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Topic of Research: A Vibrational Study of Biomolecules and Their Derivatives

Findings

This study presents the theoretical (DFT) and experimental investigations of the vibrational spectra of 5-substituted uracils (F, Cl, NH_2 and CH_3) bio-molecules and these are the *three different types* of structural substitutions on the *fifth position* of pyrimidine ring of uracil. And *all of the normal modes* of vibration and other structural parameters of the respective different bio-molecules are evaluated, which the rare pyrimidine bases are naturally occurring in thymine (in DNA) and uracil (in RNA). Here in our work, 5-chloro-uracil has been studied and reported for the stability and reactivity of *heterocyclic molecules* for the analysis of antiviral-drugs against the new corona virus; COVID-19. 5-Fluorouracil is a derivative of uracil and one of the most often used drugs to treat solid tumors and colorectal carcinoma.

The scaled quantum mechanical (SQM) force fields method has been implemented by Pulay et al. and Nishimura et al. to adjust force constants for the vibrational frequencies of the molecules to compare with experimental results involves risk of misinterpretation of other modes of vibrations for the molecules. The effects of substituent groups on uracil ring have been studied experimentally and theoretically by a few authors in a few cases. *Ab initio* and density functional theory (DFT) calculations have been made in rare cases. Here, this study has been done with a detail comparison of the results and discussions obtained for *three different structural substitution* reveals the certain intriguing facts. In our work, it is found that the theoretical density functional theory (DFT) calculations using Gaussian-09 program provide extremely valuable detailed information about the experimentally observed IR and Raman band peaks as well as the theoretically predicted optimized the vibrational frequencies along with their corresponding intensities in IR and Raman scattering activities and depolarization ratios

of the Raman bands with optimized molecular geometries, atomic charges (APT/Mulliken charges), HOMO-LUMO, MEPs/ESPs and thermodynamics functions.

In the pyrimidine ring of uracil, 5-halosubstituted uracils, 5-amino-uracil and 5-methyluracil, one of the double C=C bond ring stretching mode has been reported in both the experimentally observed and theoretically calculated frequencies in the region 1715–1650 cm^{-1}. The Kekule ring mode like the mode (ν_{14}) of benzene has been reported in the both results at the frequency ~1085 cm^{-1} for uracil, ~1150 & 1163 cm^{-1} for the 5-halogenated uracils (F & Cl), ~1205 cm^{-1} for the 5-aminouracil and ~1150 cm^{-1} for the 5-methyluracil in which the mode of substituted uracils appears to have higher magnitude than the parent uracil molecule due to the involvement of substituted halogen atoms and hydrogen bonding of substituted amino and methyl group atoms in the respective molecules. One of the mass sensitive mode, the ring-breathing like the mode (ν_1) of benzene has been assigned at lower in the magnitude for 5-halosubstituted uracils, 5-amino-uracil and 5-methyluracil than the parent uracil molecule due to the mass of the respective substituted group of atoms. Similarly, the trigonal angle ring bending like the mode (ν_{12}) of benzene is also the mass sensitive mode like the ring-breathing mode.

All the corresponding dihedral angles of pyrimidine ring of the uracil, 5-halosubstituted uracils and 5-methyluracil are mostly either 0^0 or 180^0, which indicate that all the twelve atoms of pyrimidine ring of these molecules are in the same plane. . But, all the corresponding dihedral angles of pyrimidine ring of 5-amino-uracil are found to have some distortion in the ring from planarity (of about 0.5^0-1.5^0). All 5-Substituted-uracils have changed the electro-negativity with a noticeable - or +ve sign charge for the purpose of drug-design. In our results, the 5-fluoro-uracil, 5-amino-uracil and 5-methyl-uracil are having the energy gap -5.330415, -4.5579 and -5.4192 eV respectively. Where, the 5-amino-uracil has the smallest energy gap than above two molecules as well as uracil (-5.61896 eV) and 5-chloro-uracil (-5.1605067 eV). Therefore, the 5-amino-uracil is most bio-active in all of the molecules.

Finally, it provides a firm basis for future development in the use of anti-carcinogenic drugs synthesis against the new corona virus; COVID-19, cancers, anti-HIV viruses and DNA repairing.