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N. Jayamani
Spectroscopy deals with the transitions induced in a chemical species by its interactions with the photons of electromagnetic radiations. Spectroscopic methods are generally used to measure the energy difference between various molecular energy levels and to determine its atomic and molecular structures.

Vibrational spectroscopy is the simple instrumental and versatile method for structural analysis and molecular vibrations. The molecular vibrations may be studied by IR and Raman scattering spectroscopy. Vibrational spectroscopy gives a dynamical picture of the molecule. With the development of computational methods of theoretical chemistry and more powerful personal computers, have led to higher accuracy in frequency and intensity measurements on relatively large polyatomic molecules. The results yield useful information about to the physical and chemical properties of the compounds.

In the present investigation, various compounds of some specific applications have been used for vibrational spectroscopic analysis. The density functional theory (DFT) in combination with B3LYP functional and the basis sets 6-31G* and 6-31G** have been used to carry out geometry optimization, to determine the geometrical parameters, energy calculations, force fields and the intensities of vibrational spectra. For reliable vibrational analysis, scaling of computed harmonic force field is required and it is done using scaled quantum mechanical method (SQM).

Molecular geometry optimizations and vibrational frequencies of selected molecules are calculated with Gaussian 03W software package. The
transformation of force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of total energy distribution (TED), prediction of IR and Raman spectra were performed by the software package MOLVIB. Comparing the simulated and experimental spectra, rational interpretation is provided for physical and chemical properties of the molecules and the role of functional group present in the molecules by the investigation.

The thesis consists of ten chapters. The first chapter deals with the theory of vibrational spectroscopy and group theory to determine the symmetry and normal modes of vibrations. The selection rules for IR and Raman spectroscopy have also been discussed.

In the second chapter, procedure of quantum chemical calculations and normal coordinate analysis of vibrational spectra are explained.

In the third chapter, instrumentation aspects, sample handling techniques and advantages of Fourier -Transform techniques are discussed briefly.

The density functional theory of vibrational spectra and assignment of fundamental vibrational modes of pyrazole and 3, 5-dimethyl pyrazole are explained in fourth chapter. The methyl groups are generally referred to as electron donating substituents in the ring systems. The CH₃ interacts with nearby π-systems via hyper conjugation. This mechanism implies electronic delocalization and is taken into account by the molecular orbital approach.

The density functional theory calculations and vibrational analysis of p-bromonitrobenzene and p-chloronitrobenzene are discussed in fifth chapter. The role of Nitro group which is electron withdrawing group in an aromatic ring
system makes a remarkable effect on the geometric and spectroscopic properties of the title compounds are also discussed.

The FTIR and FT-Raman spectral analysis of 2-chloro-4-nitrophenol and 2, 4-dichlorophenol have been analyzed by applying quantum chemical calculations are discussed in the sixth chapter. The effects of hydrogen bonding on the molecular vibrations are described satisfactorily by the scaled DFT force field.

The effect of hydrogen bonding on the structure and vibrational frequencies of p-bromobenzoic acid and p-fluorobenzoic acid forms the subject matter of chapter seven. Intra and inter molecular forces that affect the carbonyl absorption due to inductive, mesomeric, field and conjugation effects are also dealt.

FTIR and FT-Raman spectra of 2, 4-difluoroacetophenone and 2-chloroacetophenone form the content of the eighth chapter. The change in ionization potential, electrons affinity and excitation energy of the molecule due to highly electronegative fluorine and chlorine substituents that present in the title compounds are also discussed in detail.

The structural properties of 1, 5-dimethyl naphthalene and its complete vibrational spectroscopic analysis have been discussed in ninth chapter.

The density functional theory and vibrational assignments based on normal coordinate analysis for 2-acetonaphthone is discussed in the last chapter. The influence of Ketonic and methyl group on the vibrational frequencies of title compound is analyzed.
LIST OF PUBLICATIONS


PARTICIPATION AND PAPER PRESENTATION IN SEMINARS / CONFERENCES

1. Participated in the workshop on Recent trends in Physical Sciences Research at Department of Physics, Periyar University, Salem, 29-30 August 2005.


3. Participated in the National Seminar on Recent Advances in Material Science (RAMS 2008) at Department of Physics, Sri Sarada College for Women, Salem, 10th January 2008.

4. Presented a paper in the National Level Seminar on Emerging Trends in the Research Field of Physics at Post Graduate and Research Department of Physics, Erode Arts College, Erode-9, 6th March 2009.

5. Presented a paper in the National Seminar on Glimpses of Material Science at Department of Physics, Sri Sarada College for Women, Salem, 1st February 2010.

6. Participated in the workshop on Recent trends in Crystal Growth at Crystal Growth Center, Anna University, Chennai, 30th March 2010.