dimethyl naphthalenes in gas phase, **Prasanta Das**, E. Arunan, Puspendu K. Das, *Vibr. Spectrosc.* **2008**, *47*, 1-9.

2. Production of paclitaxel by Fusarium solani isolated from Taxus celebica, B.V.S.K Chakravarthi, **Prasanta Das**, Kalpana Surendranath, Anjali A. Karande and Chelliah Jayabaskaran, *J. Biosci.* **2008**, *32*, 259–267.

3. Infrared Spectra of Dimethylquinolines in the Gas Phase: Experiment and Theory, **Prasanta Das**, S. Manogaran, E. Arunan and Puspendu K. Das, *J. Phys .Chem. A* **2010**, 114, 8351-8358.

4. Isomeric identification of methylated naphthalenes using gas phase infrared spectroscopy, Shubhadip Chakraborty, **Prasanta Das**, and Puspendu K. Das, **Accepted** in *Ind. J. Phys.* **2010**.

5. Is there Intramolecular Hydrogen Bonding in Diols? An FT-IR and DFT investigation, **Prasanta Das**, Puspendu K. Das and E. Arunan, *Manuscript ready for submission in J. Phys. Chem. A* **2010**.

6. An Experimental and Theoretical investigation of IR spectra of dimethylphenanthrenes in the gas phase, **Prasanta Das**, E. Arunan and Puspendu K. Das, *Manuscript under correction*.