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FTIR, FT-Raman and UV–Vis spectral studies of D-tyrosine molecule

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ABSTRACT

In the present work, experimental and theoretical studies on the structure, vibrational spectra and electronic spectra of D-tyrosine molecule are reported. The FTIR (4000–400 cm^{-1}) and FT-Raman (4000 –50 cm^{-1}) spectra were recorded and analysed using anharmonic frequency calculations at PT2-VSCF and VPT2 levels in gas and solution phases. The solute–solvent interactions were treated using the integral equation formalism of the polarisation continuum model (IEF-PCM). The calculated anharmonic frequencies were compared with the experimental ones. It was found that PT2-VSCF anharmonic frequencies are closer to the experimental data. The VPT2 frequencies in gas and solution phases have small differences. The magnitudes of coupling between pair of modes were also computed. In addition, studies on the excitation energies, oscillator strengths, HOMO and LUMO energies and MEP of D-tyrosine at TD-DFT level are also reported.

1. Introduction

Amino acids, the building block of proteins, are a group of bioactive molecules mostly existing in L- and D-forms. For proper understanding of the protein structure and its properties, it is important to understand the structure and properties of amino acids. Tyrosine is a nonessential amino acid which exhibits interesting biological behaviour. The presence of the hydroxyl group allows phosphorylation of tyrosine side chain by the intermediate of kinases, a chemical transformation necessary for enzyme regulation. The level of D-tyrosine in human body is closely related to the health. The patients suffering from chronic renal failure have significantly greater amounts of D-tyrosine as compared to the normal humans [1]. Tyrosine helps to stimulate the nervous system. It is an essential component for the production of several important brain chemicals called neurotransmitters such as dopamine, norepinephrine and epinephrine [2] which are helpful to improve memory under psychological stress. Tyrosine is also essential for the normal functioning of organs like thyroid, pituitary and adrenal glands responsible for making and regulating hormones. It is also used in the treatment of allergies, headaches, Parkinson's disease and vitiligo [3,4]. Owing to the vast applications, the spectroscopy of tyrosine molecule has been studied extensively [1–11]. For tyrosine, the vibronic assignments in a jet cooled LD-R2P1 spectrum [1], DFT calculations, solvation studies and pH dependent SERS on silver colloidal nanoparticle [5] and the electronic spectrum in a supersonic jet using laser-induced fluorescence spectroscopy [6] have been carried out. The conformational and vibrational analysis of L-proline-tyrosine dipeptide has been studied by Kecel et al. [3]. For L-tyrosine, molecular mechanics and quantum chemical calculations of the structure, IR spectra and Raman spectra in solid and aqueous phases [7], vibrational analysis in hydrated media [8] and the photochemical pathways of isomerisation of the molecule at DFT and TD-DFT level of theory [9] have been reported. A rapid and sensitive microchip electrophoresis method with laser induced fluorescence detection was developed for the quantification of D-tyrosine in biological samples [10]. The matrix-isolation FTIR and theoretical computations of tyrosine molecule are reported by Ramaekers et al. [4], wherein the scaling procedure is taken into account. The empirical scaling factor is used to bring computed frequencies in closer agreement with the experimental ones for compensating the anharmonicity. The vibrational frequencies calculated by the usual harmonic approximation differ from the observed values up to 5–10%, partly because of the strong anharmonic character of some vibrations [11]. The second-order vibrational perturbation theory (VPT2) is an effective way for the study of medium and large size molecules in gas phase and the inclusion of anharmonic contributions predicts the results in close agreement with the experiments [12]. Apart from the VPT2 computations in vacuum, several studies have proved the advantage of computing vibrational frequencies in solution phase [13,14]. In this framework, continuum solvation methods are

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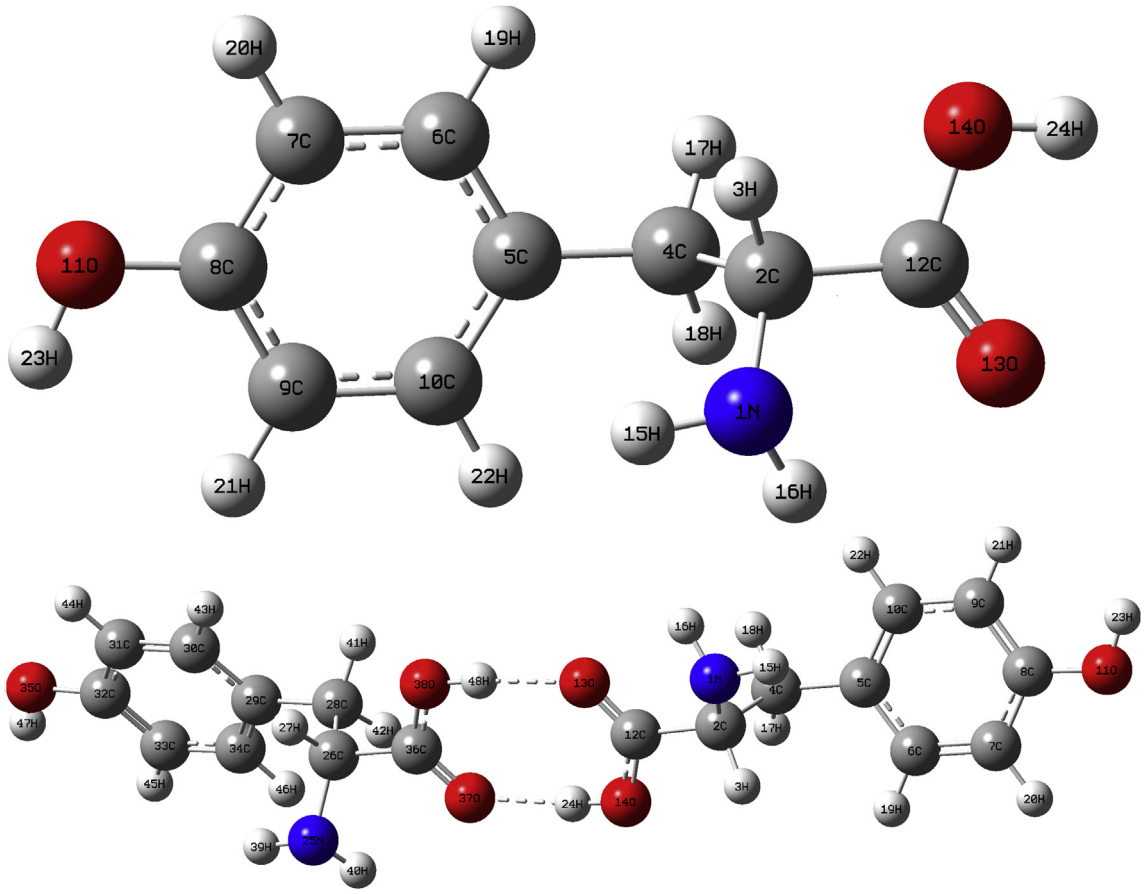

Fig. 1. Optimized monomer and dimer structure of D-tyrosine using B3LYP/6-311G(d,p) theory.

particularly attractive due to their reliability coupled to computational costs fully comparable with those of the corresponding computations in the gas phase [15]. The second order perturbation corrected vibrational self-consistent filed method (PT2-VSCF) is also an efficient method to predict the anharmonic vibrational frequencies, although it is more time demanding [16,17]. To the best of our knowledge, the FTIR, FT-Raman and anharmonic vibrational analysis of D-tyrosine molecule have not been reported so far. Therefore, in the present study, vibrational analysis of the FTIR and FT-Raman spectra of the title molecule is performed within DFT/6-311G(d,p) framework using PT2-VSCF and VPT2 methods in gas and solution phases. Anharmonicity, which causes coupling between different vibrational modes, affects the frequencies of the modes. In order to understand the coupling behaviour between pairs of modes, mode–mode coupling strengths based on two mode coupling representation of the quartic force field (2MR-QFF) for the ground state [18] are computed and the effect of mode–mode coupling on vibrational frequencies is discussed. The harmonic frequency calculations of the dimer structure are also carried out to study the effect of intermolecular interactions on structure and frequencies. The UV–Vis spectrum, HOMO–LUMO and molecular electrostatic potential (MEP) analysis of D-tyrosine molecule are also reported.

2. Experimental details

D-tyrosine compound was purchased from Sigma Aldrich Chemicals, USA in the solid form and was used as such without further purification to record the spectra. The FTIR spectrum of the title molecule in 4000–400 cm^{-1} region was recorded using KBr pellet technique on Bruker Tensor-37 spectrometer. To increase the signal-to-noise ratio, a minimum of 32 scans were accumulated. The FT-Raman spectrum in 4000–50 cm^{-1} region was recorded on Bruker RFS-27 spectrometer using 1064 nm line of Nd:YAG laser source. Both the FTIR and FT-Raman spectra were recorded at a spectral resolution of 2 cm^{-1}. The UV–Vis spectrum was recorded in ethanol in the region 800–200 nm using Lambda-950 UV–Vis–NIR spectrophotometer. All the spectra were measured at room temperature.

3. Computational details

The quantum chemical calculations for D-tyrosine molecule were performed using DFT (B3LYP) method with 6-311G(d,p) basis set. The optimized structural parameters were evaluated for the calculations of vibrational frequencies by imposing C1 point group symmetry. In order to overcome the disagreement between harmonic frequencies and experimental data and to avoid the scaling procedure, anharmonic frequencies of the title molecule were computed using 2 s order perturbative approaches. Using VPT2 method implemented by Barone [12] in Gaussian 09 program [19], the anharmonic frequencies in gas and solvent (CCl_4) phases were computed and the solvent dependence of the frequencies was investigated using integral equation formulation of the polarizable continuum model (IEF-PCM) [20]. The anharmonic frequencies were also calculated using PT2-VSCF approach implemented in Gamess-US program [21]. In order to know the coupling between pair of modes, the magnitudes of anharmonic mode–mode coupling for the ground state, based on 2MR-QFF potential energy function, have been estimated. The harmonic frequencies were also computed for the dimer structure of the title molecule. The