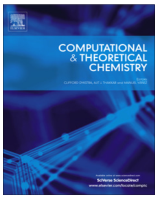
Computational and Theoretical Chemistry 1057 (2015) 43–53

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Effect of external electric field on ground and singlet excited states of phenylalanine: A theoretical study

Pradip Kr. Bhattacharyya

Department of Chemistry, Arya Vidyapeeth College, Guwahati, Assam 781016, India

ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form 31 December 2014
Accepted 23 January 2015
Available online 4 February 2015

Keywords:
TDDFT
External electric field
Excited state
Phenylalanine
Amino acid

ABSTRACT

The effect of external electric field on the ground and few singlet excited states of phenyalanine are studied in the light of TDDFT (time dependent density functional theory) and DFRT (density functional reactivity theory). The excited state geometries are compared with the ground state ones. Sensitivity of the reactivity parameters such as total electronic energy, energy of the HOMO (highest occupied molecular orbital), global hardness (η), electrophilicity (ω) etc. towards the external electric fields are measured by varying the applied field strength. Variation of aromaticity of the ground and excited states are gauged in terms of nucleus independent chemical shift (NICS). Geometry, reactivity and aromaticity of the ground as well as excited states are responsive to the presence of external electric field.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Being the principal constituent, amino acids occupy the centre stage of protein research over decades [1–6]. Among the naturally occurring amino acids; phenylalanine (Phe), tryptophan (Trp) and tyrosine (Try) possess fluorescent aromatic chromophores. The fluorescence spectra of aromatic amino acids depend on the surrounding environments and thus the measurement of their fluorescence may be used to study different aspects of protein structure [7–9]. Phenylalanine is the only aromatic amino acid present in many native biopolymers [10]. Therefore the study of the photophysical parameters of phenylalanine is a prerequisite for conformational studies of proteins and peptides, especially for the estimation of interchromophoric distances [11]. Understanding of the dynamics and the mechanism of the fluorescence of a molecule again entails an in-depth study of the geometries, reactivity and aromaticity of the ground and excited states.

Moreover, the ground and excited state of phenylalanine is envisaged to be influenced by the presence of external electric field, especially in the context of biological systems where the ions present in cellular environment, polar sugar-phosphate back bone and charged histones impart strong local electric field [12]. This proposition is further substantiated by some recent works which show that biological systems can experience a strong electric field with magnitude ranging from $\sim 10^8$ to $\sim 10^{10}\,\mathrm{Vm}^{-1}$ [12,13].

In recent years Time Dependent Density Functional Theory (TDDFT) has become a popular tool for computing the electronically excited states of molecules [14–20]. On the other hand density functional reactivity theory (DFRT) has been particularly impressive in estimating reactivity parameters of molecular systems. These parameters, called reactivity descriptors, defined within the framework of density functional theory are global hardness (η) (also called chemical hardness), electrophilicity (ω), chemical potential (μ) etc [21]. These descriptors have been tested and studied extensively by several research groups and are reported to be very useful in rationalizing the reactivity patterns in the molecular systems [22–26]. Geerlings et al. and Chattaraj et al. have reviewed the theoretical basis of these descriptors and also their applicability [27,28]. Some of the recent developments and applications of these descriptors are greatly commendable [29–33].

The effect of electric field on the chemical reactivity has been illustrated in several earlier studies [34–44]. Particularly, the chemical reactivity as a function of orientation in the electric field has been thoroughly investigated [34,35]. Chattaraj and his co-workers have observed the effect of electric field on the global and local reactivity indices and confirms that electric field impinge on all the local reactivity indices substantially [36]. Pal and co-workers also studied the behaviour of these descriptors in presence of external electric field as well as solvent media [37–40]. That the introduction of electric field influences both physical and chemical properties of various molecular systems are evident from these studies. Recently a number of works has been devoted to the study

---

E-mail address: prdpbhatta@yahoo.com

http://dx.doi.org/10.1016/j.comptc.2015.01.017
2210-271X/© 2015 Elsevier B.V. All rights reserved.

of application of external electric field on biological molecules [41–44].

Herein TDDFT and DFRT are exploited to study the effect of external electric fields on reactivity, stability and aromaticity of the ground and first three singlet excited states of phenylalanine.

2. Theoretical and computational details

In DFT, chemical potential (μ) and global hardness (η) are defined as the first and second derivative of energy with respect to the number of electrons respectively [45,46]. Use of finite difference approximation and Koopmans' theorem [47] leads to the working formulae for μ and η as $\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2}$ and $\mu = \frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2}$. Electrophilicity ($\omega$) [48] is expressed as $\omega = \frac{\mu^2}{2\eta}$.

The ground state geometrical minima of the species are obtained using 6-31+G(d,p) with Becke three parameter exchange and Lee, Yang and Parr correlation functional (B3LYP) [49,50] and are ascertained by frequency calculations. After locating the minima, single point energy calculations have been carried out at different external electric field strengths applied along six directions (along positive and negative directions of x, y and z-axes, the sign + means that the field is applied along + direction of the axis and – sign means that the field is applied along the – direction of the axis). The range of the strength of the external field chosen to be 0.00–0.01 a.u. [1 a.u. = 51.4 V/Å = 51.4×10^{10} Vm^{-1}]. The global reactivity descriptors (μ, η and ω) are calculated using expressions mentioned above. The excited states are obtained from the B3LYP/6-31+G(d,p) optimized structure using TDDFT method and involved single excitations only. Further, to observe the effect of functional on the chosen parameters, we repeated the calculations using CAM-B3LYP functional. This functional was tested and confirmed to provide results with acceptable accuracy [51]. Moreover to test the effect of basis set, the calculations are repeated with 6-311++G(d,p) basis set.

Nucleus independent chemical shift (NICS) is used to evaluate aromaticity of the system [52,53] Rings with large negative NICS values are considered aromatic. The more negative the NICS values, the more aromatic the rings are. Non-aromatic species have NICS values close to zero and positive NICS values are indicative of anti-aromaticity. NICS is usually computed at ring centres (NICS(0)) determined by the non-weighted mean of the heavy atoms coordinates. However, it can also be calculated at certain distance above or below the centre of the ring. In fact, the NICS value obtained at 1 Å above the molecular plane (NICS(1)) or its corresponding out-of-plane tensor component ($\mathrm{NICS(1)}_{zz}$) is considered to reflect the *p*-electron effects better than NICS(0) [54,55] Therefore, both NICS(0), and NICS(1) together with $\mathrm{NICS(1)}_{zz}$ values are calculated [54,56] in presence of external electric fields using the Gauge-Including Atomic Orbital method (GIAO) [57,58] by placing a ghost atom (Bq) at the geometric mean of the ring atoms (and 1 Å above the molecular plane of the six member ring) and computed the isotropic chemical shift (σ_{iso}) at this ghost atom. We report $-\sigma_{\mathrm{iso}}$ values (NICS) = $-\sigma(\mathrm{Bq})_{\mathrm{iso}}$), throughout the manuscript. All the calculations are carried out using Gaussian09 [59].

3. Results and discussion

The adsorption spectra of phenylalanine were performed some time ago and are still the primary source [60]. In this work the calculated adsorption spectra of phenylalanine are observed at 220 nm in aqueous phase (224 nm in gas phase) which is closer to the experimental value 258 nm. The deviation from the experimental value is due to the fact that the computations are performed in a single molecule whereas in experiment we have a large number of molecules that might interact themselves. However, this result is appreciably closer to the experimental values compared to that obtained earlier [61] where Hameka et al. reported the calculated peak at 201 nm. The peak at 220 nm is associated with the HOMO → LUMO transition with oscillator strength 0.1393. The shape of the HOMO and the LUMO are depicted in Fig. 1 which shows that the transition is basically $\pi \rightarrow \pi^*$ in nature. Apart from the peak at 220 nm, the other two prominent peaks at 213 nm and 205 nm (with oscillator strength 0.0289 and 0.0234 respectively) associated with the HOMO → LUMO + 3 and HOMO → LUMO + 4 transitions respectively. Excitation of a molecule leads to change in the geometry of the molecule.

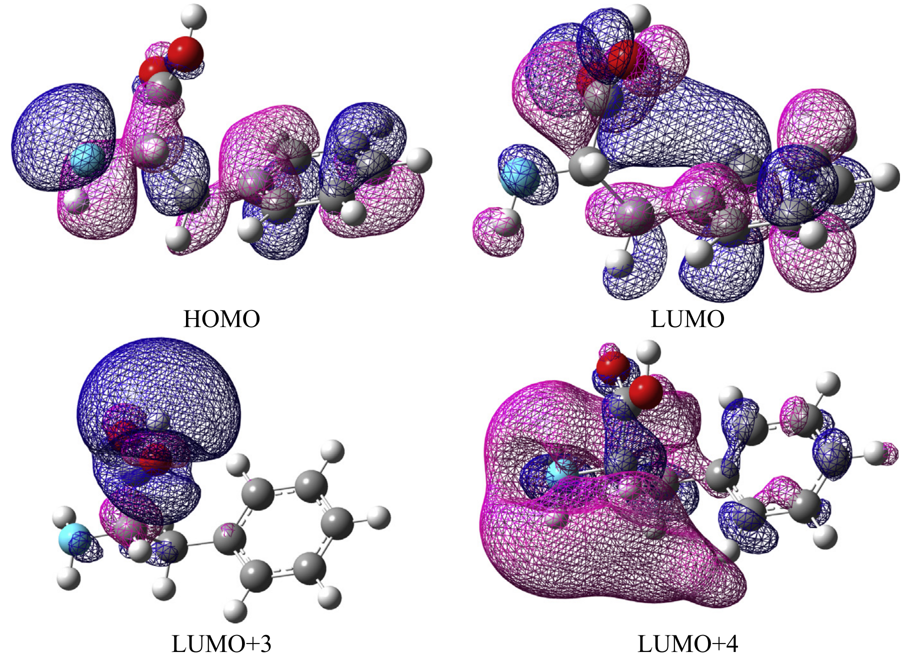


Fig. 1. Molecular orbital involved in electronic transition in phenylalanine.

Download English Version:

https://daneshyari.com/en/article/5393360

Download Persian Version:

https://daneshyari.com/article/5393360

Daneshyari.com