

CONTENTS

CHAPTER NO.	TITLE	PAGE NO.
	ABSTRACT	ii
	LIST OF TABLES	ix
	LIST OF FIGURES	xii
	LIST OF ABBREVIATIONS	xiv
	LIST OF SYMBOLS USED	xvii
1	INTRODUCTION	1
	1.1 Aims and Objectives	1
	1.2 Review of Literature	2
	1.3 Scope of the present work	6
	1.4 Suggestions for future work	6
2	EXPERIMENTAL METHODS	8
	2.1 Crystallization	8
	2.2 Molecular vibrations	8
	2.3 Infrared Spectroscopy	9
	2.3.1 Selection rules	10
	2.3.2 Fourier Transform Infrared Spectroscopy	11
	2.3.3 Sample preparation	13
	2.4 Raman Spectroscopy	14
	2.4.1 Quantum theory of Raman effect	15
	2.4.2 Selection rules	15
	2.4.3 Fourier Transform Raman Spectroscopy	16
	2.5 Factors affecting vibrational spectra	17
	2.5.1 Hydrogen bonding	17
	2.5.2 Hyperconjugation	18
	2.5.3 Inductive effect	18
	2.6 Electronic Spectroscopy	18

	2.6.1	Principle	19
	2.6.2	Electronic transitions	19
	2.6.3	Instrumentation	20
3		COMPUTATIONAL METHODS	23
	3.1	Quantum chemical computation	23
	3.1.1	<i>Ab initio</i> method	23
	3.1.2	Density functional theory	24
	3.2	Gaussian basis sets	25
	3.2.1	STO-3G minimal basis set	25
	3.2.2	6-31G and 6-311G split valence basis sets	26
	3.2.3	6-31G* and 6-311G** polarization basis sets	26
	3.3	Computer Software	27
	3.4	Optimization of geometry	27
	3.5	Normal Coordinate Analysis	28
	3.6	Natural Bond Orbital (NBO) Analysis	30
	3.7	Frontier molecular orbital (FMO) analysis	32
	3.8	Hyperpolarizability	32
	3.9	Mulliken population analysis	33
	3.10	Harmonic oscillator model of aromaticity (HOMA)	34
	3.11	Electron localization function analysis	35
4		VIBRATIONAL SPECTROSCOPIC INVESTIGATION AND NORMAL COORDINATE ANALYSIS OF THE FIBRATE HYPOLIPIDEMIC AGENT 5-(2,5- DIMETHYLPHENOXY)-2,2-DIMETHYL PENTANOIC ACID (GEMFIBROZIL)	36
	4.1	Experimental details	37
	4.1.1	Sample preparation	37
	4.1.2	IR and Raman measurements	37
	4.2	Optimized geometries	37
	4.3	NBO analysis	41
	4.4	Vibrational analysis	43
	4.4.1	Phenyl ring vibrations	45

	4.4.2 Methyl group vibrations	46
	4.4.3 Methylene group vibrations	50
	4.4.4 Carboxylic acid group vibrations	51
	4.5 HOMO – LUMO energy gap	57
	4.6 Mulliken atomic charges	59
	4.7 Conclusion	60
5	AN EXPERIMENTAL AND THEORETICAL APPROACH ON THE MOLECULAR STRUCTURE AND EFFECT OF HYDROGEN BONDING IN THE VIBRATIONAL SPECTRA OF SULFASALAZINE, AN ANTIBACTERIAL DRUG	62
	5.1 Experimental details	63
	5.2 Optimized geometries	64
	5.3 NBO analysis	72
	5.4 Vibrational analysis	76
	5.4.1 Pyridine ring vibrations	79
	5.4.2 Phenyl ring vibrations	83
	5.4.3 Sulfonamide group vibrations	84
	5.4.4 Hydroxyl group vibrations	85
	5.4.5 Carboxylic acid group vibrations	86
	5.5 Harmonic oscillator model of aromaticity (HOMA)	93
	5.6 Conclusion	94
6	ANALYSIS OF VIBRATIONAL SPECTRA OF 4-AMINO-N-(4-METHYL-2-PYRIMIDINYL) BENZENE SULFONAMIDE (SULFAMERAZINE) BASED ON DENSITY FUNCTIONAL THEORY CALCULATIONS	95
	6.1 Experimental details	96
	6.2 Optimized geometries	96
	6.3 Natural bond orbital analysis	101
	6.4 Electron localization function (ELF) analysis	103
	6.5 Vibrational analysis	104
	6.5.1 Pyrimidine ring vibrations	105

	6.5.2	Phenyl ring vibrations	107
	6.5.3	Sulfonamide group vibrations	110
	6.5.4	Methyl group vibrations	116
	6.5.5	Amine group vibrations	117
	6.6	Harmonic oscillator model of aromaticity (HOMA)	117
	6.7	Conclusion	118
7		MOLECULAR MODELING AND SPECTRAL COMPARISON FOR THE CHANGE IN METHYL POSITION OF NITROPHENOL COMPOUNDS 2-METHYL-4-NITROPHENOL AND 3-METHYL-4-NITROPHENOL: A DENSITY FUNCTIONAL THEORETICAL STUDY	119
	7.1	Experimental details	120
	7.1.1	Sample preparation	120
	7.1.2	IR and Raman measurements	120
	7.2	Optimized geometries	120
	7.3	NBO analysis	124
	7.4	Vibrational analysis	127
	7.4.1	Phenyl ring vibrations	130
	7.4.2	Methyl group vibrations	134
	7.4.3	Nitro group vibrations	135
	7.4.4	Hydroxyl group vibrations	142
	7.5	Physiochemical properties	143
	7.6	Conclusion	143
8		DENSITY FUNCTIONAL THEORY STUDIES ON THE MOLECULAR STRUCTURE, SPECTRA (FT-IR, FT-RAMAN AND UV) AND NBO ANALYSIS OF ETHYL CENTRALITE	144
	8.1	Experimental details	144
	8.2	Optimized geometries	145
	8.3	Natural bond orbital analysis	151
	8.4	Vibrational analysis	153

	8.4.1	Phenyl ring vibrations	155
	8.4.2	Ethyl group vibrations	160
	8.4.3	Urea group vibrations	169
	8.5	Electronic absorption spectra	169
	8.6	Hyperpolarizability calculation	171
	8.7	Conclusion	172
9		SUMMARY AND CONCLUSION	173
		REFERENCES	176
		APPENDICES	
	i.	LIST OF PUBLICATIONS	
	ii.	REPRINT OF JOURNAL PUBLICATION	
	iii.	BIO-DATA	