

# First Order Hyperpolarizability of 6-Chloromethyl 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 behavior. 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 6-Chloromethyl Uracil 6-CMU.

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

## I. INTRODUCTION

Pyrimidine cytosine, uracil and their derivatives are of great biological importance. Recent spectroscopic studies of uracil and its derivatives have been motivated because of their biological and pharmaceutical importance. Uracil's use in the body is to help carry out the synthesis of many enzymes necessary for the cell function through bonding with riboses and phosphates. Uracil and its derivatives serves as allosteric regular and coenzymes for reactions in the human body and in plants. Some of its derivatives used as an anticancer drug (These drug inhibits RNA replication enzymes, thereby diminishing RNA synthesis and stopping the growth of cancerous cell). Some of them are the basic constituents of DNA and RNA and play an important role in constitution properties of nucleic acids. [1-3] 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 [4]. 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 [5]. 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 [6]. 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 [7].

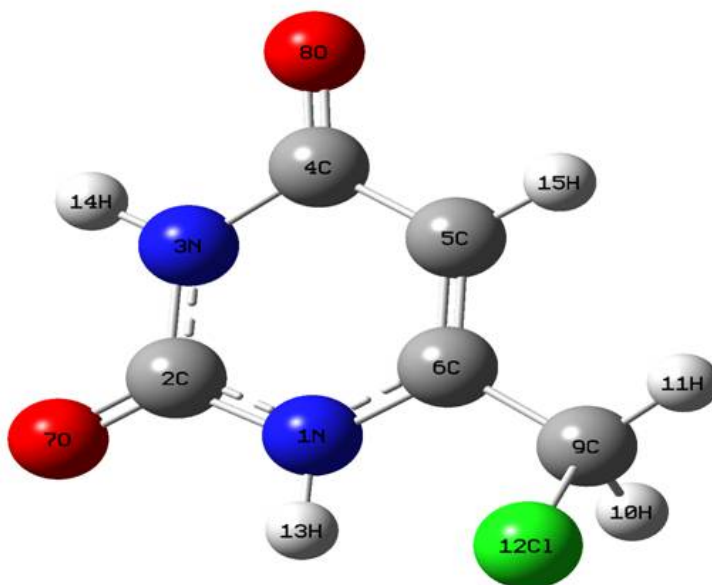
## II. COMPUTATIONAL DETAILS

Quantum chemical calculations for 6-Chloromethyl Uracil (6-CMU) 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 [8]. DFT method employs Becke's three-parameter hybrid functional [9] (B3) combined with the electron correlation functional of Lee, Yang and Parr (LYP) [10]. The basis sets used for 6-CMU 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 [11]. 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 ( $\mu$ ), the isotropic polarizability and the first order hyperpolarizability of the 6-CMU are also calculated by HF and DFT methods.

### III. RESULTS AND DISCUSSION

**Molecular Geometry:** 6-Chloromethyl Uracil (6-CMU) having  $C_s$  point group symmetry are shown in Fig. 1 The molecular structures of 6-CMU have 15 atoms and belonging to the point group  $C_s$ . The three Cartesian displacements of the 15 atoms provide 39 internal modes. All 39 fundamental vibrations are active in both IR & Raman. The 39 normal modes of 6-Chloromethyl Uracil are distributed among the symmetry species as  $13N-6 = 26A'$  (in-plane) +  $13A''$ (out-of-plane),



**Fig. 1: Molecular structure of the 6-Chloromethyl Uracil**

**Molecular Polarizability:** The first order hyperpolarizability  $\beta_{total}$  along with dipole moment  $\mu$ , 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 6-Chloromethyl Uracil. If a molecule is exposed to an external electric field E [12], 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,  $\mu_i$ ,  $\alpha_{ij}$  and  $\beta_{ijk}$  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 [13]. The total static dipole moment  $\mu$ , mean polarizability  $\langle\alpha\rangle$ , anisotropy of the polarizability  $\Delta\alpha$  and total first order hyperpolarizability  $\beta_{total}$  using x, y, z components can be defined as:

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

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

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

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

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 calculation.

The calculated polarizabilities  $\alpha$  and hyperpolarizabilities  $\beta$  in esu are given in Tables 1.  $\alpha$  and  $\beta$  values of Gaussian 03W output are reported in atomic units (a.u.) and converted to electrostatic units (esu). 1 a.u. =  $0.1482 \times 10^{-24}$  esu (for  $\alpha$ ); 1 a.u. =  $8.6393 \times 10^{-33}$  esu (for  $\beta$ ). The magnitude of the molecular hyperpolarizability  $\langle \alpha \rangle$  is one of key factors in a NLO (non-linear optical) system. The B3LYP/6-311++G(d,p) calculated first order hyperpolarizability value  $\beta_{total}$  of 6-CMU is equal to  $0.07109 \times 10^{-37}$  esu while this value is  $0.05149 \times 10^{-37}$  esu at HF/6-311++G(d,p) for 6-CMU.

**Table 1. Non linear optical properties of 6-Chloromethyl Uracil calculated using HF/6-311++G(d, p) and B3LYP/6-311++G(d, p) basis set.**

NLO behavior	Values	
	HF/6-311++G(d, p)	B3LYP/6-311++G(d, p)
Mean polarizability $\langle \alpha \rangle$	$0.55375 \times 10^{-25}$ esu	$0.55295 \times 10^{-25}$ esu
Anisotropy of the polarizability ( $\Delta\alpha$ )	$1.00439 \times 10^{-25}$ esu	$1.08134 \times 10^{-25}$ esu
First hyperpolarizability ( $\beta$ )	$0.05149 \times 10^{-37}$ esu	$0.07109 \times 10^{-37}$ 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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