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NON LINEAR OPTICAL PROPERTIES OF ACETONITRILE USING QUANTUM CHEMICAL METHODS

V.P.Deshmukh[1]*, S.R.Mitkar[2], C.S.Kodarkar[3]

[1,2,3]Department of Physics, Shri Siddheshwar Mahavidyalaya, Majalgaon-431131, India
*Corresponding author email: dvinayaka@gmail.com

Abstract: This work reports nonlinear optical properties (NLO) of acetonitrile using quantum chemical methods. The static first and second hyperpolarizability (β and γ) are obtained by using the Finite-Field approach. The finite field is applied either in X, Y or Z direction. The geometrical parameters of acetonitrile molecule at B3LYP/6-311++G** level are in excellent agreement with the available experimental values. The calculated dipole moment is also close to the experimental value. A systematic change have observeed in β and γ values in acetonitrile. The γ values are higher than β values.

Keywords: Acetonitrile, NLO properties, Quantum Chemical Methods, Hyperpolarizabilities.

1. INTRODUCTION

Non Linear Optical (NLO) properties are important for the development of photonic devices optically based computers, optically based telecommunication systems, and for dat/images etc.. Several efforts have been made to understand the NLO properties of organic molecules for the last two decades [1-9]. Theoretical methods such as Quantum chemistry methods play a important role for the prediction of NLO properties of a material and its suitability use in photonic applications.

Acetonitrile(ACN) is a widely used dipolar aprotic solvent. ACN role as a common solvent in a verity of chemical processes and its unusually high dipole moment (3.92D) [10] for such a small organic molecule, has caught the attention of several experimental and theoretical works.

In the present work we have investigated the geometrical parameters and NLO properties by carrying out quantum chemical methods. This paper is structured as follows. The next section gives computational details. Results are presented and discussed in the third section. Conclusions are in ferret in the last section.

2. COMPUTATIONAL DETAILS

The geometries of ACN molecule is optimized using quantum chemical methods with different basis set. In particular we have used ab initio and density functional theory methods. Density functional theory with B3LYP, B3PW91 and PBEPBE exchange and correlation functionals have been used for the geometry optimization of ACN molecules Geometries of ACN molecule have also been optimized at Hatree-Fock level. The basis sets used in geometry optimization are split valence triple zeta basis set with and without added diffuse and polarization functions on hydrogen and heavy atoms. Using these calculations we level of theory at which ACN molecule shows the lowest energy and the minimum energy structure.

First and second hyperpolarizabilities are then obtained by using Finite-Field method.[11-19]

$$\beta_i = \{-E(2F_i) + E(-2F_i) + 2[E(F_i)-E(-F_i)]\}/4(F_i)^3$$

$$\gamma_i = \{E(3F_i) - 12E(2F_i) + 39E(F_i) - 56E(0) + 39E(-F_i) - 12E(-2F_i) + E(-3F_i)\}/36(F_i)^4$$

Here E(Fi) indicates the total energy in the presence of field (F) applied in i direction (i = x , y or z).

All the calculations are performed using Gaussian suit of program[20].

3. RESULT AND DISCUSSION

We first optimized geometries of ACN molecule at different level of theory to obtain the lowest energy structure. We have used Hatree-Fock (HF) and Density Functional theory with exchange and correlation functionals viz. B3LYP, B3PW91 and PBEPBE with split valence triple zeta basis set with and without diffuse and polarization functions. The ACN molecule shows lowest energy at B3LYP/6-311++G** level. Fig. 1 shows the optimized structure of ACN at B3LYP/6-311++G** level of theory.

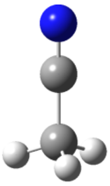

Fig. 1 *Optimized structure of ACN at B3LYP/6-311++G** level*

Table 1 gives bond lengths, angles and dipole moment for ACN at B3LYP/6-311++G** level along with experimental determinations [21]. As can be seen from Table 1, bond lengths, angles and dipole moment for ACN molecule is in excellent agreement with the respective experimental value. The bond lengths C-C are slightly longer than C=N and C-H bond lengths. ∠C-C-H is smaller than ∠C-C=N.

Table 1 Structural parameters for ACN B3LYP/6-311++G level alongwith available experimental values for acetonitrile. Bond lengths in Å and bond angles in degrees.**

Parameters	Exp	CH3CN
C-C	1.458	1.520
C=N	1.157	1.144
C-H	1.102	1.070
∠C-C-H	109.5	109.4
∠C-C=N	–	180
μ (Debye)	3.92	4.05

NLO Properties

The dipole moments or total energy of a molecule can be used to calculate hyperporizabilities. However both these approach do not give the same results but energy based equations are more stable with respect to field strength than the dipole moment based equation. Here also we have used energy based equations to obtain hyperporizabilities using Finite-Field method. Finite-Field method is a derivative method for obtaining the hyperporizabilities and therefore one can not avoid the numerical problem. For the accurate determination of hyperporizabilities , suitable field strength needs to be decided in order to obtain the numerical stability. Since hyperporizabilities calculations using the Finite-Field involves energy of molecules, the numerical accuracy of the hyperporizabilities calculations using Finite –Field method will be sensitive to the precision in the energy calculations. Therefore hyperporizabilities using Finite-Field method need to be calculated at different levels of theory.

Here we first applied different Finite-Field strength in x, y and z direction to ACN molecule to obtain the suitable field strength to obtain the numerical stable hyperporizabilities. The geometry of ACN optimized at B3LYP/6-311++G** level have been used here. Once the suitable field strength is decided to prevent the numerical instability, we then obtained hyperporizabilities for ACN molecule at different levels and basis sets.

Fig. 2 shows variation of β and γ of the ACN with field strengths applied in x, y and z direction using Finite-Field method. From fig. 2 it can be said that ACN molecule shows numerical stable hyperporizabilities at a certain range of field strength applied in x, y and z direction. Therefore we have chosen field strength of 0.006 a.u. to calculate the hyperporizabilities of ACN using different methods and basis sets. WE have obtained hyperporizabilities using different levels of theory with field strength of 0.006 a.u. applied in x, y and z direction.

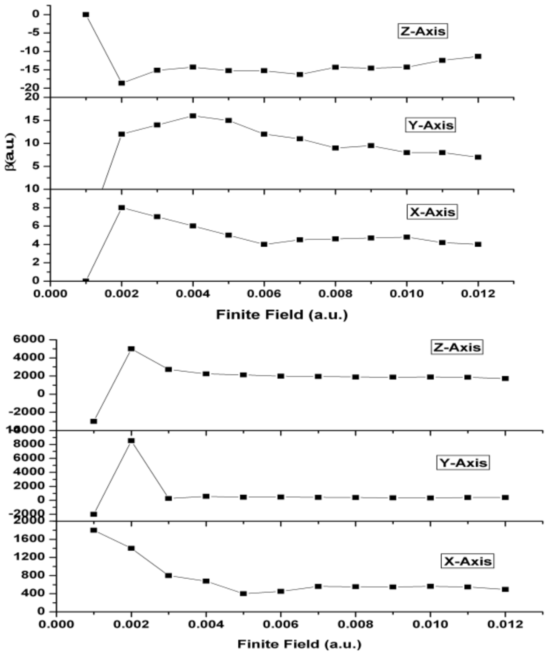

Fig. 2 *Variation of β and γ for ACN with field strength at B3LYP/6-311++G** level.*

From fig.3 (a) the β values for the field applied in y direction it can be seen that electron correlation effect at MP2 level increases β values significantly than the HF level. β values obtained using MP2 level are higher than those obtained using density function theory with different exchange and correlation functionals. There is no large difference in β values obtained using different exchange and correlation functionals employed in DFT method. Here also the split valence triple zeta basis set without diffuse and polarization functions gives lower β values than those obtained with inclusion on diffuse and polarization function in the same basis set at all the levels of theory used. MP2 gives highest values of β among all the methods used and for all the basis sets with field applied along y axis.

Fig. 3(b) shows the variation of γ ACN obtained with different methods and basis sets with field strength of 0.006 a.u. applied in x, y or z direction. Similar to β values, here also ACN shows highest γ values when field is applied along y axis. The split valence triple zeta basis set without diffuse and polarization functions gives γ values lower than those with diffuse and polarization functions on hydrogen and heavy atoms. Here also the electron correlation effect in MP2 method increases the γ values than the HF method. The γ values obtained with different exchange and correlation functional employed in DFT are almost equal for all the basis sets and applied field direction. On comparing the β and γ values of ACN for the field applied in y direction, it can be seen that the γ values latter are more than ten times higher than the latter.

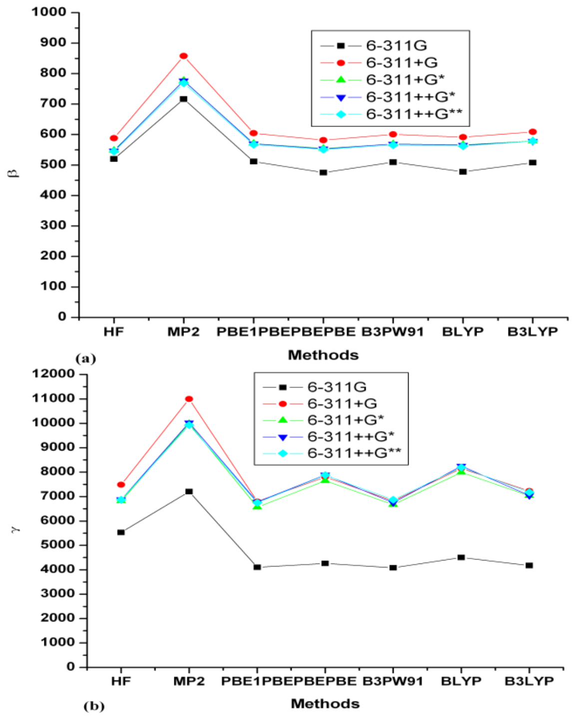

Fig. 3 *Variation of β and γ obtained using various methods and basis sets using field strength of 0.006 a.u.*

4.CONCLUSIONS

We have studied NLO properties of ACN molecule using quantum chemical methods. It is found that ACN molecule is stable B3LYP/6-311++G** level of theory and optimized geometry are in excellent agreement with the experimental values. Using the finite field approach, the first and second hyperpolarizabilities are obtained. To prevent numerical instability, we have applied different field strengths for ACN. The numerically stable hyperpolarizabilities are obtained around 0.006 a.u. Using this field strength to ACN hyperpolarizabilities are obtained with different methods and basis sets. The calculated dipole moment is also close to the experimental value. A systematic change have observeed in β and γ values in ACN. The γ values are higher than β.

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