

# Analysis of vibronic–mode coupling structure in vibrational spectra of fuzeon as a 36 amino acid peptide for hiv therapy beyond the multi–dimensional franck condon integrals approximation

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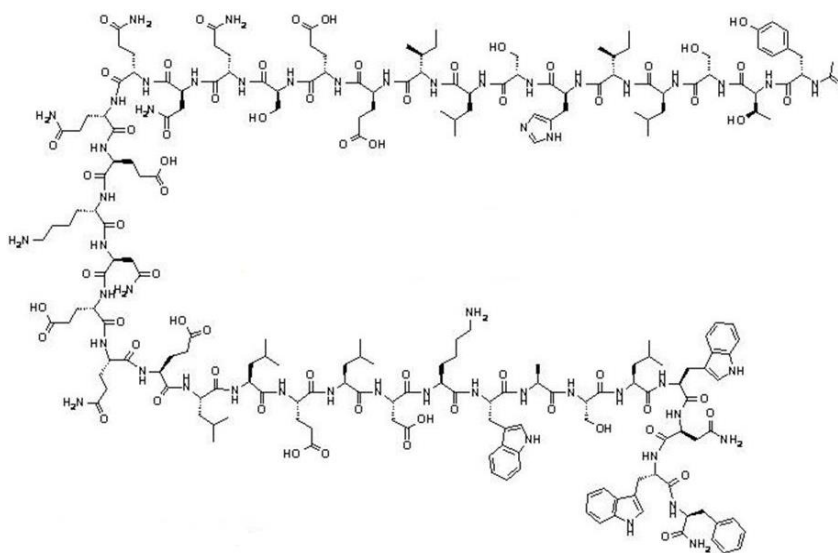
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## Abstract

Parameters such as FT–IR and Raman vibrational wavelengths and intensities for single crystal Fuzeon are calculated using density functional theory and were compared with empirical results. The investigation about vibrational spectrum of cycle dimers in crystal with carboxyl groups from each molecule of acid was shown that it leads to create Hydrogen bonds for adjacent molecules. The current study aimed to investigate the possibility of simulating the empirical values. Analysis of vibrational spectrum of Fuzeon is performed based on theoretical simulation and FT–IR empirical spectrum and Raman empirical spectrum using density functional theory in levels of HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP/6–31–HEG\*\*. Vibration modes of methylene, carboxyl acid and phenyl cycle are separately investigated. The obtained values confirm high accuracy and validity of results obtained from calculations.



Molecular Structure of Fuzeon [1–42].

**Keywords:** Vibronic Structure; Vibrational Spectra; Multi–Dimensional Franck–Condon Integrals Approximation; Density Functional Theory (DFT); Fuzeon; Non–Focal Functions of Becke; Correlation Functions of Lee–Yang–Parr.

## 1. Introduction

Fuzeon as a 36 amino acid peptide for HIV therapy is one of the most complex drugs chemically synthesized (Figure 2) on large scale. In fact, Enfuvirtide (INN) is an HIV fusion inhibitor, the first of a class of antiretroviral drugs used in combination therapy for the treatment of HIV–1 infection. It is marketed under the trade name Fuzeon (Roche) (Figure 1). Density Functional Theory (DFT) is one of the most

powerful calculation methods for electronic structures [5–7]. Numerous results have been previously studied and indicate successful use of these methods [8–10]. The theory is one of the most appropriate methods for simulating the vibrational wavenumbers, molecular structure as well as total energy. It may be useful to initially consider the calculated results by density functional theory using HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP6–31–HEG\*\* approach [11–16]. It should be noted that calculations are performed by considering one degree of quantum interference as well as polarization effects of 2d orbitals in interaction [17–362].

## 2. Details of calculations

All calculations of molecular orbital in the base of ab are performed by Gaussian 09. In calculation process, the structure of Fuzeon molecule (graphical abstract figure) is optimized and FT–IR and Raman wavenumbers are calculated using HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP6–31–HEG\*\* base. All optimized structures are adjusted with minimum energy. Harmonic vibrational wavenumbers are calculated using second degree of derivation to adjust convergence on potential surface as good as possible and to evaluate vibrational energies at zero point. In optimized structures considered in the current study, virtual frequency modes are not observed which indicates that the minimum potential energy surface is correctly chosen. The optimized geometry is calculated by minimizing the energy relative to all geometrical quantities without forcing any constraint on molecular symmetry. Calculations were performed by Gaussian 09. The current calculation is aimed to maximize structural optimization using density functional theory. The calculations of density functional theory are performed by HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP6–31–HEG\*\* function in which non-focal functions of Becke and correlation functions of Lee–Yang–Parr beyond the Franck–Condon approximation are used. After completion of optimization process, the second order derivation of energy is calculated as a function of core coordination and is investigated to evaluate whether the structure is accurately minimized. Vibrational frequencies used to simulate spectrums presented in the current study are derived from these second order derivatives. All calculations are performed for room temperature of 320 (K).

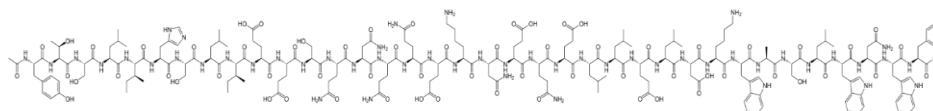


Fig. 1: Structure Formula of Fuzeon [43–93].

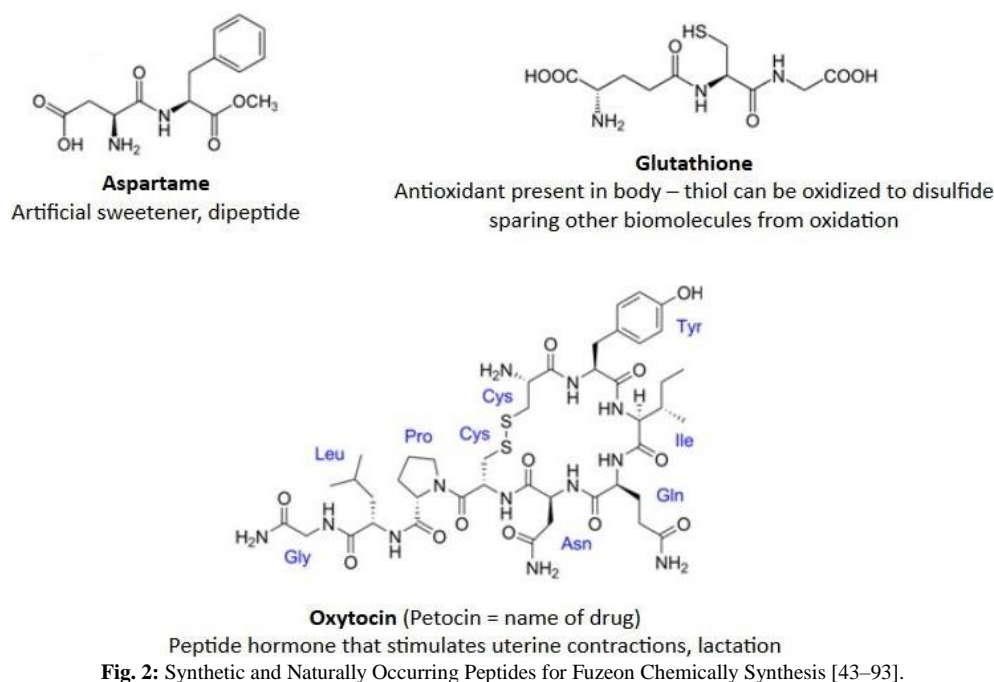


Fig. 2: Synthetic and Naturally Occurring Peptides for Fuzeon Chemically Synthesis [43–93].

## 3. Vibration analysis

Analysis of vibrational spectrum of Fuzeon is performed based on theoretical simulation and FT–IR empirical spectrum and Raman empirical spectrum using density functional theory in levels of HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP6–31–HEG\*\*. Vibration modes of methylene, carboxyl acid and phenyl cycle are separately investigated.

C–H stretching vibrations in single replacement of benzene cycles are usually seen in band range of 3300–3600  $\text{cm}^{-1}$ . Weak Raman bands are at 3173  $\text{cm}^{-1}$  and 3207  $\text{cm}^{-1}$ . C–C stretching mode is a strong Raman mode at 1201  $\text{cm}^{-1}$ . Raman weak band is seen at 1699  $\text{cm}^{-1}$ , too. Bending mode of C–H is emerged as a weak mode at 1333  $\text{cm}^{-1}$  and 1183  $\text{cm}^{-1}$  and a strong band at 1227  $\text{cm}^{-1}$  in Raman spectrum. Raman is considerably active in the range of 1250–1650  $\text{cm}^{-1}$  which 1197  $\text{cm}^{-1}$  indicates this issue.

C–H skew–symmetric stretching mode of methylene group is expected at 3211  $\text{cm}^{-1}$  and its symmetric mode is expected at 3101  $\text{cm}^{-1}$ . Skew–symmetric stretching mode of  $\text{CH}_2$  in Fuzeon has a mode in mid–range of Raman spectrum at 3120–3270  $\text{cm}^{-1}$ . When this mode is symmetric, it is at 3117  $\text{cm}^{-1}$  and is sharp. The calculated wavenumbers of higher modes are at 3081  $\text{cm}^{-1}$  and 3091  $\text{cm}^{-1}$  for symmetric and skew–symmetric stretching mode of methylene, respectively.

Scissoring vibrations of CH<sub>2</sub> are usually seen at the range of 1539–1547 cm<sup>-1</sup> which often includes mid-range bands. Weak bands at 1564 cm<sup>-1</sup> are scissoring modes of CH<sub>2</sub> in Raman spectrum. Moving vibrations of methylene are usually seen at 1473 cm<sup>-1</sup>. For the investigated chemical in the current study, these vibrations are at 1343 cm<sup>-1</sup> were calculated using density functional theory. Twisting and rocking vibrations of CH<sub>2</sub> are seen in Raman spectrum at 935 cm<sup>-1</sup> and 1191 cm<sup>-1</sup>, respectively, which are in good accordance with the results at 915 cm<sup>-1</sup> and 1167 cm<sup>-1</sup>, respectively.

In a non-ionized carboxyl group (COOH), stretching vibrations of carbonyl [C=O] are mainly observed at the range of 1847–1889 cm<sup>-1</sup>. If dimer is considered as an intact constituent, two stretching vibrations of carbonyl for symmetric stretching are at 1749–1784 cm<sup>-1</sup> in Raman spectrum. In the current paper, stretching vibration of carbonyl mode is at 1787 cm<sup>-1</sup> which is a mid-range value.

Stretching and bending bands of hydroxyl can be identified by width and band intensity which in turn is dependent on bond length of Hydrogen. In dimer form of Hydrogen bond, stretching band of O–H is of a strong Raman peak at 1334 cm<sup>-1</sup> which is due to in-plane metamorphosis mode. Out-of-plane mode of O–H group is a very strong mode of peak at 1085 cm<sup>-1</sup> of Raman spectrum. The stretching mode of C–O (H) emerges as a mid-band of Raman spectrum at 1329 cm<sup>-1</sup>.

Lattice vibrations are usually seen at the range of 0–850 cm<sup>-1</sup>. These modes are induced by rotary and transferring vibrations of molecules and vibrations and are including Hydrogen bond. Bands with low wavenumbers of Hydrogen bond vibrations in FT-IR and Raman spectrum (Figure 3) are frequently weak, width and unsymmetrical. Rotary lattice vibrations are frequently stronger than transferring ones. Intra-molecular vibrations with low wavenumbers involving two-bands O–H ...O dimer at 95 cm<sup>-1</sup>, 199 cm<sup>-1</sup> and 272 cm<sup>-1</sup> are attributed to a rotary moving of two molecules involving in-plane rotation of molecules against each other.

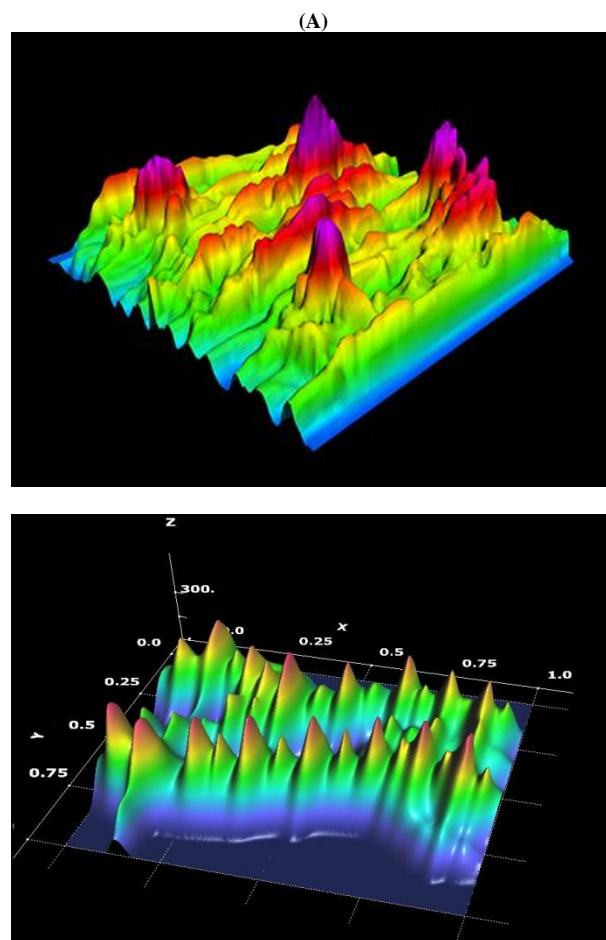


Fig. 3: 3D Simulation of (A) FT-IR Spectrum and (B) Raman Spectrum of Fuzeon.

#### 4. Conclusion and summary

Calculations of density functional theory using HF/6–31G\*, HF/6–31++G\*\*, MP2/6–31G, MP2/6–31++G\*\*, BLYP/6–31G, BLYP/6–31++G\*\*, B3LYP/6–31G and B3LYP6–31-HEG\*\* levels were used to obtain vibrational wavenumbers and intensities in single crystal of Fuzeon. Investigation and consideration of vibrational spectrum confirm the formation of dimer cycles in the investigated crystal with carboxyl groups from each Hydrogen molecule of acid protected from adjacent molecules. The calculated vibrational spectrum which obtains from calculations of density functional theory is in good accordance with recorded empirical values which indicates successful simulation of the problem. The obtained results indicate that the results obtained from theoretical calculations are valid through comparing with empirical recorded results.

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