

DECLARATION

I hereby declare that the thesis entitled “**SPECTRAL STUDIES OF SOME POLYATOMIC MOLECULES BASED ON QUANTUM CHEMICAL CALCULATIONS**” submitted to Periyar University in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy in Chemistry** is a record of original research work carried out by me under the guidance and supervision of **Dr. A. SANKAR**, Assistant Professor, Department of Chemistry, Kandaswami Kandar’s College, P. Velur- 638 182 and that it has not formed before the basis for the award of any Degree, Diploma, Associateship, Fellowship or any other similar titles in this or any other University or Institution of higher learning.

Signature of the Candidate

Place:

Date:

(S. P. SARAVANAN)



ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

It is a moment to express my gratitude to those who have contributed greatly to the success of my research work. First of all I would like to thank the almighty.

I am extremely obliged to my most respectable research supervisor **Dr. A. SANKAR**, Assistant Professor, Department of Chemistry, Kandaswami Kandar's College, P.Velur for his kind support with lots of encouragement throughout the whole period of my Ph.D., career. The completion of research work and also this thesis would have not been possible without his patience, desire, precious comments and scientific suggestions.

I express my hearty and sincere gratitude and thanks to **Dr. R. SOMASUNDARAM, M. D.**, Secretary, Kandaswami Kandar's College, P.Velur for providing all facilities to do my research work in successful manner.

I submit my sincere thanks to **Dr. N. THANGARAJ, Principal**, Kandaswami Kandar's College, P. Velur for his kind support in completing my research work.

I thank to **Dr. S. VEDANAYAKI**, Associate Professor and Head, Department of Chemistry, Kandaswami Kandar's College, P.Velur for her keen interest and encouragement for the completion of this study.

My sincere thanks to Doctoral Committee Member **Dr. B. S. KRISHNAMOORTHY**, Assistant Professor, Department of Chemistry, Vivekanandha College of Arts and Sciences for Women (Autonomous), Elayampalayam, Tiruchengode for his kind support, encouragement and assistance in various forms.

I express my heartfelt thanks to **Dr. K. MOHAN KUMAR, Dr. N. LATHA, Dr. M. SENTHIL and Mr. J. PRAKASH** Assistant Professors, Department of Chemistry, Kandaswami Kandar's College, P.Velur for their most valuable support during my research period.

I gratefully acknowledge the help rendered by the **OTHER FACULTY MEMBERS, NON TEACHING STAFF MEMBERS, RESEARCH SCHOLARS**

AND PG STUDENTS Department of Chemistry, Kandaswami Kandar's College, P.Velur for their support during my research period.

I owe a special word of gratitude and thanks to "Vidhya Rathna" **Prof. Dr. M. KARUNANITHI**, Chairman and Secretary, Vivekanandha Educational Institutions and Hospitals, Tiruchengode and Sankari for his valuable support.

I submit my thanks to **Dr. K. PARIMALA**, Trichy for providing Gaussian software for my research work. I also express my sincere thanks to **Prof. Dr. L. R. GOPINATH**, Dean-Research, and **Dr. S. ARCHAYA**, Assistant Professor, Department of Biotechnology, Vivekanandha College of Arts and Sciences for Women (Autonomous), Elayampalayam, Tiruchengode, for their timely help in my thesis work.

I thank to my beloved parent **Mr. S. M. PALANIAPPAN** and **Mrs. K. JAYAMANI** for their co-operation with deep appreciation for their meticulous care and everlasting source of encouragements and love to complete my task.

I express my special thanks to my beloved wife **Mrs. M. SUMATHI** and my lovable daughter **S. NIKHITHA** for their keen desire, patience, moral support and continuous encouragement for my research work.

My heartfull thanks to **Prof. Dr. N. RAJENDRAN**, Principal and Faculty members of Chemistry Department, Vivekanandha Arts and Science College for Women, Sankari for their unflagging support that give me strength and keep me motivated from the beginning to till the end of my research work.

(S. P. SARAVANAN)



PLAGIARISM CERTIFICATE

Declaration by the Candidate

I hereby declare that the thesis entitled **SPECTRAL STUDIES OF SOME POLYATOMIC MOLECULES BASED ON QUANTUM CHEMICAL CALCULATIONS** submitted by me for the award of Ph.D. degree in **CHEMISTRY** is my original contribution and it is not plagiarized or copied from any other thesis/books/ any other copy right materials.

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I hereby declare that the candidate **Mr. S. P. SARAVANAN**, Department of Chemistry, Kandaswami Kandar's College, P Velur, has carried out the Ph. D. programme under my supervision during the period April 2015 to April 2019 and the thesis entitled **SPECTRAL STUDIES OF SOME POLYATOMIC MOLECULES BASED ON QUANTUM CHEMICAL CALCULATIONS** submitted by him is verified and it is not plagiarized or copied from any other thesis/books/any other copy right materials.

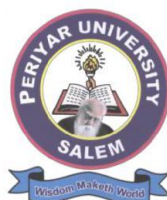
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LIST OF PUBLICATIONS

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1. **Saravanan, S. P.**, Sankar, A. and Parimala, K. Spectroscopic investigations of 2,5-Difluoronitrobenzene using Hartree-Fock (HF) and Density Functional Theory (DFT) calculations. *Journal of Molecular Structure*, 1127 (2017) 784-795.
2. **Saravanan, S. P.**, Sankar, A. and Parimala, K. Vibrational (UV and NMR) analysis of 4-(Trifluoromethoxy)benzylbromide by Density Functional Theory calculations. *International Journal of Scientific Research in Science, Engineering and Technology*, (July-August-2017) 3(5) 296-299.
3. **Saravanan, S. P.**, Sankar, A. and Parimala, K. Vibrational spectral characterization of 2-(Methylamino)pyridine by Hybrid Functional Theory calculations. *International Journal of Science and Research Methodology*, 7(3) (September 2017) 74-82.
4. **Saravanan, S. P.**, Sankar, A. and Parimala, K. Structure, spectroscopic measurement of 4-(Diethoxymethyl)benzaldehyde. *International Journal of Scientific Research in Science and Technology*, 4(2) (2018) 42-45.
5. **Saravanan, S. P.**, Sankar, A. and Parimala, K. Synthesis and spectroscopic characterization of 2-Chloro-5-(trifluoromethyl)benzotrile an experimental and theoretical approach. Communicated to *Journal of Molecular Structure*.



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ABBREVIATIONS

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TFMBN	2-Chloro-5-(Trifluoromethyl)benzonitrile
CC	Couple Cluster
DEMB/DTMB	4-(Diethoxymethyl)benzaldehyde
DNB	2,5 Difluronitrobenzene
DFT	Density Functional Theory / Hybrid Functional Theory
FF	Fukui Function
FT-IR	Fourier Transform Infrared
GIAO	Gauge Independent Atomic Orbital
GTO	Gaussian Type Orbital
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
HOFF	Hybrid Orbital Force Field
IRC	Intrinsic Reaction Coordinate
LSDA	Local Spin-Density Apporximation
LUMO	Lowest Unoccupied Molecular Orbital
MAP	2-(Methylamino)Pyridine
MEP	Molecular Electrostatic Potential
NBO	Natural Bond Orbital
NLO	Non-Linear Optical
NCA	Normal Coordinate Analysis
NMR	Nuclear Magnetic Resonance
OVFF	Orbital Valence Force Field
PPP	Parisor-Parr-Pole
PED	Potential Energy Distribution
QCC	Quantum Chemical Calculations
RSPT	Rayleigh Schordinger Perturbation Theory
SQM	Scaled Quantum Mechanical
SCF	Self-Consistent Procedure
SAM	Semi Ab initio Method
SHM	Simple Huckle Method
STO	Slater Type Orbital
TD-DFT	Time Dependent -Density Functional Theory
TMB	4-(Trifluoromethoxy)benzylbromide
UV-Vis	Ultra Violet-Visible
UBFF	Urey-Bradley Force Field
MPPT	Moller Plesset Perturbation Theory
EHM	Extende Huckle Method



Preface

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PREFACE AND REVIEW OF LITERATURE

Vibrational spectroscopy is an important tool for the elucidation of molecular structure and gives a dynamical picture of the polyatomic molecule. The study of vibrational spectroscopy provides wealth of data on the vibrations of polyatomic molecules, which, when properly interpreted, yields information regarding the molecular structure, bonds holding the structure, forces behind the bonds, interplay between the inter molecular forces, molecular dynamics etc. Infrared spectroscopy is a mature research tool, which has enjoyed a renaissance in recent years due to the introduction of Fourier transform techniques. The qualitative interpretation of IR spectroscopy has been enhanced by the computer assisted data analysis and the infrared spectrum pictures the vibrational modes of the molecule and has enfolded within much information on chemical structure.

Raman spectroscopy is also an important spectroscopic technique which provides more structural insights into the molecular structures. In conventional Raman spectroscopy, the strongly interfering fluorescence has always been a great nuisance and obscures the Raman signal. Introduction of FT-Raman spectroscopy has been a great boon to reduce the problems occurred in classical Raman spectroscopy. It has allowed the study of materials that were previously “impossible” because of fluorescence and provides ready access in the extensive data handling facilities that are available with a commercial FT-IR spectrometer. Thus, Raman scattering has been proved to be a powerful technique, complementary to in elastic neutron scattering and infrared spectroscopy.

The electronic absorption spectroscopy can be used quite extensively to study the energies involved in the electronic transitions and to explain the effect of different substituents and their positions. The electronic spectra of a molecule when recorded in a solvent generally shifts the band in comparison to those obtained in a vapour phase. This is called solvent shift effect and is believed to arise due to the weak physical interactions between the solute and solvent molecules. The interactions are classified as specific effects, whereas the former includes hydrogen bonding, ionization, charge

transfer and molecular aggregation, the later are due to the dispersive, inductive and electrostatic forces occurring between the solute and the surrounding molecules. The spectra of the solutions of different polyatomic molecules in various polar and non-polar solvents shift either towards shorter wavelength (blue shift) or towards longer wavelength (red shift). The $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions are red shifted while the $n \rightarrow \pi^*$ transition is blue shifted as the ground state is more stabilized than the excited stated.

Nuclear Magnetic Resonance (NMR) has been extensively used as a very sensitive tool for probing the various phenomena in the solid state. As the effectiveness of the method mostly depends on the sensitivity and perfectness of the electronic instrumentation adopted for the NMR spectrometer design, great importance and care have to be devoted towards the different aspects of the instrumentation involved. The present thesis elucidates an altogether novel and innovative approach to instrumentation for wideline NMR aimed at achieving enhanced performance of the spectrometer. The spectrometer thus designed, with improved instrumental capabilities has then been successfully utilised for carrying investigations of different types.

Computational chemistry that generates data which complements experimental data obtained through chemical experiments. The calculations are based primarily on Schrodinger's equation. Further it supports evaluation of properties such as structure, absolute interaction energy and relative interaction energies, dipoles, electronic charge distributions and higher multipole moments, vibrational frequencies, reactivity and cross sections for collision with other particles can be evaluated. In certain cases it could also predict an unobserved chemical phenomenon which is also used for new drug designing and materials. Computational chemistry also supports the experimental chemist in finding entirely new chemical objects. In view of the above, the present thesis comprises by five molecules such as 2,5-Difluoronitrobenzene, 4-(Trifluoromethoxy)benzylbromide, 2-(Methylamino)pyridine, 4-(Diethoxymethyl) benzaldehyde and 2-Chloro-5-(trifluoromethyl)benzonitrile.

Various spectroscopic studies of halogen substituted nitrobenzene compound have been reported in the literature (Mukherjee *et al.*, 2010) from time to time.

Vibrational spectra of fluorobenzene were studied extensively (Eaton and Steele., 1973; Lipp and Seliskar., 1978). The molecular structure of *o*-fluoronitrobenzene has been investigated by gas phase electron diffraction and Ab initio MO calculations (Shiskovet *al.*, 2003).

Benzylbromide can be used as fullerene indicator and an octant booster in gasoline fuels used in internal combustion of engine. Industrial utilization of toluene is dealkylation of benzene and is disproportionate to a mixture of benzene and xylene. In several clinical tests, it is used to break red blood cells in order to take out hemoglobin. Towards electrophilic aromatic substitution, toluene reacts as a normal aromatic hydrocarbon (Wade., 1992; Furnell and Vogel., 1989).

Amino pyridines are extensively used in pharmacological and medical applications. Some of them exhibit anesthetic properties and have been used as drugs for certain brain diseases (Okamoto *et al.*, 1997; Carmona *et al.*, 1993). 2-Aminopyridine tagged oligosaccharides have been widely used for sensitive qualitative and quantitative analysis by high performance liquid chromatography with fluorescence detection (Okamoto *et al.*, 1997), in preparation of cytidine analogs (Hildbrandet *al.*, 1997) and it is also immensely used as a reagent in analytical chemistry the ring nitrogen of most pyridines that undergoes reactions such as protonation, alkylation and acylation. The harmonic frequencies of pyridine derivatives were calculated by several authors (Yamamoto *et al.*, 1980; Destexheet *al.*, 1994). The FT-IR and FT-Raman spectra of 2-methyl pyridine-1-oxide have been recorded. These spectra have been interpreted employing the scaled quantum mechanical force field (SQMFF) methodology, by directly transferring the scale factors obtained for pyridine (Arenas *et al.*, 1997).

Benzaldehyde is one of the essential aromatic aldehyde and the substitution of a functional group in benzaldehyde that changes the spectra markedly. The vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many earlier researchers (Kattiet *al.*, 1992; Mathew *et al.*, 1993).

Dimitrova has studied the vibrational spectra of benzonitrile and its radical anion (1997), the molecular structure and vibrational properties of 2-formylbenzonitrile (Misra *et al.*, 2007) and 3-chloro-4-fluorobenzonitrile (Balachandran and Parimala., 2013), 4-bromobenzonitrile (Krishnakumar., 2009), 4-(dimethylamino) benzonitrile and its isotopomers (Okamoto *et al.*, 2000), 4-(1H-pyrrol-1-yl) benzonitrile and 5-cyano-2-(1-pyrrolyl)-pyridine (Schweke., 2007) were carried out. From a theoretical point of view, 4-acetylbenzonitrile, 4-formylbenzonitrile and 4-hydroxybenzonitrile molecules are interesting because it contains different binding sites for its interaction with the metal surface and it contains an aromatic ring, the CN group and isolated pair of electrons on nitrogen and oxygen atoms (Loo *et al.*, 1985).