



Research Article

**VIBRATIONAL ANALYSIS AND ELECTRONIC PROPERTIES OF
ZWITTERIONIC D-PHENYLALANINE**

**Abdelali BOUKAOU^{*1}, Djamel SEBBAR², Nouara GUESSABI³,
Samiya AISSOU⁴**

¹Laboratoire de Physique des Techniques Expérimentales et ses Applications, Université de Médéa,
ALGERIA; ORCID: 0000-0003-2190-9152

Faculté des Sciences, Département des Sciences de la Matière, Université de Médéa, ALGERIA

²Laboratoire de Physique des Techniques Expérimentales et ses Applications, Université de Médéa,
ALGERIA; ORCID: 0000-0003-4463-1982

³Faculté des Sciences, Département des Sciences de la Matière, Université de Médéa, ALGERIA ;
ORCID: 0000-0001-7662-3149

⁴Faculté des Sciences, Département des Sciences de la Matière, Université de Médéa, ALGERIA;
ORCID: 0000-0003-2767-5481

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ABSTRACT

In this study, the experimental FT-IR spectrum of zwitterionic D-phenylalanine has been recorded at room temperature and interpreted by density functional theory (DFT) calculations. The optimized geometry and vibrational wavenumbers have been calculated using the DFT/B3LYP method with the def2-TZVP basis set. Some interesting electronic properties like the HOMO and LUMO energy levels and HOMO-LUMO energy gap have also been calculated.

Keywords: D-phenylalanine, IR spectroscopy, HOMO and LUMO analysis, DFT calculations.

1. INTRODUCTION

An amino acid is an organic compound characterized by the presence of a carboxyl group (COOH), an amino group (NH₂), a hydrogen atom and a characteristic side chain group (-R group), all bonded to the same carbon atom called α -carbon [1] (Fig.1 (a)).

^{*} Corresponding Author: e-mail: a.boukaoud@gmail.com, tel: +231(0)553266943

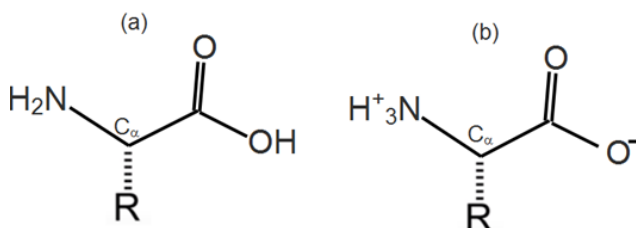


Figure 1. Unionized form (a) and zwitterionic form (b) of amino acids.

In the solid phase, the amino acids exist in the zwitterionic form, which means that the NH₃⁺ group is protonated (positively charged) and the -COO⁻ group is deprotonated (negatively charged) (Fig. 1. (b)).

Phenylalanine (Phe) is one of the nine essential amino acids that our body cannot synthesize [2]. As the case of all others α -amino acids (except for glycine), Phe possess an intimate property of chirality: it may exist in two enantiomers, right handed form (D-phe) or left handed form (L-Phe) [1].

Today, it is well known that proteins are constituted exclusively of L-amino acids, however, the question about the origin of this preferential tendency remains unanswered [3,4].

The use of IR spectroscopy for studying the hydrogen-bonded systems like the amino acid compounds can be revealed important information about their hydrogen bond networks [5,6].

The IR spectrum of L-phe was previously reported [7]. More than ten years later, the behavior of IR spectra of L-phe in aqueous solutions (at several pH values) were investigated by S. Olsztynska et al. [8]. Moreover, X. Cao et al. proposed a tentative assignment of the observed bands in the IR spectrum of L- β -phenylalanine (L- β -phe) using DFT calculations [9].

To the best of our knowledge, a detail study of the vibration and electronic behavior of D-phe using a combination of IR spectroscopy and DFT calculations has not yet been performed.

This work aims to investigate the effects of hydrogen bonding on the vibrational normal modes of D-phe using a combination of IR spectroscopy and DFT calculations. To this end, the prominent observed bands in the IR spectrum of D-phe have been compared to those previously observed for L-phe [7] and L- β -phe [9]. In addition, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, as well as the gap energy for D-phe have been predicted.

2. EXPERIMENTAL DETAILS

The zwitterionic form of D-phe ($\geq 99\%$) was purchased from Sigma Aldrich (Japan) and used without further purification.

The FT-IR spectrum of polycrystalline sample of D-phe was recorded, at room temperature, in the region 400–4000 cm⁻¹ using KBr pellets on a FTIR-8400S spectrometer with a spectral resolution of about 4 cm⁻¹.

3. COMPUTATIONAL DETAILS

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were carried out with the ORCA 3.0.3 program [10].

In order to take into account the effects of the local environment of D-phe molecule in our calculations, the Conductor-like Screening Model (COSMO) was employed, using water as solvent [11].

The optimized structural parameters, vibrational frequencies and predicted FT-IR spectrum were performed at the B3LYP [12,13] level using the def2-TZVP basis set [14,15], in all calculations the RIJCOSX algorithm [16-17] was also utilized.

4. RESULTS AND DISCUSSIONS

4.1. Vibrational Analysis

The vibrational wavenumbers are calculated at the optimized molecular structure of D-phe shown in Fig. 2.

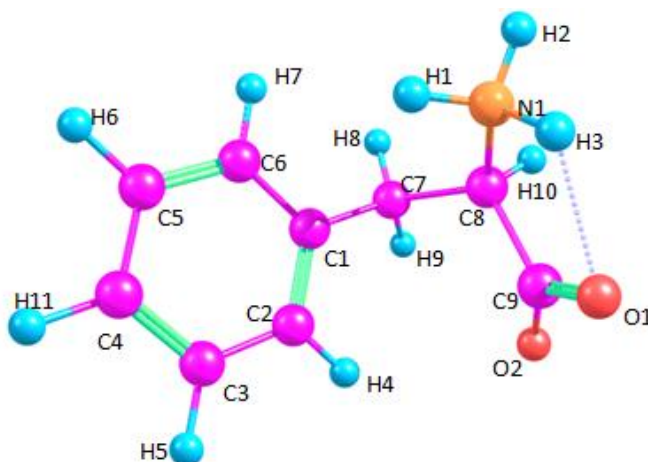


Figure 2. Optimized molecular structure of D-phe with numbering of atoms.

The global minimum energy of the equilibrium structure is computed to be -554.718965 a.u.

In this section, we focus on the vibrational assignments of the observed bands in the FT-IR spectrum. The D-phe molecule belongs to C_1 symmetry point group, it consists of 23 atoms, which gives 63 normal modes of vibration.

Our first observation is that the FT-IR spectra of D-phe (Fig. 3) and L-phe [7] samples obtained at room temperature using KBr pellets are similar, but not identical.

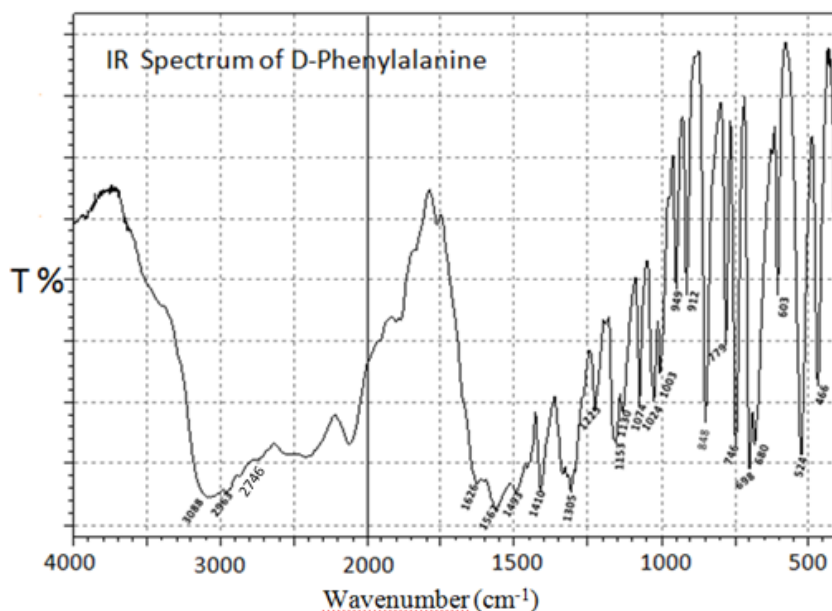


Figure 3. FT-IR spectrum (KBr pellet) of D-phe observed at T=293 K.

It is important to note that the region between 1627 and 2700 cm^{-1} in the observed FT-IR spectrum of D-phe is characterized by the presence of multiple broad and overlapping bands, which is a peculiarity common to KBr pellet spectra of amino acids [18].

Some selected observed and calculated wavenumbers with their assignments are listed in Table 1.

Table 1. The observed (ω_{obs}), calculated (ω_{cal}) vibrational wavenumbers and vibrational assignments of D-phe molecule.

ω_{obs} (cm ⁻¹)	ω_{cal} (cm ⁻¹)		Assignments
	Unscaled	Scaled*	
3088	3514	3022	ν_{as} (NH ₃ ⁺)
2963	3423	2943	ν_{s} (NH ₃ ⁺)
2866	3201	2752	ν (NH)
2746	3173	2728	ν (CH)
1626	1654	1621	ν_{as} (COO ⁻)
1562	1606	1573	β (NH ₃ ⁺)
1493	1532	1470	β (ring-CH)
1410	1432	1403	β (NH ₃ ⁺)
1305	1394	1366	β (ring-CH)
1225	1293	1267	γ (CH)
1074	1091	1069	γ (CH)
1024	1032	1011	ρ (NH ₃ ⁺)
949	950	931	ρ (NH ₃ ⁺)
848	860	842	ρ (NH ₃ ⁺)
698	722	707	ρ (CH ₂)
603	613	600	β (CCC)
524	512	501	def (ring)
466	498	488	def (ring)

vs (symmetric stretching), ν_{as} (antisymmetric stretching), β (in-plane deformation), γ (out of plane deformation), def (deformation)

* scaled by 0.86 for N-H and C-H stretching vibrations and by 0.98 for all other modes.

a) 2700-4000 cm⁻¹ SPECTRAL RANGE

In the FT-IR spectrum of D-phe, the N-H stretching vibrations appeared in the region 2866-3088 cm⁻¹. The calculated wavenumbers in the region 2700-2800 cm⁻¹ are assigned to the C-H stretching vibrations. However, a unique C-H mode is observed experimentally at 2746 cm⁻¹. The band observed at 3088 cm⁻¹ (our case) is practically in the same position compared to the corresponding band in the IR spectrum (KBr pellet) of L- β -phe (observed at 3087 cm⁻¹) [9]. This insignificant shift (1 cm⁻¹) is due to the same effect of N-H...O hydrogen bonding interactions in D- and L- β -phe crystals.

b) 1800-400 cm⁻¹ SPECTRAL RANGE

In the IR spectra of amino acids, the 1700-1200 cm⁻¹ range is usually characterized by the presence of intense bands ascribed to the stretching modes of the carboxylate group (ν_{COO^-} asym and ν_{COO^-} sym) [18].

In our study, the band observed at 1626 cm⁻¹ is assigned to the asymmetric ν_{COO^-} vibrations. The corresponding ν_{COO^-} vibration mode for L-phe [7] was previously observed at 1625 cm⁻¹. The result shows a great similarity between the H-bond energies formed by the COO⁻ groups in L- and D-phe crystals.

The vibrational coupling is well known to be particularly significant in the region 400-1200 cm⁻¹ [5]. In this region, the benzene ring in-plane or out-of-plane bending vibrations are coupled with certain other bending or stretching vibrations. For example, the bands observed at 466 and 524 cm⁻¹ are assigned to the benzene ring deformation.

4.2. Electronic Properties

The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). They serve to determine most of electric and optical properties of a molecule. The gap between HOMO and LUMO characterizes the molecular electrical transport properties [19].

The three-dimensional plots of HOMO, LUMO, HOMO-1 and LUMO+1 orbitals were computed at the B3LYP/ def2-TZVP level using water as solvent. As shown in Fig. 4, the two different colored regions exhibit a completely opposite phase. The energy values of HOMO and LUMO are calculated to be -6.8832 eV and -0.5567 eV, respectively. While, the calculated energy gap is found to be 6.3264 eV.

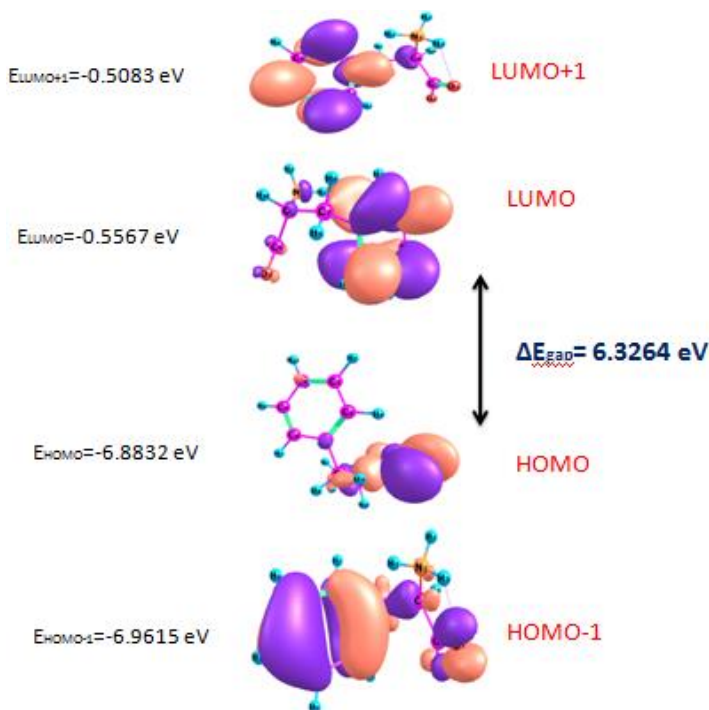


Figure 4. The three-dimensional plots of HOMO, LUMO, HOMO-1 and LUMO+1.

It is important to compare the energy gaps of aromatic amino acids to know which one is the most stable. Our calculations show that the energy gap for D-phe (6.3264 eV) is larger than that predicted for L-tyrosine (4.567 eV) [20]. Consequently, the molecule with the largest energy gap is generally more stable.

5. CONCLUSIONS

In this study, the vibrational and electronic properties of zwitterionic D-phenylalanine were studied.

The experimental IR spectrum of D-phenylalanine was compared with the corresponding ones for L-phenylalanine [7] and L-β-phenylalanine [9].

The insignificant shifts of the band positions in the FT-IR spectra of D-phenylalanine, L-phenylalanine and L- β -phenylalanine show a great similarity between the H-bond energies formed by the $-\text{NH}_3^+$ and COO^- groups in the three crystals.

The HOMO-LUMO gap of D-phenylalanine was predicted and compared to the corresponding one for L-tyrosine [20].

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