# FT-RAMAN AND FT-IR SPECTROSCOPIC STUDY AND VIBRATIONAL ANALYSIS OF BENZIMIDAZOLE

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## ABSTRACT

The structure of nonlinear optical crystal benzimidazole is confirmed by powder X-ray diffraction method. The optimization of the structure has been done by density functional theory (DFT) with B3LYP level and 6-311G++(d,p) basis set. The fundamental vibrational frequencies of benzimidazole (BZE) are calculated using density functional theory (DFT) methods at different levels of calculation. The HOMO-LUMO energies have been investigated which proposes that the probability of charge transfer to take place inside the molecule. Mulliken population study on atomic charges was also calculated.

Keyword : Powder XRD, FTIR, Raman, HOMO-LUMO, Mulliken analysis

## INTRODUCTION

Organic crystals are increasingly being recognized as materials of the future because of their molecular nature combined with the versatility of synthetic chemistry can be used to alter and optimize their molecular structure in order to maximize nonlinear properties. Organic crystals were completely scrutinized due to their high nonlinearities, rapid response in electro-optic effect and tailor made flexibility [1–6]. These compounds need to form in a non-Centro symmetric crystal in view of applications with quadratic optically nonlinear effects. The organic NLO crystals performed well in second harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability, etc. [7-8]. However, their practical applications are limited by poor chemical stability, poor phase matching properties caused by a large birefringence [9] and difficulties stiller main in crystal growth with sufficient quality and hardness for applications, such as optical and electro-optical (EO) sampling devices. The basic necessities for an NLO crystal to be effectively applied in frequency conversion are a nonzero NLO coefficient, transparency at all wavelengths involved, proficient transfer of energy between the optical waves scattering through the crystal, and noble physical (low vapor pressure, high thermostability) and optical (high damage threshold, large birefringence, low dispersion) properties. Crystal growth from solution is a significant procedure that is utilized in numerous applications from laboratory to industrial scale. An innumerable number of organic and inorganic crystals are grown in this fashion [10].

In the present work, we have done the computational studies of benzimidazole by density functional theory with B3LYP/6-311G++(d,p) basis set. The benzimidazole was subjected to powder X-ray diffraction (XRD) studies. The XRD study spectacles the benzimidazole belongs to the crystal system of Orthorhombic and space group P21na. FTIR and Raman studies reveal the functional group of the grown crystal. The Mulliken charge analysis was completed to survey the intra-molecular charge transfer interaction. The investigation from HOMO-LUMO orbitals explained the charge distribution among the molecules.

## POWDER XRD ANALYSIS

Powder XRD studies were carried out to demonstrate the crystallinity by Stoe STADI powder diffractometer. The X-ray powder data were collected using a position-sensitive detector (PSD) with an angular range of 2.1 $^{o}$. The step size was 2.0$^{o}$ and the nominal detector resolution is 70.02$^{o}$. The radiation is CuK$_{\alpha}$ ($\lambda$ = 1.54178A$^{o}$). Well crushed powder was used for the study. The observed 2θ values are given in the input of the PROSZKI software package and the lattice parameters are calculated. The data obtained from powder XRD are in good agreement with the reported literature [11,12]. The powder XRD pattern of benzimidazole is shown in Fig. 1.

## COMPUTATIONAL DETAILS

The DFT calculations of BZE have been performed by using the Gaussian 09 program kit [13] at the Becke3-Lee-Yang- Parr functional (B3LYP) [14,15] with 6-311G++(d,p) basis set to obtain energy minimization. The equation was solved by the method of self-consistent interactively to acquire all the optimized geometry. The optimization of BZE is shown in Fig. 2. From the full-featured Gauss View approach [16], the fact concerning molecular displacement vectors with vibrations was achieved. Anisotropic scaling factor 0.9615 was used to obtain the molecular vibrations from B3LYP/6-311G++(d,p) level of theory. The transformation of relative intensities of the Raman Spectrum ( Ii ) from the Raman activities ( Si ) was achieved by the Raman Scattering [17, 18] . The generated Infrared and Raman spectral peaks by the Gaussian 09 program were charted adopting pure spectral line shapes of full bandwidth at half maximum of 10 cm $^{-1}$.

## MULLIKEN ANALYSIS

The atomic charge has been utilized to explain the process of electro negativity equalization and charge transfer in chemical reactions [19,20]. Also, it has been used to model the electrostatic potential at outside molecular surfaces [21-24]. The Mulliken atomic charge was calculated through DFT at B3LYP/6-311G++(d,p) method and the graphical representation is shown in Fig. 3. The atom C4 has a maximum positive charge of 0.37146 and every hydrogen atom have exposed a positive charge. The magnitude of hydrogen atom changed between 0.324142 and 0.179948. The atoms N2 and N5 have the top value of negative charges -0.554573 and -0.809969 respectively. All the carbon atoms have exhibited a negative charges except C1, C3 and C4.

## Energy gap of HOMO-LUMO

To obtain the information about the molecular orbital (MO) structure, the energies of HOMO ( π-donor) and LUMO ( π- acceptor) of BZE molecule are investigated through the B3LYP level with the 6-311G++(d,p) level. The expansion of the word HOMO is the highest occupied molecular orbital. The expansion of the word LUMO is the lowest unoccupied molecular orbital. Orbital of HOMO and LUMO are displayed in Fig. 4. HOMO, LUMO energies and their band gap energy exhibit the actual molecular chemical reaction. Naturally, HOMO is called as an electron donor due to having the capability to contribute an electron. LUMO is called as an electron acceptor due to having the capacity to grab an electron. The energies of HOMO and LUMO are reckoned at **- 6.1486 eV** and **-0.3532 eV** correspondingly. The band gap between HOMO and LUMO is observed as **5.7954 eV**. The computed energies of HOMO and LUMO has revealed that the charge transformation takes place in the molecule itself. The low value of energy gap declares that the appropriateness of the grown BZE in the field of NLO [25].

## SPECTROSCOPIC ANALYSES

The various fundamental vibrational modes of benzimidozole (stretching, in-plane and out-of-plane) such as C-H vibrations, C-N vibrations and N-H vibrations are depicted in the Table 1. The FTIR and Raman spectra are displayed in Fig. 5 and Fig. 6.

### C–H vibrations

The hetro aromatic arrangement displays the presence of C–H stretching vibrations in the region 3100–3000 cm$^{-1}$ which is the region for prepared identification of C–H stretching vibrations. The band appeared at 1544 and 240 cm$^{-1}$ in the benzimidazole have been assigned to C–H ring stretching vibrations. The C–H in-plane ring bending vibrations are generally befallen as a number of strong to weak intensity bands in the region 1300-1000 cm$^{-1}$.

### C–C vibrations

The aromatic carbon–carbon stretching vibrations of the title compound are observed at 1656 and 1616 cm$^{-1}$ in IR spectrum. Some ring modes were exaggerated by the substitution to the aromatic ring of the title compound. In the present study, the IR bands for benzimidazole compound have been assigned to ring in-plane modes and the out-of-plane deformation modes, are considered carefully by their quantitative descriptions.

### N-H Vibrations

In plane vibrational modes N-H stretching. These modes have been observed and located within the IR-spcetral range 3200 and 100-1700cm$^{-1}$.The values of 456-1136cm$^{-1}$.benzimidazole compound have been bending ,asymmetric stretching of vibrations.

## CONCLUSION

The lattice parameters were found by powder XRD technique. The FTIR spectrum reveals that the functional groups of The Vibrational spectral analysis of BZE was performed using DFT calculations. From the FT-IR analysis it is concluded that the major portion of the lattice force is largely derived from hydrogen bonding of the NH group of the heterocyclic ring. From the Raman analysis the ring breathing vibrations, which are observed at 1464 and 1544 cm$^{-1}$ in the IR spectrum are also observed in the Raman spectrum nearly at these wavenumbers. The collaborations of the charge between the molecules have been established by Mulliken charge investigation. The HOMO-LUMO showed the charge transfer interaction in cation and anion groups.

List of Figures :

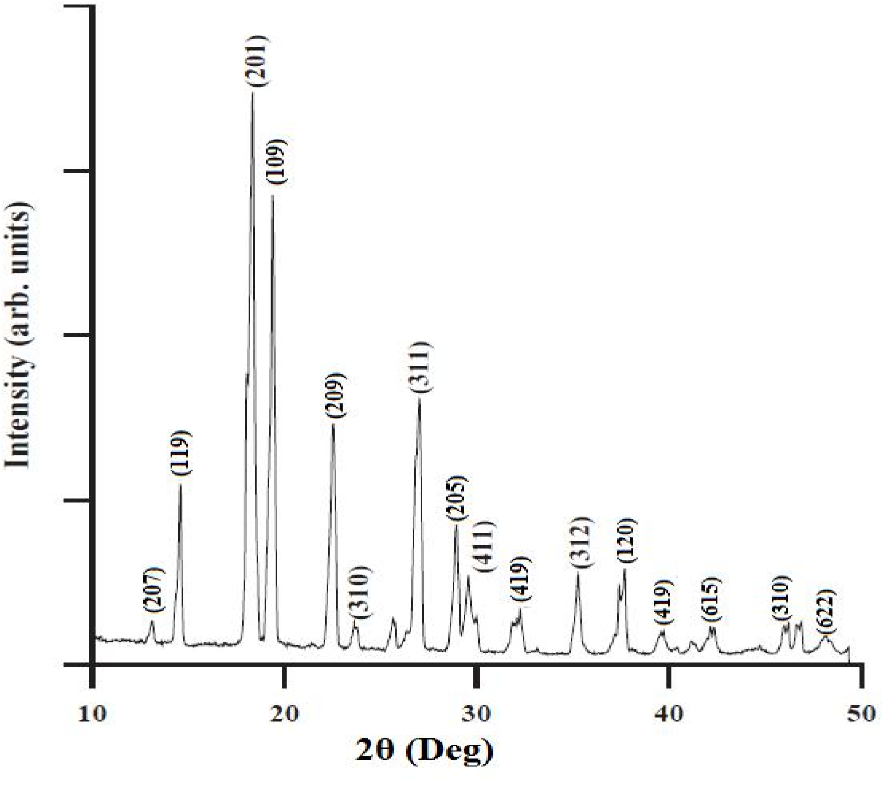

**Fig. 1 Powder XRD pattern of BZE**

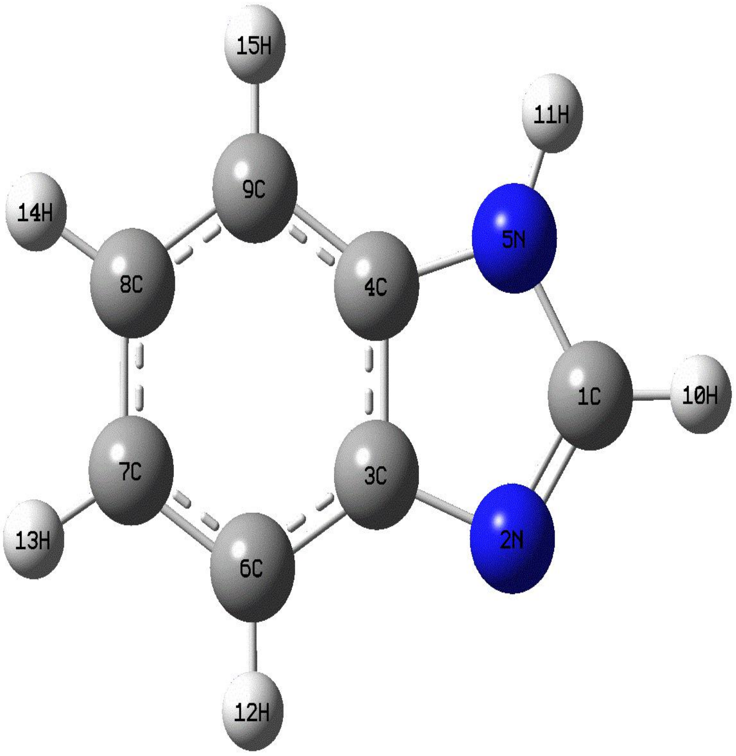

**Fig. 2 Optimized structure of BZE**

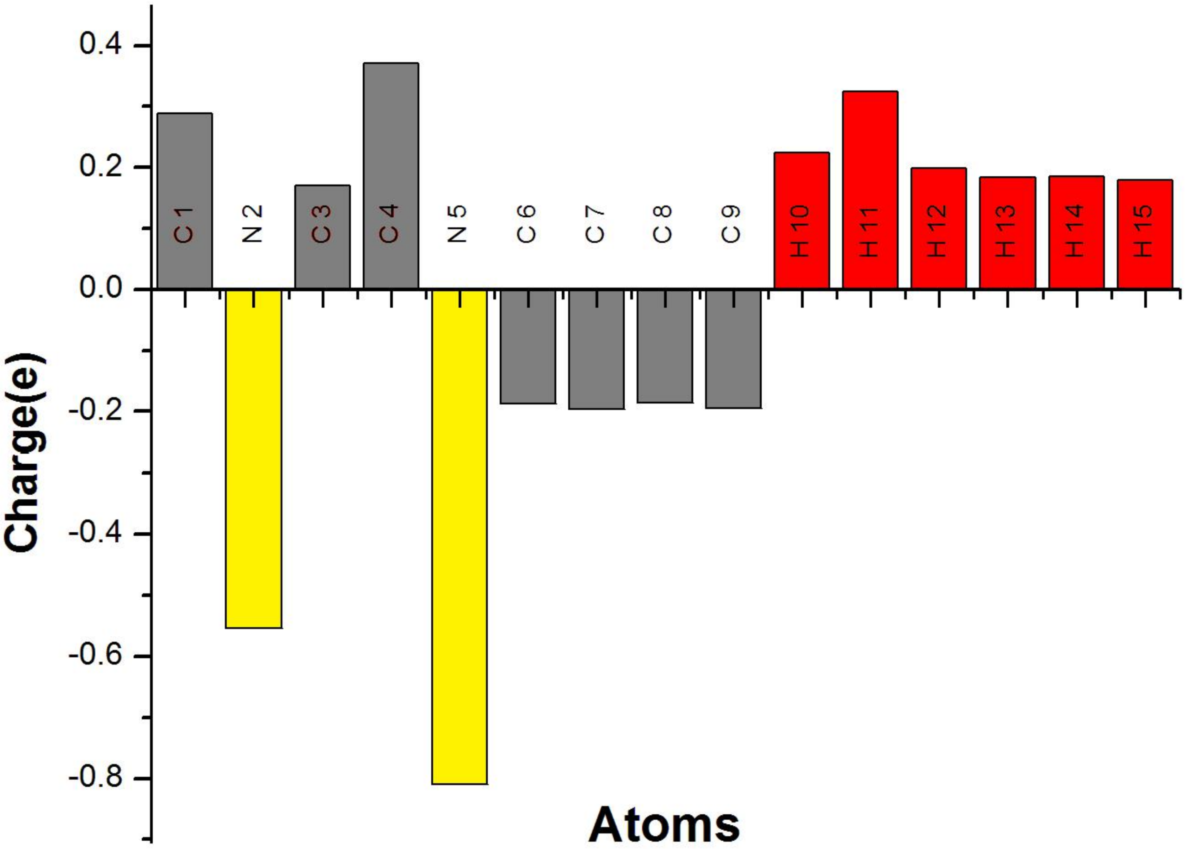

**Fig. 3 Mulliken charge distribution of BZE**

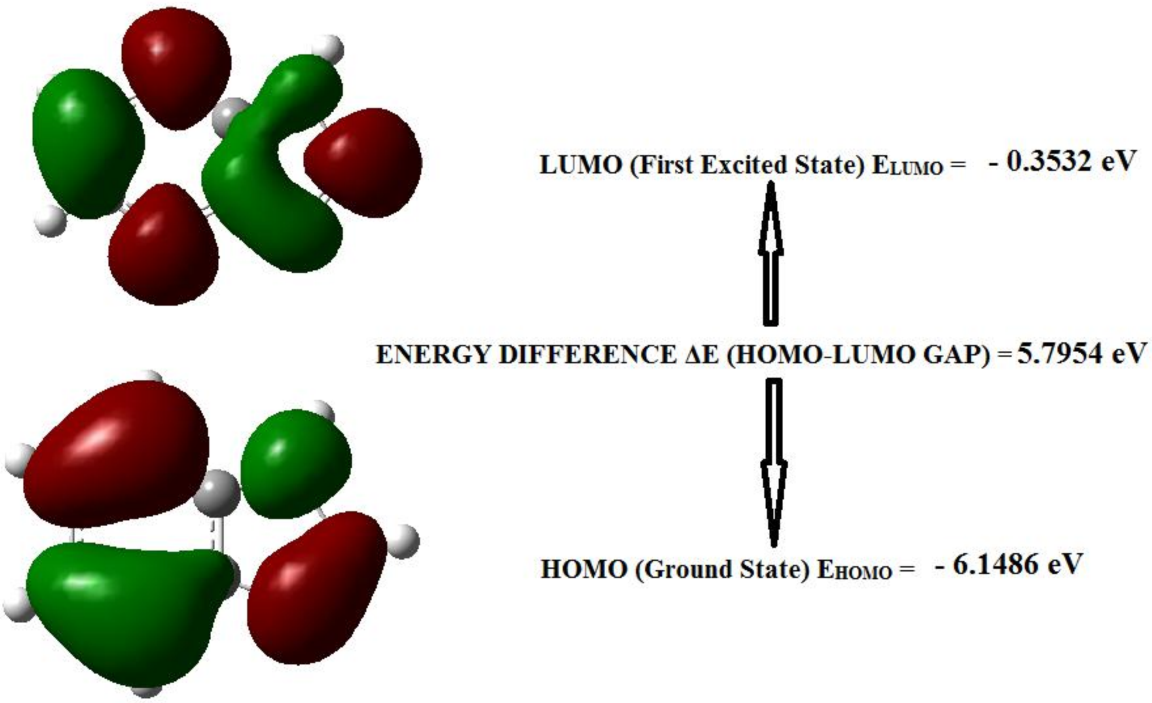

**Fig. 4 HOMO –LUMO plot of BZE**

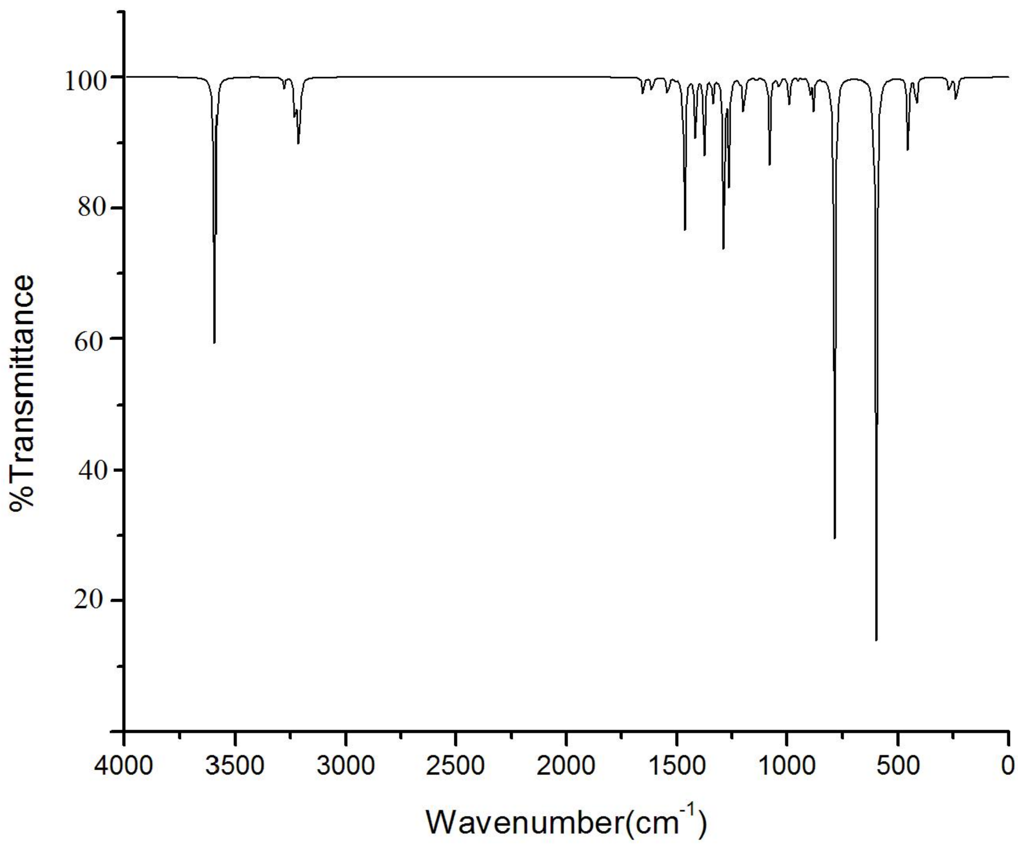

**Fig. 5 FT-IR spectrum of BZE**

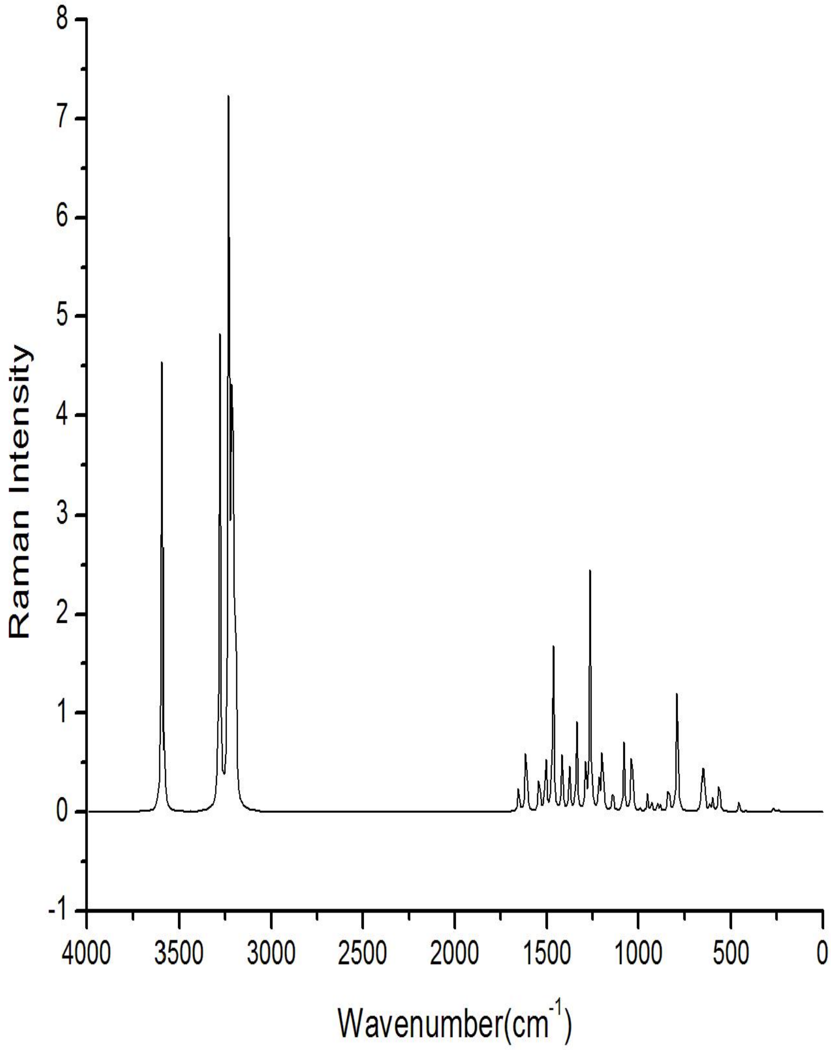

**Fig. 6 FT-RAMAN spectrum of BZE**

**List of Table :**

**Table 1 Vibrational assignments of BZE**

| IR | RAMAN | ASSIGNMENTS |
|---|---|---|
| 240 | … | CH wags(symmetric) |
| 456 | 456 | C2H,C5H,and Im NH wags |
| 600 | 568 | C3H,C4H and NH wags |
| … | 648 | CH & NH wags(asymmetric) |
| 784 | 792 | CH strong wags(asymmetric) |
| 880 | 928 | CH strong and Im CH wags |
| 992 | 952 | C2H and NH bending |
| 1080 | 1040 | CH strong bending(symmetric) |
| … | 1080 | CH strong bending(symmetric) |
| … | 1136 | CH and NH bending |
| 1200 | 1200 | C2H,C3H, and C5H bending(asymmetric) |
| 1288 | 1264 | C2H,C3H,and C5H bending (symmetric) |
| 1376 | 1336 | C2H, and C3H bending (symmetric) |
| … | 1416 | C2H,C4H,and C5H bending (asymmetric) |
| 1464 | 1464 | CH strong and Im XH strong bending (symmetric) |
| 1544 | 1544 | CH strong and Im XH strong bending (symmetric) |
| 1656 | 1616 | XH strong bending and CC strong Stretching |
| 3200 | 3200 | NH Vibrations |

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