

Using Density Functional Theory Approach for Vibrational Analysis

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Abstract

Vibrational spectroscopy is more than just an analytical instrument. A molecule's electrical structure, bond strength, and conformational flexibility are recorded in the normal vibrational modes. This information can only be accessed via local vibration modes and their associated local features, which is why regular vibrational modes are often delocalized. For determining a molecule's electronic structure, the Density Functional Theory (DFT) approach, notably the hybrid functional method, has developed into a potent quantum chemistry instrument. Density functional theory (B3LYP) approaches invoked by the 6-31G (d,p) basis set optimized geometrical parameters, atomic charges, vibrational wavenumbers, and vibrational frequency intensities of cuscohygrine in the ground state. Predicted FTIR and FT-Raman spectra of molecule based on the optimised chemical structure.

Keywords: *Geometry Optimization; Vibrational Analysis; Electronic.*

I. INTRODUCTION

Heterocyclic compounds may be found all over the place in nature and play an important role in many aspects of life. The pharmaceutical industry is the most common place where they are employed. Antibacterial, antifungal and antitubercular effects of Cuscohygrine substance are being studied extensively. In the scientific literature, there hasn't been a new, complete study on this subject in a while. However, as can be observed from real online writings, the fundamental ideas and practises have remained constant. The relevance of the cuscohygrine sample prompted the selection of the substance for use in Quantum chemical calculations to identify all of its physicochemical features.

In order to do QCCs, the GAUSSIAN 09 software package is used. Based on the molecule's size and the number of orbitals, the applicable technique and basis set are selected (C13H24N2O). Based on Becke's three-parameter hybrid exchange function and the LeeYange-Parr correlation functions, density functional theory (DFT) for organic molecules has shown impressive results in the literature. The primary goal of this theoretical investigation is to get a better understanding of the structural, magnetic, electrical, and vibrational characteristics of the aforementioned substance. DFT/B3LYP methods were used to investigate Cuscohygrine's structural properties, bond lengths, bond angle and vibrational assignments, type of charge transfer between the orbitals, distribution of electrons in orbitals, electronic properties ionisation potential, electron affinity, electro negativity, global hardness, global softness, NBO and hyperpolarizability. The antituberculosis activity of Cuscohygrine is further shown by a molecular docking investigation.

II. VIBRATIONAL ANALYSIS

Vibrational wavenumbers and IR and Raman intensities of the title compound, as well as their experimental and calculated wavenumbers, are depicted in this diagram. Figure 1 depicts the FT-IR spectra obtained experimentally as well as the theoretical IR spectra. Figure 2 depicts the computed B3LYP, M06-2X, and MPWLYP functional Raman spectra in comparison to the measured data. According to B3LYP/6-311+G(d,p) level calculations, the vibrational wavenumbers are overestimated under the harmonic approximation. Due to the C1 point group and lack of symmetry, all 54 of the basic vibrations are IR and Raman-active and dispersed across the functional and fingerprint areas of the molecule.

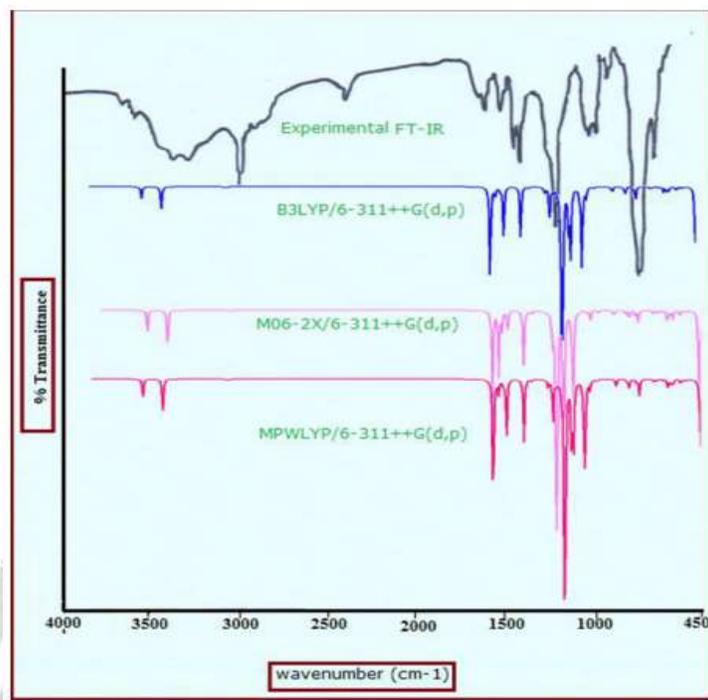


Figure 1: Comparative FT-IR and theoretical IR spectra of the title compound.

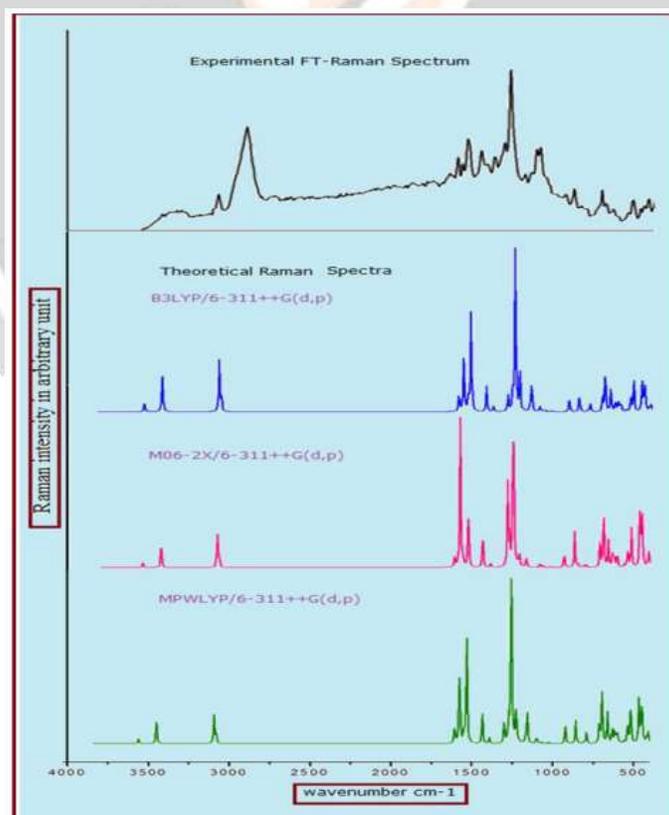


Figure 2: Simulated Raman spectra at B3LYP, M06-2X, MPWLYP.

Vibrational modes are broken down into three categories for the purpose of thorough vibrational analysis:

- (i) Benzothiazole ring vibrations,
- (ii) Amino group vibrations and
- (iii) O-CF₃ vibrations.

i Benzothiazole ring vibrations

There are many benzothiazole rings (thiazol ring fused with the phenyl ring) in the title chemical, hence the spectrum is heavily dominated by bending vibrations of C-H, C-C, C=C, C-N, and C-S stretching. There are a number of weak to moderate bands in the 3100–3000 cm⁻¹ range due to the phenyl ring straining the C–H bonds. The phenyl ring's C-H stretching vibrations cause a wide shoulder band about 3020 cm⁻¹ in FT-IR. Scaled wavenumbers of 3086, 3085, and 3072 cm⁻¹ have been determined. In the IR spectra, the aromatic C–H in-plane bending modes of 2-amino-4-methylbenzothiazole were found at 1120 and 995 cm⁻¹. C-H inplane bending vibrations are detected across the range of 1585–1042 cm⁻¹ in the case of 2(3H)-Benzothiazolone. Phenyl ring's dominating 1221 and 1097 C-H in-plane bending modes were predicted in this situation. The predicted range of 1000–600 cm⁻¹ is detected for the C–H out-of-plane bending vibrations of the title chemical, as it is for most benzene derivatives. All three modes have been given wavenumbers between 758 and 785 cm⁻¹ in the FT-IR/FT-Raman spectra, indicating that they are substantially pure. A fused thiazole ring and a hefty O-CF₃ group on each side of the benzene ring change its breathing mode. The ring breathing mode (RBM) has been allocated based on the visualisation of vibrations in the GAUSSVIEW software and PED, and it matches well with experimentally observed bands at 933 cm⁻¹ in FT-IR and at 938 cm⁻¹ in FT-Raman. This vibration has a wavenumber of 915 cm⁻¹. The phenyl ring's trigonal bending is also significantly altered, with the mode for 2(3H)-Benzothiazolone being 870 cm⁻¹ and the predicted value for the title compound being 1020 cm⁻¹.

At 1570, 1540, 1429, 1385, 1294 and 1249 cm⁻¹ are the computed wavenumbers that correspond to dominant C-C squeezing. Puckering torsional modes (Puckering) are seen at 708 and 690 cm⁻¹ in this example. The 370 cm⁻¹ value assigned to the ring butterfly mode is a conservative estimate. The vibrations of the two hetero atoms (Sulfur and Nitrogen) in the thiazole moiety are impacted and changed by the conjugated -C=C-N=C-S system. In the 700-600 cm⁻¹ range, the C-S linkage's stretching vibration is detected. Mixed mode at 611 cm⁻¹ was used to derive compound dominant C-S stretching for this paper's title. FT-IR/FT-Raman spectroscopy shows the C=N stretching vibration at 1535/ 1539 cm⁻¹ for the title chemical, whereas C-N stretching is computed at 1266 cm⁻¹. All other systems with a thiazole moiety have the same assignment patterns as these.

ii Amino group vibrations

There are three distinct amino group vibrations: N-H stretching, scissoring, and rocking deformation all occur in the 3500-3300 cm⁻¹ range. According to this study, the NH₂ group's scaled asymmetric and symmetric modes are at 3549 and 3439 cm⁻¹, respectively, while the equivalent empirically measured modes are at 3398 and 3307 cm⁻¹. The hydrogen-induced red shift in the N-H stretching modes might be the cause. There are three distinct amino group vibrations: N-H stretching, scissoring, and rocking deformation all occur in the 3500-3300 cm⁻¹ range. Experimentally, we found that the experimentally observed modes in the far-infrared spectrum match to the scaled asymmetric and symmetric modes at 3549 and 3439 cm⁻¹, respectively, in the current investigation on the NH₂ group. There is a possibility that the red shift in the N-H stretching modes is due to hydrogen bonding in the system. The NH₂ scissoring mode band is located at 1620/ 1603 cm⁻¹ in FT-IR/FT-Raman. NH₂'s rocking and wagging deformation vibrations contribute to various low-frequency normal modes. It is believed that the NH₂ rocking and wagging vibrations are prevalent in the bands located at 1062 cm⁻¹ and 450 cm⁻¹.

iii O-CF₃ group vibrations

The motion of the O-CF₃ group is also related with nine basic vibrations, three stretching, three bending, two rocking modes, and one torsional mode, as is the case with the methoxy group. When fluorine atoms are present in aromatic methoxy compounds, the asCH₃ are predicted to be in the vicinity of 2985 20 cm⁻¹ and 2955 cm⁻¹,

however this is not the case. There are four asymmetric C-F stretching modes predicted at 1160, 1148, 1097, and 1085 cm^{-1} , according to the calculations. At 915, 853, and 785 cm^{-1} , the symmetric C-F stretching modes may be discovered. At a wavelength of 1094 cm^{-1} , an experimental Raman antisymmetric CF stretching mode may be identified. At 628 cm^{-1} , the CF_3 umbrella flexes. C-O stretching vibrations are responsible for the strong band at 1300-1200 cm^{-1} . The bands at 1196 cm^{-1} and 1148 cm^{-1} (modes 16 and 18) are mixed modes that include C-O stretching vibrations, according to the results of this investigation. It is also possible to find C-O group bending vibrations that are both in-plane and out-of-plane.

III. THERMODYNAMIC PROPERTIES

This compound's thermodynamic properties were determined via vibrational analysis. The following fitting equations and correlation graphs in Figure 3 indicate that these thermodynamic functions are directly proportional to temperatures in the range of 100-700 K.

$$S = 58.835 + 0.2042T - 6.0 \times 10^{-5} T^2 \quad (R^2 = 1)$$

$$C_V = 0.1258 + 0.1916 T - 10.0 \times 10^{-5} T^2 \quad (R^2 = 0.9999)$$

$$\Delta H = -0.9453 + 0.0159 T - 5.0 \times 10^{-5} T^2 \quad (R^2 = 0.9997)$$

Thermodynamic data like the ones shown here might be useful in future research on the substance in question. Other thermodynamic energy may be calculated using the relationships between thermodynamic functions; chemical processes can be assessed using the second rule of thermodynamics and the relationship between thermodynamic functions. Because all thermodynamic calculations were performed in the gas phase, these results cannot be applied to solutions.

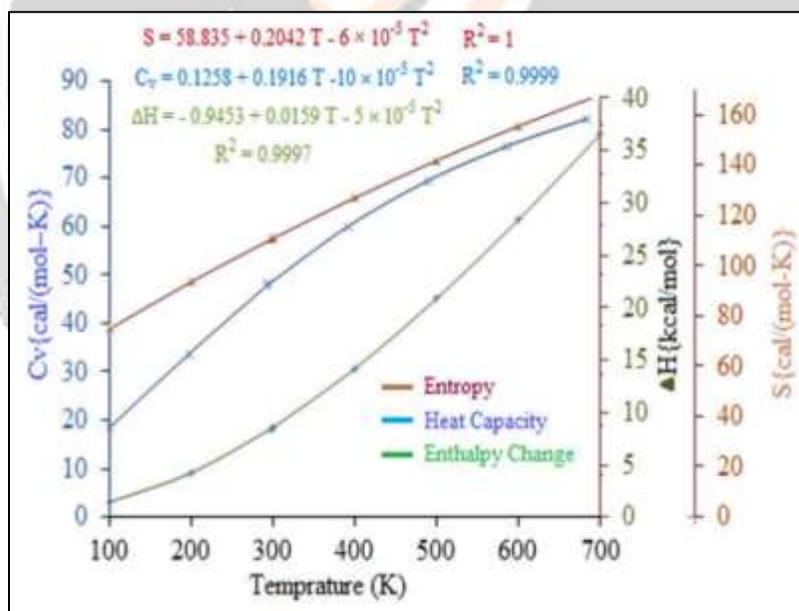


Figure 3: Correlation graph of calculated heat capacity, entropy and change in enthalpy of Riluzole.

IV. CONCLUSION

Cuscohygrine's molecular geometry, vibrational frequencies, infrared intensities, and Raman scattering activities were all analysed. Even in the low frequency area, the estimated values accord well with the published values. According to the HOMO and LUMO energies computed, it is very reactive. It is possible to foretell the reactive behaviour of the title molecule by the use of MEP visualisation. Electronegative atoms' impact on ^{13}C and ^1H NMR

chemical shifts are explored. The chemical has NLO uses based on the tot value. A novel anti-tuberculosis medicine can be developed using the docking findings.

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