

FT-IR and FT RAMAN SPECTRA of 4-Chloro 2 Methyl Benzonitrile

Virendra Kumar Sharma

Associate Professor, Department of Applied Sciences (Physics),
Greater Noida Institute of Technology, Greater Noida, Uttar Pradesh, India

ABSTRACT

FT-IR spectrum of 4-chloro 2 methyl benzonitrile in the region 400-4000 cm^{-1} has been recorded in KBr pellet technique with a Bruker IFS-66 Fourier transform spectrometer. FT-Raman spectrum in powder form has been recorded in the region 50-4000 cm^{-1} on a Bruker IFS 66 optical bench with an FRA 106 Raman module attachment interfaced to a microcomputer. Geometry and vibrational wavenumbers were calculated using ab-initio calculations with HF method. The results were compared with experimental values. The observed FT-IR and FT-Raman vibrational frequencies were analyzed and assigned to different normal modes of the molecule. Most of the modes have wavenumbers in the expected range and the error obtained was, in general, very low. Using PEDs, the contributions were determined for different modes to each wave number. From the PED, it is apparent that the frequency corresponding to $\text{C}\equiv\text{N}$ stretching contains 88% contribution from the $\text{C}\equiv\text{N}$ stretching force constant and it mixes with C-CN stretching mode to the extent of 12%.

KEYWORDS: FT-IR, RAMAN, SPECTRA, 4-chloro 2 methyl benzonitrile, spectrometer, PED

INTRODUCTION

Nitrile group is one of the common groups occurring in nature which is a versatile precursor and intermediate for amines, aldehydes, drugs, agrochemicals, electronic materials and herbicides. Recently drugs manufactured from nitriles are used for a variety of pathological conditions. The recent importance of nitriles in the field of medicine is due to its versatility which is due to the presence of polarized triple bond which allows it to undergo a variety of interactions. Dyes having nitrile group are very common because they have good mechanical property and thermal stability. [1,2]

Hence, they produce fructuous outputs in the field of solar technology. Since nitriles have a peak temperature of 350 $^{\circ}\text{C}$ at the end of its life period, the derivatives of nitriles find application in spacecrafts, marine engineering, electronic and integrated circuit package systems. Non- linear optics is related to the interaction of applied electromagnetic in several materials to generate new electromagnetic fields which is altered in wave number, phase, and other physical properties. Quantum chemical calculations

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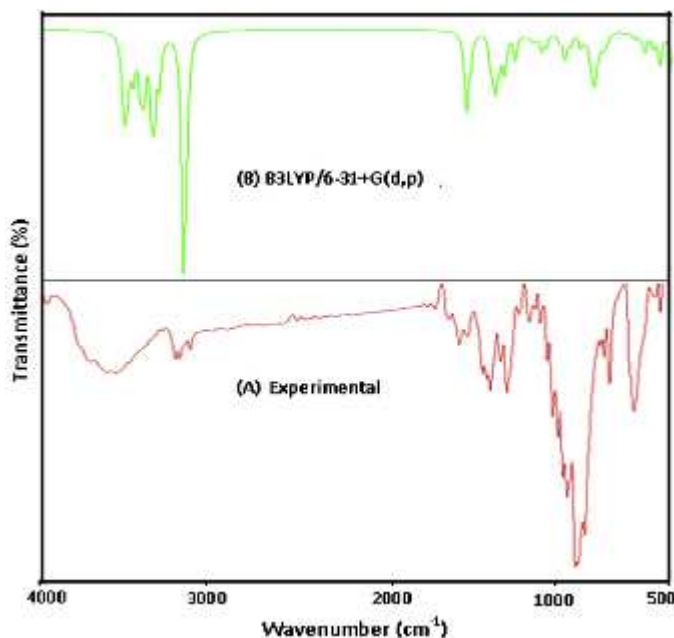


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are helpful in the description of the relationship between the electronic structure of the systems and in NLO response. The computational approach allows the calculation of molecular NLO properties inexpensively by determining higher order polarizability tensors of the molecule. Benzonitrile, a phenyl cyanide compound was derived by heating benzoic acid with lead thiocyanate.

When it reacts with strong acid, it produces toxic hydrogen cyanide but on heating it decomposes and produces very toxic vapours of hydrogen cyanide and nitrous oxide. Benzonitrile and most of its derivatives are used in industrial and medical field for manufacturing dyes, rubber chemicals, polymers, anhydrous metal salts, food preservatives, drugs and as intermediates for pharmaceuticals, organic chemicals, antiseptics, natural products, herbicides, epoxy curing agent, agrochemicals etc. Benzonitrile compounds are well known solvents in physical science laboratories. The substitution benzonitrile compounds possess strong and weak inhibitory effects based on their positions. The para or meta

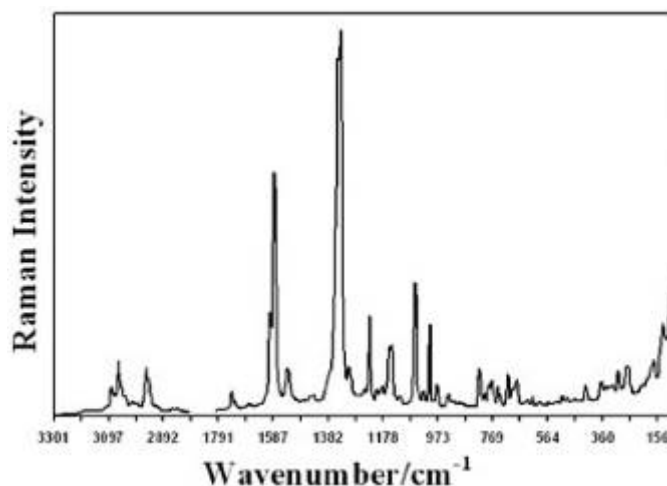
position of benzonitrile is an example for weak catalytic effect in nitrilase enzyme. But the substitution in the orthoposition of benzonitrile is a consequence of strong effect because of steric hindrance. Recently Dye-Sensitized Solar Cells (DSSCs) are found to be the most systematic and cheapest third-generation solar technology, which has the magnificent interest, as green and renewable energy converting device. [3,4]



In DSSC, the dye sensitizers plays a supercilious and significant part which enhances future researches. Properties like physical, electronic and the thermal properties of dye sensitizers has to be taken into account for DSSC synthesis. Hence computational and experimental investigations of these dye sensitizers has become an essential technique for identifying innovatory dye sensitizers with enhanced properties. Results obtained from theoretical methods for large molecules are applied for finding their applications in various fields in addition to their physico-chemical properties. Theoretical calculations are powerful tools for determining specific answers which can be authenticated with experimental values.[5,6]

Discussion

The vibrational fundamental frequencies of 4-chloro 2 methyl benzonitrile have been investigated with DFT-B3LYP through 6-31+G(d,p) and 6-311++G(d,p) level calculations.

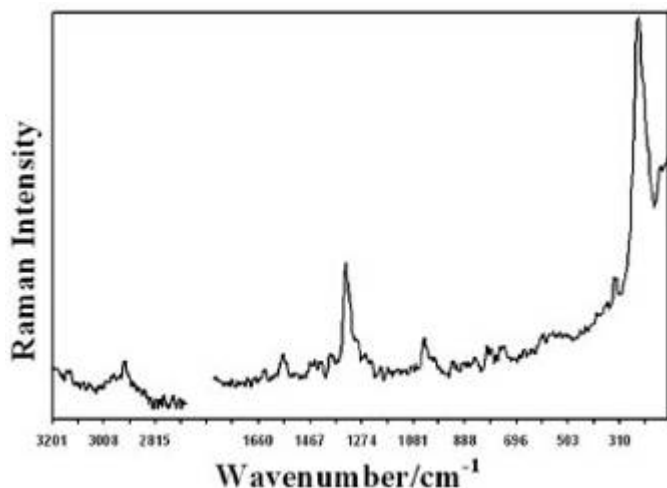


Various parameters such as stabled geometries and frequencies of CHAP were confirmed by FTIR and FT-Raman spectroscopies on the basis of C1 point group symmetry. The frequency assignment for normal modes is supported by the TED calculation. The perceptive of CHAP chemical activity and properties might be confirmed through smaller HOMO-LUMO band gap. In addition, the thermodynamic properties and results of Mulliken's charge of CHAP have been designed and discussed. These outcomes will be of support in the quest of the experimental and theoretical evidence for 5-chloro-2-hydroxy acetophenone in reaction intermediaries, pharmaceuticals and agrochemicals industries.[7,8]

Structural, Vibrational, Electrical, optical and Stability studies of 4-chloro 2 methyl benzonitrile has pore over by computational methods. The equilibrium geometry (atomic length, atomic angle and dihedral angle), frequency vibrational assignments, IR activities and Raman intensities in scattering bustles was premeditated by B3LYP method employing 6-311 ++G (d, p) / (2d, p) as the basis sets. The Raman and IR spectra of FMBN are traced and the frontier orbital energy gap has predicted. The electrostatic potential, contour map and electron density have also drawn to clarify the electronic activity of 2C3MOBN. For the future applications in nonlinear optics (NLO) of the molecule has investigated threth the hyper polarizability (β) and electric dipole moment (μ) of 2C3MOBN are calculated using second basis set on the finite-field approach denote above. Intra Charge Transfer (ICT), hyper conjugative interactions, charges delocalization of the molecule has explored by Natural Bond Orbital (NBO) Fock matrix cram on the way to locate the Stability. Mulliken population analysis and Natural population analysis on charges also evaluated. Eventually investigate thermodynamic parameters like enthalpy, Gibbs free energy, zero point energy, entropy, heat capacity, dipole moment, and atomic charges.[9,10]

Results

The first task of the computational work was to determine the optimized geometry of the compound.



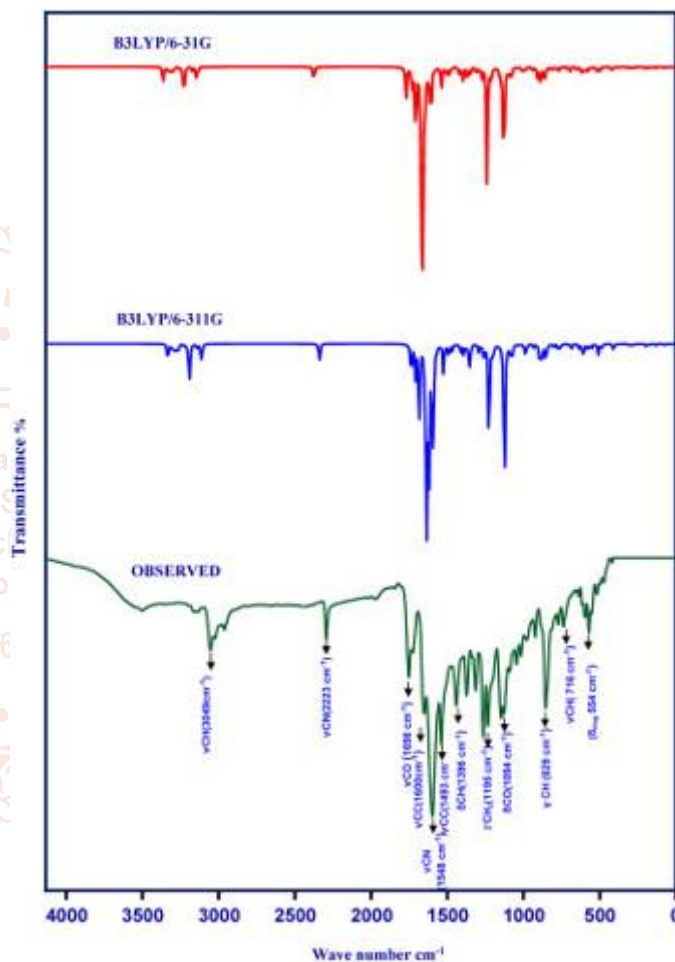
Both the geometry optimizations and wave number calculations for 4-chloro 2 methyl benzonitrile were carried out using both ab initio HF and the hybrid density functional B3LYP (Becke–Lee–Young–Parr composite of exchange correlation) functional with the 6-311++G(d,p) basis set, using the Gaussian 03 W program package, invoking gradient geometry optimization. Geometries of the model 4M2MBA have been first optimized with full relaxation on the potential energy surfaces at the HF/6-31G(d,p) level and the resultant geometries have been used as inputs for further calculations at the DFT(B3LYP) level. Polarization functions have been added for the better treatment of the methoxy, methyl and carboxyl groups. Analytic frequency calculations at the optimized geometry were done to conform the optimized structure to be an energy minimum and to obtain the theoretical vibrational spectra. The total energy distribution (TED) was calculated by using the scaled quantum mechanics (SQM) program and the fundamental vibrational modes were characterized by their TED.[11,12]

This paper presents the experimental and theoretical vibrational IR and Raman spectra of the title molecule. The FT-IR (gas and solid phase) and FT-Raman spectra have been recorded in the range of 400–4000 cm^{-1} and 10–3500 cm^{-1} , respectively. Because of the lack of experimental information on the geometric structure available in the literature, theoretical calculations were compared with those of a similar molecule. All observed vibrational bands have been discussed and assigned with the help of TED values on the basis of our calculations. The molecular geometry at all the vibrational wave numbers of 4-chloro 2 methyl benzonitrile have been calculated by using the HF density functional method at the B3LYP/6-311G(d,p) level. A complete assignment of the fundamentals was proposed on the

basis of the TED calculations. Furthermore, the thermodynamic, non-linear optical, first-order hyperpolarizabilities and total dipole moment properties of the compound have been calculated in order to get an insight into the compound. We hope that the results are of assistance in the quest for experimental and theoretical evidence for the title molecule is reaction intermediates and for non-linear optical and photo-elastic materials.

Conclusions

The FTIR, FT-Raman and UV-visible Spectra of 4-chloro 2 methyl benzonitrile were recorded experimentally and theoretically.



The optimized geometrical structure, harmonic vibration frequencies, and chemical shifts were computed using a hybrid-DFT (B3LYP) method and 6-31G (d,p) as the basis set. The complete assignments of fundamental vibrations were performed on the basis of the experimental results and Total Energy Distribution (TED) of the vibrational modes. The first order hyperpolarizability and relative properties of furosemide were calculated. The UV-Visible spectrum of the compound was recorded in the range 200–400 nm and the electronic properties, such as HOMO and LUMO energies, were determined by Time-Dependent DFT approach. Furthermore, Mulliken population analysis and thermodynamic properties were performed using

B3LYP/6-31G (d,p) level for the furosemide compound.[13,14]

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