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Cyanotoxin Time–Resolved Absorption and Resonance FT–IR and Raman Biospectroscopy and Density Functional Theory (DFT) Investigation of Vibronic–Mode Coupling Structure in Vibrational Spectra Analysis

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ABSTRACT

Cyanotoxins are toxins produced by bacteria called cyanobacteria (also known as blue–green algae). Cyanobacteria are found almost everywhere, but particularly in lakes and in the ocean where, under high concentration of phosphorus conditions, they reproduce exponentially to form blooms. Blooming cyanobacteria can produce cyanotoxins in such concentrations that they poison and even kill animals and humans. Cyanotoxins can also accumulate in other animals such as fish and shellfish, and cause poisonings such as shellfish poisoning. Parameters such as FT–IR and Raman vibrational wavelengths and intensities for single crystal Cyanotoxin 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 bounds for adjacent molecules. The current study aimed to investigate the possibility of simulating the empirical values. Analysis of vibrational spectrum of Cyanotoxin is performed based on theoretical simulation and FT–IR empirical spectrum and Raman empirical spectrum using density functional theory in levels of F/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. The obtained values confirm high accuracy and validity of results obtained from calculations.

Keywords: Vibronic Structure, Vibrational Spectra Analysis, Density Functional Theory (DFT), Cyanotoxin, Non–Focal Functions of Becke, Correlation Functions of Lee–Yang–Parr, Time–Resolved Absorption and Resonance, FT–IR and Raman Biospectroscopy

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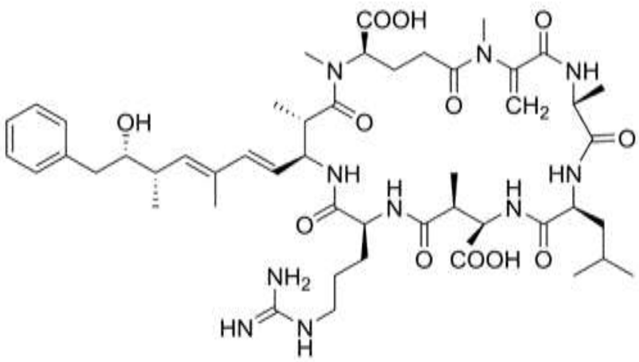
INTRODUCTION

Cyanotoxins are toxins produced by bacteria called cyanobacteria (also known as blue–green algae). Cyanobacteria are found almost everywhere, but particularly in lakes and in the ocean where, under high concentration of phosphorus conditions, they reproduce exponentially to form blooms. Blooming cyanobacteria can produce cyanotoxins in such concentrations that they poison and even kill animals and humans. Cyanotoxins can also accumulate in other animals such as fish and shellfish, and cause poisonings such as shellfish poisoning. 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 F/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 [17–320].



Molecular structure of Cyanotoxin [1–42].

Details of Calculations

All calculations of molecular orbital in the base of ab are performed by Gaussian 09. In calculation process, the structure of Cyanotoxin molecule (Figure 1) is optimized and FT–IR and Raman wavenumbers are calculated using F/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 is performed by F/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 555 (K).

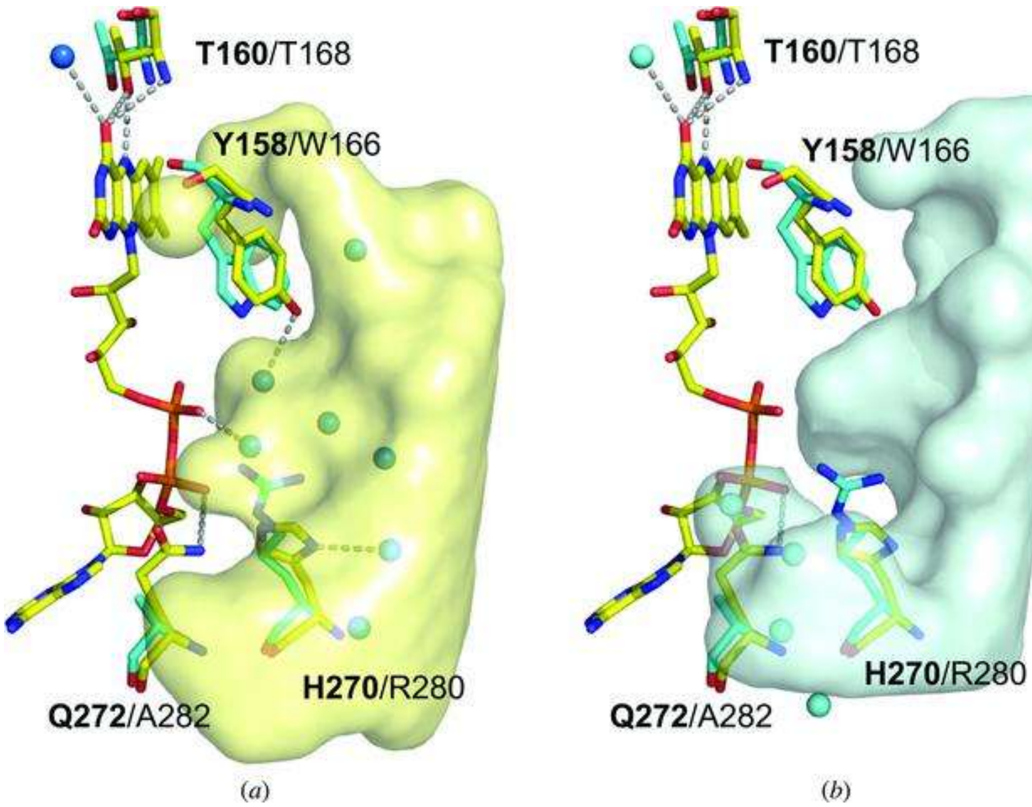


Figure (1): Different sections of the Cyanotoxin [43–93].

Vibration Analysis

Analysis of vibrational spectrum of Cyanotoxin is performed based on theoretical simulation and FT–IR empirical spectrum and Raman empirical spectrum using density functional theory in levels of F/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 3000–4000 cm^{-1}. Weak Raman bands are at 3789 cm^{-1} and 3702 cm^{-1}. C–C stretching mode is a strong Raman mode at 1899 cm^{-1}. Raman weak band is seen at 2373 cm^{-1}, too.

Bending mode of C–H is emerged as a weak mode at 2098 cm^{-1} and 2897 cm^{-1} and a strong band at 2081 cm^{-1} in Raman spectrum. Raman is considerably active in the range of 2000–3000 cm^{-1} which 1893 cm^{-1} indicates this issue.

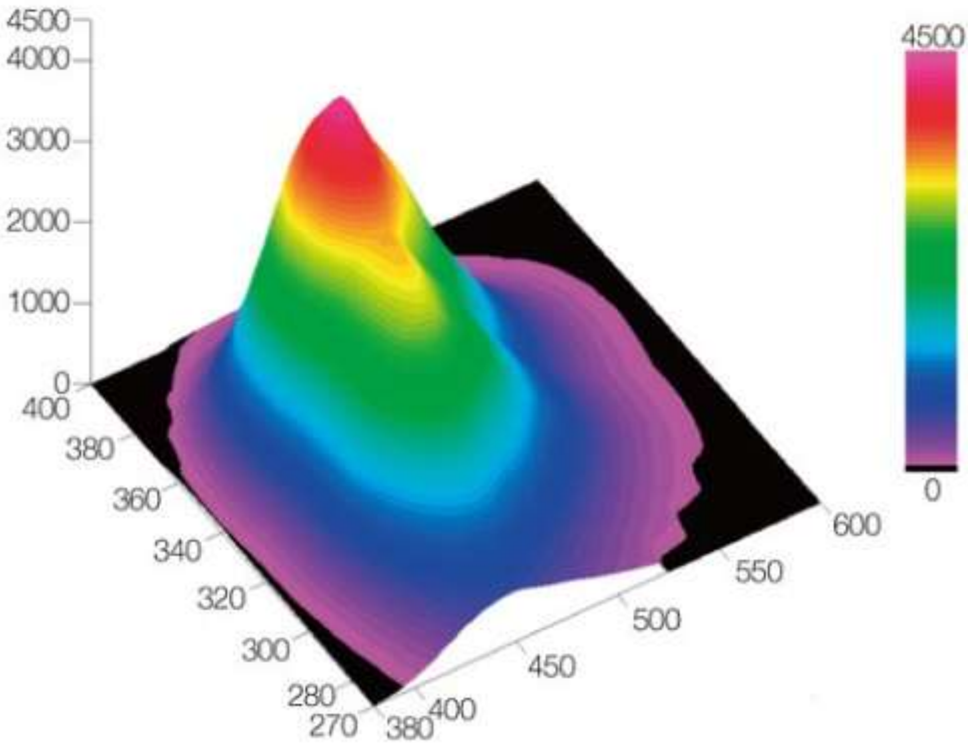
C–H skew–symmetric stretching mode of methylene group is expected at 3885 cm^{-1} and its symmetric mode is expected at 2699 cm^{-1}. Skew–symmetric stretching mode of CH_2 in Cyanotoxin has a mode in mid–range of Raman spectrum at 3000–4000 cm^{-1}. When this mode is symmetric, it is at 3795 cm^{-1} and is sharp. The calculated wavenumbers of higher modes are at 3763 cm^{-1} and 3793 cm^{-1} for symmetric and skew–symmetric stretching mode of methylene, respectively.

Scissoring vibrations of CH_2 are usually seen at the range of 2027–2081 cm^{-1} which often includes mid–range bands. Weak bands at 2740 cm^{-1} are scissoring modes of CH_2 in Raman spectrum. Moving vibrations of methylene are usually seen at 2169 cm^{-1}. For the investigated chemical in the current study, these vibrations are at 2039 cm^{-1} were calculated using density functional theory. Twisting and rocking vibrations of CH_2 are seen in Raman spectrum at 1615 cm^{-1} and 1889 cm^{-1}, respectively, which are in good accordance with the results at 1599 cm^{-1} and 1864 cm^{-1}, respectively.

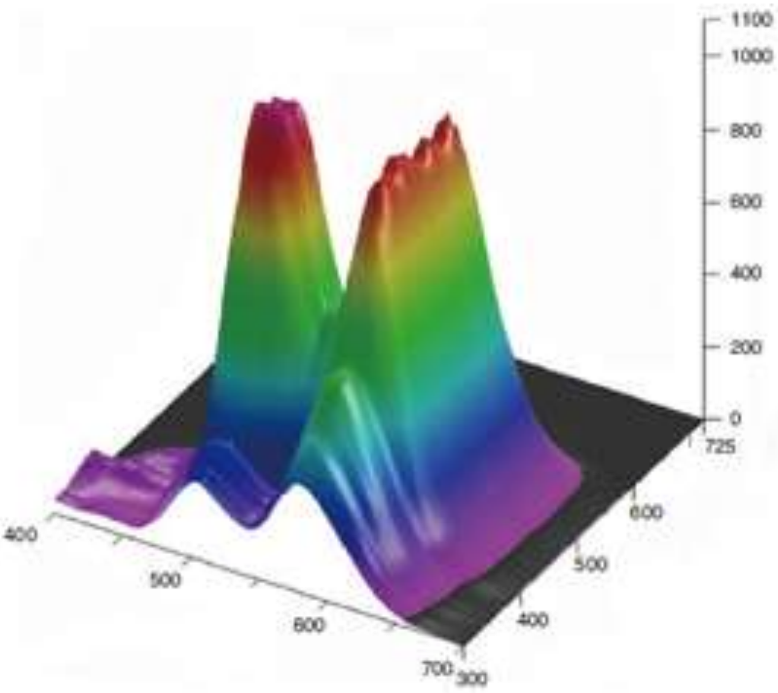
In a non–ionized carboxyl group (COOH), stretching vibrations of carbonyl [C=O] are mainly observed at the range of 2540–2588 cm^{-1}. If dimer is considered as an intact constituent, two stretching vibrations of carbonyl for symmetric stretching are at 2440–2485 cm^{-1} in Raman spectrum. In the current paper, stretching vibration of carbonyl mode is at 2497 cm^{-1} 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 2067 cm^{-1} which is due to in–plain metamorphosis mode. Out–of–plain mode of O–H group is a very strong mode of peak at 1749 cm^{-1} of Raman spectrum. The stretching mode of C–O (H) emerges as a mid–band of Raman spectrum at 1947 cm^{-1}.

Lattice vibrations are usually seen at the range of 0–1250 cm^{-1}. 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 2) 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 788 cm^{-1}, 893 cm^{-1} and 949 cm^{-1} are attributed to a rotary moving of two molecules involving in–plain rotation of molecules against each other.



(a)



(b)

Figure (2): 3D Simulation of (a) FT–IR spectrum and (b) Raman spectrum of Cyanotoxin.

CONCLUSION AND SUMMARY

Calculations of density functional theory using F/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 Cyanotoxin. 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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