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Molecular structure, vibrational spectroscopic (FT-IR, FT-Raman),UV-Vis spectra, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis, thermodynamic properties of 2,6-dichloropyrazine by ab inito HF and density functional method

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Abstract. FT-IR and FT-Raman spectra of 2,6-dichloropyrazine were recorded and analyzed. The vibrational wavenumbers were examined theoretically using DFT/B3LYP /6-311G(d,p) level of theory. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in infrared spectroscopy of the studied molecule. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of nonlinear optics. The assignments of the vibrational spectra have been carried out with the help of normal co-ordinate analysis (NCA) following the Scaled Quantum Mechanical Force Field Methodology (SQMFF). UV-visible spectrum of the title molecule has also been calculated using TD-DFT/6-311G(d,p) method. The calculated energy and oscillator strength exactly reproduces reported experimental data. The Mulliken population analysis on atomic charges and the HOMO-LUMO energy are also calculated.

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Key words: 2, 6-dichloropyrazine, FT-IR, FT-Raman, UV-Vis, NBO, HOMO-LUMO

1 Introduction

Pyrazine and its derivatives are one of the most studied and important class of N-heterocycles. Pyrazines possess unique and extremely potent flavor and aroma characteristics [1,2]. Some of the derivatives of pyrazines find use as pharmaceutical intermediates[3],

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marking volatiles[4], antifungal and antiviral agents[5] and hence they find extensive applications in flavor and pharmaceutical industries. alkyl-substituted pyrazine, is widely used as a key intermediate for pyrazineamide, an effective anti-tubercular drug [6,7].

Vibrational spectroscopy has been proven to be a useful probe of the structural properties of pyrazine.The pyrazines are the most extensively investigated class of diazines [8].Pyrazine (1,4-diazabenzene) is a diaza analogs of the benzene molecule. It is isoelectronic with benzene as it contain 6π electrons for aromatic delocalization. However, the perfect aromaticity of benzene is disturbed by centric substitution of 2 nitrogen atoms in the case of the systems under consideration, such that the electronegative nitrogens hold some of the ring electrons to prevent the perfect delocalization of the 6π electrons. The inclusion of a substituent group in aromatic rings leads to the variation of charge distribution in molecules, and consequently this greatly affects the structural, electronic and vibrational parameters. In general electron deficient pyrazines undergo electrophilic substitution reactions under normal conditions with the substitution of electron-donating group. That is the pyrazine system become more nucleophilic. Chlorine is generally referred to as highly electronegative and hence it withdraw the electrons from the ring which results in the change in ionization potential, electron affinity and excitation energies of the system.

Literature survey reveals that detailed interpretations of the infrared and Raman spectra have been reported on pyrazine [9-19] and dichloro substituted pyrazine [8]. For 2,6-dichloropyrazine the experimental results compared with the DFT/B3P86 method with 6-311G(d,p) basis set by assuming C_{2v} symmetry. We have assumed C_1 symmetry for this molecule, because the molecule possesses minimum energy in this conformation [For C_1 symmetry , $E=-1183.6248893$ a.u. and C_{2v} symmetry $E=-1183.62480348$ a.u.]. But the results based on density functional theory calculation with B3LYP/6-311G(d,p) and FT-IR, FT-Raman, UV-Vis spectral studies, the first order hyperpolarizabilities, the HOMO-LUMO and NBO analyses on 2,6-dichloropyrazine have no reports. This inadequacy in the literature encouraged us to make this theoretical and experimental vibrational spectroscopic research based on the structure on molecules to give a correct assignment of the fundamental bands in experimental FT-IR, FT-Raman spectra. Along with the vibrational spectra, the electronic potential should help us to understand the structural and spectral characteristic of this compound.

2 Experimental details

The compound 2,6-dichloropyrazine in the solid form was purchased from Sigma-Aldrich Chemical Company (USA) with a stated purity greater than 98% and it was used as such without further purification. Nicolet 6700 FT-IR spectrometer with an NXR FT-Raman module was used to record IR and Raman spectra. IR spectrum was recorded on samples dispersed in KBr pellets in the range of 400-4000 cm^{-1}. Raman spectrum was recorded on solid samples contained in standard NMR diameter tubes or on compressed samples con-