

FIRST ORDER HYPERPOLARIZABILITY OF 5-FLUORO-1,3-DIMETHYL URACIL USING COMPUTATIONAL METHODS

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ABSTRACT:

During the past decades it has been shown that Time Dependent Density Functional Theory (TD-DFT) is able to predict accurately and efficiently the polarizability of molecules, when using appropriate exchange-correlation potentials and (large) basis sets. In recent days organic single crystals are gaining important due to good optical behaviour. The first order hyperpolarizability along with dipole moment, mean polarizability, anisotropy of the polarizability are calculated using HF/6-311++G(d, p) and B3LYP/6-311++G(d, p) basis sets for 5-fluoro-1,3-dimethyl uracil 5-1-3FDMU.

KEYWORDS: HF, B3LYP, molecular polarizability; density functional theory.

of Lee, Yang, and Parr (LYP) [7]. The basis sets used for 5-1-3FDMU are HF/6-311++G(d, p) and B3LYP/6-311++G(d, p). These basis sets employ triple split valence wavefunctions (which allows orbitals to change size) and polarization function (which allows orbitals with angular momentum to change shape) by adding d functions to heavy atoms and p functions to hydrogen atoms. A basis set is a mathematical description of the orbitals within a system used to perform the theoretical calculation [8]. These basis sets at HF and DFT levels were used to compute optimized structural parameters, vibrational frequencies and thus the vibrational frequency assignments were made. The thermodynamic parameters, electric dipole moment (μ), the isotropic polarizability and the first order hyperpolarizability of the 5-1-3FDMU are also calculated by HF and DFT methods.

I. INTRODUCTION:

The polarizability of an atom or molecule describes the response of its electron cloud to an external field. The polarization energy due to an external electric field E is proportional to E^2 for external fields that are weak compared to the internal electric fields between its nucleus and electron cloud. Technically, polarizability is a tensor quantity, but for spherically symmetric charge distributions it reduces to a single number [1]. NLO materials have gained attention in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching and dynamic image processing [2]. In this study molecular geometry, optimized parameters are computed and the performance of the computational method for B3LYP at 6-311++G (d,p) basis set [3]. This method predicts relatively accurate molecular structure with moderate computational effort. Recently, vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds [4].

II. COMPUTATIONAL DETAILS:

Quantum chemical calculations for 5-1-3FDMU in the ground state are computed by both Ab initio Hartree-Fock (HF) and density functional theory (DFT) methods with Gaussview molecular visualisation program and Gaussian 03 program [5]. DFT method employs Becke's three-parameter hybrid functional [6] (B3) combined with the electron correlation functional

III. RESULTS AND DISCUSSION:

MOLECULAR GEOMETRY:

The molecular structures of 5-1-3FDMU having C_s point group symmetry are shown in Fig. 1. Titled compound 5-fluoro-1,3-dimethyl uracil $C_6H_7O_2N_2F$ have 18 atoms and belonging to the point group C_s . The three Cartesian displacements of the 18 atoms provide 48 internal modes. All 48 fundamental vibrations are active in both IR & Raman. For an N-atomic molecule, as already discussed, $(2N-3)$ of all the vibrations are in plane and $(N-3)$ are out of plane [9]. Thus for 5-1-3FDMU 33 of all the 48 vibrations are in-plane.

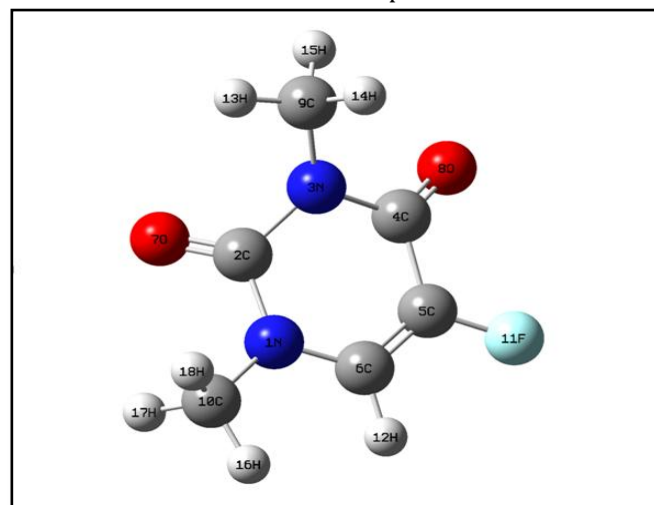


Fig. 1: Molecular structure of the 5-fluoro-1,3-dimethyl uracil

MOLECULAR POLARIZABILITY:

The first order hyperpolarizability β_{total} along with dipole moment μ , mean polarizability $\langle\alpha\rangle$, anisotropy of the polarizability $\Delta\alpha$ are calculated using HF/6-311++G(d, p) and B3LYP/6-311++G(d, p) basis sets for 5-fluoro-1,3-dimethyl uracil. If a molecule is exposed to an external electric field E [10], the charge density and hence the energy of the system will be changed. The polarizability of a molecule can be obtained from a Taylor expansion of the energy U about the electric field strength E, (i, j and k run over cartesian components, i.e. x, y and z):

$$U = U_0 - \sum_i \mu_i E_i - 1/2 \sum_i \sum_j \alpha_{ij} E_i E_j - 1/6 \sum_i \sum_j \sum_k \beta_{ijk} E_i E_j E_k + \dots$$

where U_0 is the energy of the unperturbed molecule; E_i is component of the field in the i direction, μ_i , α_{ij} and β_{ijk} are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively. The 27 components of first order hyperpolarizability can be reduced to 10 components due to the Kleinman symmetry [11]. The total static dipole moment μ , mean polarizability $\langle\alpha\rangle$, anisotropy of the polarizability $\Delta\alpha$ and total first order hyperpolarizability β_{total} using x, y, z components can be defined as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

$$\Delta\alpha = \{1/2 [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]\}^{1/2}$$

$$\beta_{total} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

The mean molecular polarizability was obtained through the knowledge of above mentioned quantities and with the help of above equation. The molecular structural data, employed in the present computation are taken from the HF/DFT calculations.

The calculated polarizabilities α and hyperpolarizabilities β in esu are given in Table 1. α and β values of Gaussian 03W output are reported in atomic units (a.u.) and converted to electrostatic units (esu). 1 a.u. = 0.1482×10^{-24} esu (for α); 1 a.u. = 8.6393×10^{-33} esu (for β). The magnitude of the molecular hyperpolarizability α is one of key factors in a NLO (non-linear optical) system. The calculated first order hyperpolarizability(β) is 0.06572×10^{-37} esu for HF/6-311++G(d,p) and 0.07243×10^{-37} esu for B3LYP/6-311++G(d,p).

Table 1. Non linear optical properties of 2,4-Dihydroxy Pyrimidine -5- Carboxylic Acid calculated using HF/6-311++G(d, p) and B3LYP/6-311++G(d, p) basis set.

NLO behaviour	Values	
	HF/6-311++G(d, p)	B3LYP/6-311++G(d, p)
Mean polarizability $\langle\alpha\rangle$	0.44306×10^{-25} esu	0.27411×10^{-25} esu
Anisotropy of the polarizability ($\Delta\alpha$)	0.78084×10^{-25} esu	0.49784×10^{-25} esu
First hyperpolarizability (β)	0.06572×10^{-37} esu	0.07243×10^{-37} esu

IV. CONCLUSION:

The present work reports a DFT-based chemical potential equalisation approach for the calculation of response properties of molecules in an external field. The induced charges and dipoles at the atomic sites are calculated from a set of linear equations derived here. A unified picture, supported by a sound theoretical framework, that has thus emerged encompasses all the earlier empirical approaches for the evaluation of molecular polarizability from the atomic ones. The calculated polarizabilities obtained here from the chosen atomic parameters are found to be in good agreement with the available experimental values.

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