



RESEARCH ARTICLE

NONLINEAR OPTICAL AND SPECTRAL PROPERTIES OF  
HYDROQUINONE & FULLERENE SYSTEMS

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ABSTRACT

Nonlinear optical materials have highly interesting photo-physical behaviors, which have a wide variety of applications, from optoelectronics to medicine. Nonlinear optical properties together with infrared and nuclear magnetic resonance analyses on the interaction between hydroquinone and pristine or boron and silicon doped C<sub>60</sub> fullerene systems have been investigated by density functional theory. Hydroquinone@C<sub>60</sub> systems in the cis and especially trans form have nonlinear optical applications. The obtained results related to optical properties such as polarizability and first hyperpolarizability may have useful predictive values which can be of interest.

**Keywords:** NLO, Fullerene, Hydroquinone, DFT

1. INTRODUCTION

Hydroquinone (HQ) is an organic aromatic molecule that consists of two hydroxyl groups that are bonded to a benzene ring in the para position. HQ drug molecule is well known for many decades. It shows antioxidant properties and is also used as the lightning agent in the cosmetics and medicine sectors [1-3].

Density functional theory (DFT) is a quantum mechanical modeling method used in physics, chemistry and materials science to investigate the electronic structure of many-body systems. It is a method of calculation to approximately solve the Schrödinger equation. DFT is giving the ability to the current technologies to model the molecular systems or materials [4]. Further, infrared (IR) and nuclear magnetic resonance (NMR) analyses are two powerful techniques to determine the structure of the molecular systems. There are many studies about vibrational spectra of HQ having two isomers, named cis and trans. Since the energy difference between two isomers is very small, previous DFT and experimental studies have agreed with both isomers could be observed in the gas phase [5-10]. Besides, the vibrational bands of the two isomers in the vibrational spectra measured in the liquid and solid phases were not distinguishable [11].

Nonlinear optical (NLO) describes the behavior of light in nonlinear media where polarization density responds nonlinearly to the electric field of the light. It explains the nonlinear response of properties such as frequency, polarization, phase or path of incident light. The non-linearity is typically observed only at very high light intensities such as those provided by lasers [12]. The early studies of NLO focused on inorganic solids. Then, with molecular optical properties, molecular NLO was formed. Due to the distinguished advantages, molecular NLO has been widely used in the bio-photonics field [13, 14]. Further, due to their large optical susceptibilities, inherent ultrafast response times and high optical thresholds for laser power, organic NLO materials have been paid a great deal of attention [15]. NLO materials have highly interesting photo-physical behaviors from optoelectronics to medicine [16].

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In 2018, we examined conformational, energetic and electronic features of HQ adsorption on pristine and silicon or boron-doped fullerenes [17]. M062X and B3LYP functionals were performed with 6-31G(d) and cc-pVDZ basis sets for gas phase and water media. HQ...SiC<sub>59</sub> showed the strongest interaction and trans conformation is slightly more stable than cis whereas the weakest interaction was observed with HQ@C<sub>60</sub>. According to the gap energy, C<sub>60</sub> was more sensitive to the presence of HQ than doped fullerenes in the gas phase while BC<sub>59</sub> showed more sensitivity in water media. In view of the literature information and continuation with our interests in the evaluation of fullerene and drug systems, the prime objective of the current search was to use the DFT method to examine the NLO properties of the interacted pristine or doped fullerene and HQ systems in the gas phase and water. Further, we were interested in understanding the conformation, doping and solvent effects on NLO properties of the investigated nanostructures, together with their IR and NMR features.

## 2. COMPUTATIONAL DETAILS

The optimization, frequency and NMR calculations were performed in Gaussian 09 program [18] whereas the computations of NLO were performed by the Multiwfn 3.3.8 program [19]. GausView 5 and VMD 1.9.3 programs were used for the visualization and interpretation of the data [20, 21]. Following the results of our previous study [17], in all calculations, B3LYP functional was used in conjunction with 6-31G(d) basis set for the gas phase and water medium.

The equations used to calculate the NLO properties are as follows. Here,  $\mu$  is total dipole moment,  $\alpha$  is isotropic polarizability,  $\Delta\alpha$  is polarizability anisotropy and  $\beta$  is static first hyperpolarizability [22].

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

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\Delta\alpha = \frac{1}{2}\{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\}^{1/2} \quad (3)$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

## 3. RESULTS AND DISCUSSIONS

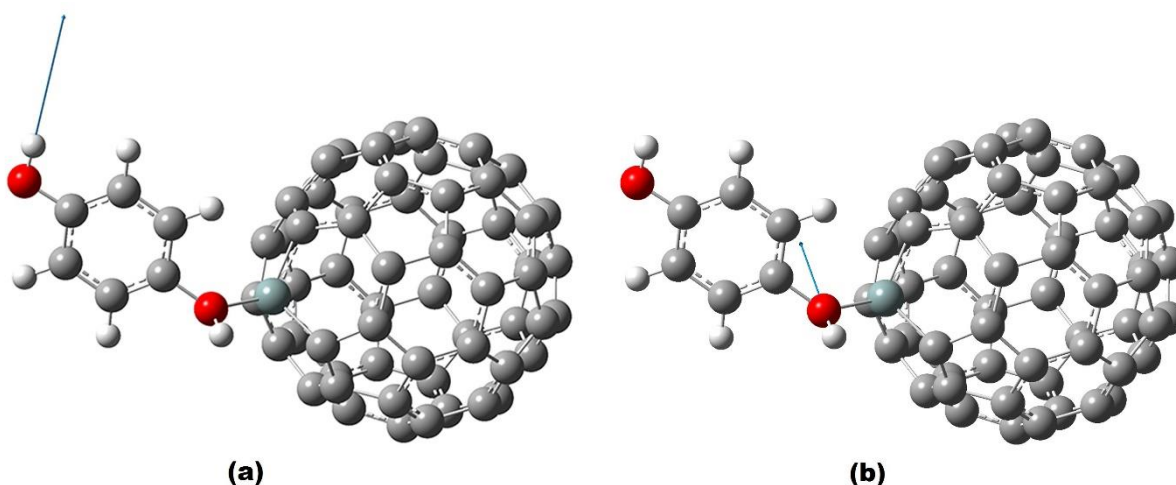
### 3.1. Spectral Analysis

In literature, there are several theoretical and experimental studies on the vibrational spectra of both cis and trans conformers of HQ in the gas and solid phase [5, 9, 23]. The OH stretching vibrations of trans and cis conformer of free HQ in the gas phase were observed at 3652 cm<sup>-1</sup> [5] and 3642 cm<sup>-1</sup> [23] while the scaled theoretical OH stretching vibrations were computed as 3613 cm<sup>-1</sup> and 3611 cm<sup>-1</sup>, respectively, in this study. The scale factor used is 0.9614 [24]. These vibrations have shifted to the lower region as 13 cm<sup>-1</sup> and 12 cm<sup>-1</sup> for water medium correspondingly. The difference between experimental and theoretical data for the gas phase is 39 cm<sup>-1</sup> for trans and 31 cm<sup>-1</sup> for cis form. B3LYP/6-31G(d) level has given very suitable results despite the high-frequency region.

Upon interaction with the pristine fullerene, on average, OH stretching bands are observed at 3605 (3595)  $\text{cm}^{-1}$  and 3607 (3600)  $\text{cm}^{-1}$  for cis and trans form. These bands have shifted with interaction as 6  $\text{cm}^{-1}$ . The values in parenthesis are for the water medium.

For the boron-doped system, interacted OH stretching bands of HQ appear at 3548 (3533)  $\text{cm}^{-1}$  and 3550 (3530)  $\text{cm}^{-1}$  for cis and trans form correspondingly whereas free OH stretching bands are observed at 3607 (3598)  $\text{cm}^{-1}$  and 3608 (3596)  $\text{cm}^{-1}$ . On the interaction, there are 63  $\text{cm}^{-1}$  shifts for boron-doped systems.

Turning to Si-doped systems, interacted OH stretching bands of HQ show at 3452 (3482)  $\text{cm}^{-1}$  and 3465 (3482)  $\text{cm}^{-1}$  for cis and trans form while free OH stretching bands are observed at 3605 (3592)  $\text{cm}^{-1}$  and 3605 (3594)  $\text{cm}^{-1}$ . Upon interacting, there are 148  $\text{cm}^{-1}$  and 170  $\text{cm}^{-1}$  shifts for silicon doped systems correspondingly. OH stretching bands are depicted in Figure 1 as an example.



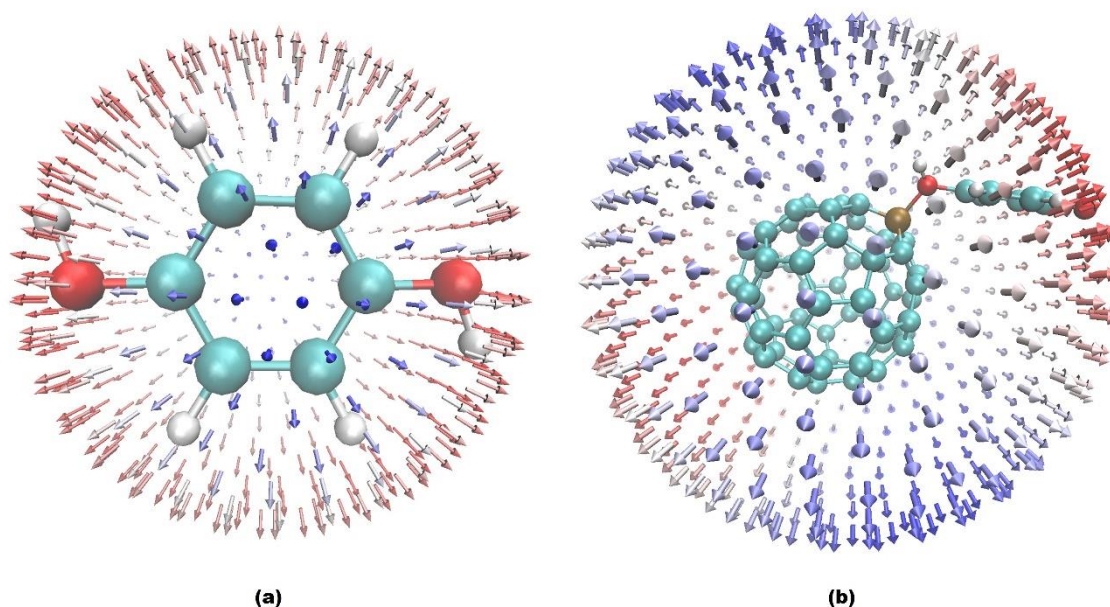
**Figure 1.** Free (a) and interacted (b) OH stretching vibrations of HQ for trans Si-doped molecular system.

To contribute to the structural identifications, NMR analyses were also carried out for the examined systems. Relative NMR frequency shifts were performed in water solvent. NMR shifts of B- and Si-nuclei change as 40 and 58 ppm from  $\text{BC}_{59}$  and  $\text{SiC}_{59}$  to the interacted molecular systems correspondingly. The shifts are attributed to changes in electron density around the dopant atom following the possible interaction with the oxygen atom of HQ. There is no significant difference in NMR shifts between cis and trans forms. Further, the shift of O and H nuclei changes as 13 ppm and 3 ppm from free HQ drug molecule to the doped fullerenes, respectively, whereas these shifts are 4 ppm and 0.1 ppm for the pristine fullerene.

### 3.1. NLO Properties

NLO properties such as dipole moment, polarizability, anisotropy of polarizability and first hyperpolarizability of the molecules are predicted to gain deeper knowledge about the relationship between molecular architecture, nonlinear response and hyperpolarizability and to support the efforts towards the discovery of new efficient products. Figure 2 represents the direction and the magnitude of the induced dipole moment when an external electric field is applied on HQ and HQ... $\text{BC}_{59}$  in trans form. If the electric field is applied parallel to the ring plane of HQ, there will be induced larger dipole moment than the situation that the electrical field is applied perpendicular to the ring plane. On the other hand, the external electric field must be applied in the direction from fullerene cage to HQ drug or vice versa, to induce a significant dipole moment. Furthermore, urea is one of the prototypical molecules used in the study of NLO properties of molecular systems [25]. For this reason, it has been frequently

used as a threshold value for comparative purposes. The calculated values of dipole moment for HQ@C<sub>60</sub>, HQ...BC<sub>59</sub> and HQ...SiC<sub>59</sub> in cis (trans) form are found to be 2.611 (0.920) D, 8.493 (8.122) D and 12.763 (12.874) D, respectively, which are approximately two, six and nine times of the value for urea (1.3732 D) [26]. The dipole moment values of free HQ are equal to 2.683 D and 0.001 D for cis and trans form correspondingly.



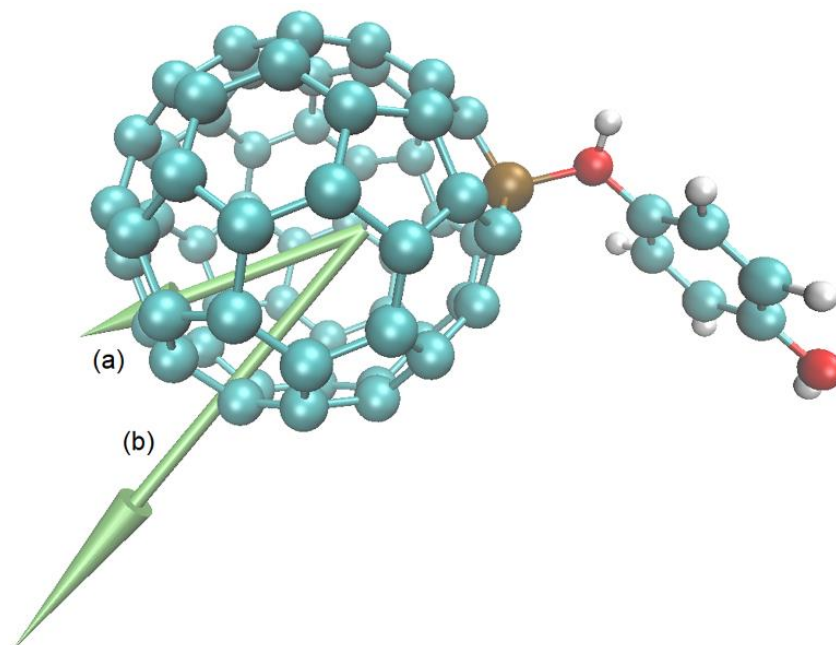
**Figure 2.** Direction and magnitude of the induced dipole moment by an external electric field: HQ (a) and HQ...BC<sub>59</sub> (b) in water medium.

The polarizability of doped fullerenes is directly proportional to the size of the dopant atom [27]. The calculated values of the polarizability of HQ@C<sub>60</sub>, HQ...BC<sub>59</sub> and HQ...SiC<sub>59</sub> in cis (trans) form are found to be 542.228 (543.043) a.u., 546.574 (564.305) a.u. and 581.780 (580.582) a.u. while the anisotropy of polarizability values are equal 95.917 (100.735) a.u., 139.072 (137.450) a.u. and 186.161 (178.995) a.u. correspondingly. According to the results, polarizability and its anisotropy of Si-doped fullerenes are larger than B-doped ones. Further, it seems the polarizability and its anisotropy are proportional to the dipole moment.

Turning to hyperpolarizability, it is one of the important key factors in the NLO system. The calculated values of the first hyperpolarizability of HQ@C<sub>60</sub>, HQ...BC<sub>59</sub> and HQ...SiC<sub>59</sub> in cis (trans) form are found to be 149.305 (185.720) a.u., 1500.852 (1479.960) a.u. and 2842.184 (2733.902) a.u., respectively, which are approximately 3.76, 37.77 and 71.53 times than to the value for urea (39.734 a.u.) [26]. The hyperpolarizability values of free HQ are equal to 45.122 a.u. and 0.012 a.u. for cis and trans form, respectively. Hyperpolarizability values in water medium have been found larger than gas phase data and the magnitude of hyperpolarizability for B-doped molecular systems (2600.445 a.u.) is larger than Si-doped fullerenes (1349.040 a.u.). Figure 3 shows the direction and the magnitude of hyperpolarizability of HQ...BC<sub>59</sub> for trans form in the gas phase and water.

Some studies introduced a correlation between first hyperpolarizability and band-gap energy. However, the character of this relationship does not seem deterministic due to positive correlations and as well as negative correlations found [28, 29]. In both cis and trans form, it seems the first hyperpolarizability is inversely proportional to the band-gap for cis and trans Si-doped (2.153 eV and 2.156 eV) and B-doped (2.176 eV and 2.173 eV) [17] molecular systems in the gas phase. In water medium, however, the hyperpolarizability is directly proportional to the band-gap for the doped systems. Further, HQ@C<sub>60</sub>

systems in the cis (2.044 eV) and trans (2.035 eV) forms that have the smallest band gap [17] have the smallest first hyperpolarizability in the gas phase.



**Figure 3.** Direction and the magnitude of hyperpolarizability of HQ...BC<sub>59</sub> for trans form in the gas phase (a) and water (b).

#### 4. CONCLUSIONS

Theoretical studies of HQ and pristine or boron and silicon doped fullerene systems have been performed on the DFT calculations. There is no significant difference between cis and trans structures from the vibrational and NMR aspects. The interaction with HQ causes a change of the electron density around the doped atom whereas there are no significant shifts for HQ@C<sub>60</sub> systems. The largest IR and NMR shifts were observed in Si-doped systems. According to NLO analyses, there is no precise relation between band-gap and the NLO properties of the examined molecular systems. Further, it clearly seems that dopant atoms definitely affect the NLO properties of fullerenes and these properties are connected with the solvent medium. The investigated molecular systems might have not NLO applications except for free HQ drug and the weakest interaction HQ@C<sub>60</sub> system in cis and especially trans forms.

#### CONFLICT OF INTEREST

There are no conflicts of interest regarding the publication of this article.

#### REFERENCES

- [1] Cotelle N, Moreau S, Cotelle P, Catteau, JP, Bernier JL, Henichart JP. Generation of free radicals by simple prenylated hydroquinone derivatives, natural antitumor agents from the marine urochordate aplidium californicum. *Chemical Research in Toxicology* 1991; 4: 300–305.
- [2] Shadyro OI, Glushonok GK, Glushonok TG, Edimecheva IP, Moroz AG, Sosnovskaya AA, Polozov GI. Quinones as free-radical fragmentation inhibitors in biological important molecules. *Free Radical Research* 2002; 36: 859-867.

- [3] Yamaguchi LF, Lago JHG, Tanizaki TM, Mascio PDi, Kato MJ. Antioxidant activity of prenylated hydroquinone and benzoic acid derivatives from *Piper crassinervium*. *Kunth. Phytochemistry* 2006; 67: 1838-1843.
- [4] Engel E, Dreizler RM. *Density Functional Theory: An Advanced Course (Theoretical and Mathematical Physics)* Springer 2011.
- [5] Wilson, HW. The vapor phase infrared spectra of hydroquinone, pyrocatechol and resorcinol. *Spectrochim. Acta A* 1974; 30: 2141.
- [6] Caminati W, Melandri S, Favero LB. Microwave spectroscopy of hydroquinone: The rotational spectrum of the cis conformer. *The Journal of Chemical Physics* 1994; 100:8569–8572.
- [7] Dunn TM, Tembreull, R, Lubman, D. M, Free-jet spectra and structure of o-, m- and p-dihydroxybenzenes. *Chemical Physics Letters* 1985; 121:453–457.
- [8] Humphrey SJ, Prat DW. High resolution S1→ S0 fluorescence excitation spectra of hydroquinone. Distinguishing the cis and trans rotamers by their nuclear spin statistical weights. *The Journal of Chemical Physics* 1993; 99:5078–5086.
- [9] Tzeng WB, Narayanan K, Hsieh CY, Tung CC. A study of the excited state structure and vibrations of hydroquinone by ab initio calculations and resonant two-photon ionization spectroscopy. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 1997; 53:2595–2604.
- [10] Gerhards M, Unterberg C, Schumm S. Structure and vibrations of dihydroxybenzene cations and ionization potentials of dihydroxybenzenes studied by mass analyzed threshold ionization and infrared photoinduced Rydberg ionization spectroscopy as well as ab initio theory. *Journal of Chemical Physics* 1999; 111:7966–7975
- [11] Varsanyi G. *Assignment of Vibrational Spectra of Seven Hundred Benzene Derivatives*. New York, NY, USA: Wiley, 1974.
- [12] Boyd R. *Nonlinear Optics*. 3rd ed. UK:Academic Press. 2008.
- [13] Kuzmin AN. Resonance Raman probes for organelle-specific labeling in live cells. *Scientific Reports* 2006; 6: 28483
- [14] Yuan Y, Lin Y, Gu B, Panwar N, Tjin SC, Song J, Qu J, Yong KT. Optical trapping-assisted SERS platform for chemical and biosensing applications: Design perspectives. *Coordination Chemistry Reviews* 2017; 339: 138
- [15] Armaković S, Armaković SJ, Šetrajić JP, Holodkov V. Aromaticity, response, and nonlinear optical properties of sumanene modified with boron and nitrogen atoms. *J Mol Model* 2014; 20:2538.
- [16] Medishetty R, Zareba JK, Mayer D, Samoc M, Fischer RA. Nonlinear optical properties, upconversion and lasing in metal–organic frameworks. *Chem Soc Rev* 2017; 46:4976.



- [17] Ergürhan O, Parlak C, Alver Ö, Şenyel M. Conformational and electronic properties of hydroquinone adsorption on C60 fullerenes: Doping atom, solvent and basis set effects. *Journal of Molecular Structure* 2018; 1167: 227–231.
- [18] Frisch MJ, Trucks GW, Schlegel HB, et al. *Gaussian 09, Revision A.1*, Gaussian Inc., Wallingford, CT. 2009.
- [19] Lu T, Chen F, Multiwfn: A multifunctional wavefunction analyzer. *Journal of Computational Chemistry* 2012; 33: 580–592.
- [20] Dennington RD, Keith TA., Millam J.M. *GaussView 5.0.8*, Gaussian Inc., 2008.
- [21] Humphrey W, Dalke A, Schulten K. VMD - Visual Molecular Dynamics'. *J Molec Graphics* 1996, 14:1:33-38.
- [22] Prasad PN, Williams DS. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. John Wiley & Soons New York, USA: 1991. pp. 66-77.
- [23] Akai N, Kudoh S, Takayanagi M, Nakata M. Cis-trans isomerization equilibrium in hydroquinone in low-temperature argon and xenon matrices studied by FTIR spectroscopy. *Chemical Physics Letters* 2002; 356: 133–139.
- [24] Scott AP, Radom L. Harmonic vibrational frequencies: An evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *Journal of Physical Chemistry* 1996; 100:16502-16513.
- [25] Vennila P, Govindaraju M, Venkatesh G, Kamal C. Molecular structure, vibrational spectral assignments (FT-IR and FT-RAMAN), NMR, NBO, HOMO-LUMO and NLO properties of O-methoxybenzaldehyde based on DFT calculations. *Journal of Molecular Structure* 2016; 1111:151–156.
- [26] Abbaz T, Bendjeddou A, Villemin D. Structural and quantum chemical studies on aryl sulfonyl piperazine derivatives. *Journal of Drug Delivery & Therapeutics* 2019; 9: 88-97.
- [27] Dheivamalar S, Sugi L. Density functional theory (DFT) investigations on doped fullerene with heteroatom substitution. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 2015; 151:687–695.
- [28] Liyanage PS, De Silva RM, De Silva, KMN. Nonlinear optical (NLO) properties of novel organometallic complexes: High accuracy density functional theory (DFT) calculations. *Journal of Molecular Structure: Theochem* 2003; 639: 195–201.
- [29] Thanthiriwatte KS, Nalin de Silva KM. Non-linear optical properties of novel fluorenyl derivatives - Ab initio quantum chemical calculations. *Journal of Molecular Structure: Theochem* 2002; 617:169–175.