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Microcystin-LR Time-resolved Absorption and Resonance FT-IR and Raman Biospectroscopy and Density Functional Theory Investigation of Vibronic-mode Coupling Structure in Vibrational Spectra Analysis

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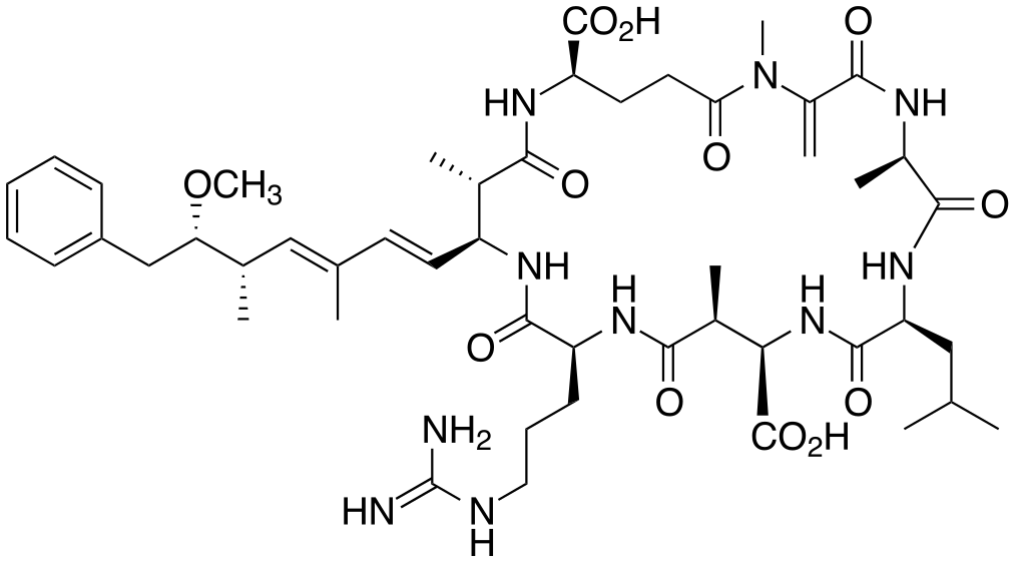
Microcystin-LR (MC-LR) is a toxin produced by cyanobacteria. It is the most toxic of the microcystins. Parameters such as FT-IR and Raman vibrational wavelengths and intensities for single crystal MC-LR are calculated using density functional theory and were compared with empirical results. The investigation about the vibrational spectrum of cycle dimers in crystal with carboxyl groups from each molecule of acid was shown that it led to create hydrogen bonds for adjacent molecules. The current study aimed to investigate the possibility of simulating the empirical values. Analysis of the vibrational spectrum of MC-LR was 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 were separately investigated. The obtained values confirmed high accuracy and validity of results obtained from calculations.



Molecular structure of microcystin–LR [1-42].

Key words: Vibronic structure; vibrational spectra analysis; density functional theory; microcystin-LR; 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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Microcystin-LR (MC-LR) is a toxin produced by cyanobacteria. It is the most toxic of the microcystins. Density functional theory 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 [17-337].

DETAILS OF CALCULATIONS

All calculations of molecular orbital in the base of ab were performed by Gaussian 09. In the calculation process, the structure of microcystin–LR molecule (Figure 1) was optimized, and FT-IR and Raman wavenumbers were 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 were adjusted with minimum energy. Harmonic vibrational wavenumbers were calculated using the second degree of derivation to adjust convergence on the potential surface as good as possible and to evaluate vibrational energies at zero points. In optimized structures considered in the current study, virtual frequency modes were not observed which indicated that the minimum potential energy surface was correctly chosen. The optimized geometry was 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 was aimed to maximize structural optimization using density functional theory. The calculations of density functional theory were 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 was used. After completion of optimization process, the second order derivation of energy was calculated as a function of core coordination and was investigated to evaluate whether the structure was accurately minimized. Vibrational frequencies used to simulate spectrums presented in the current study was derived from these second order derivatives. All calculations were performed for a room temperature of 515 (K).

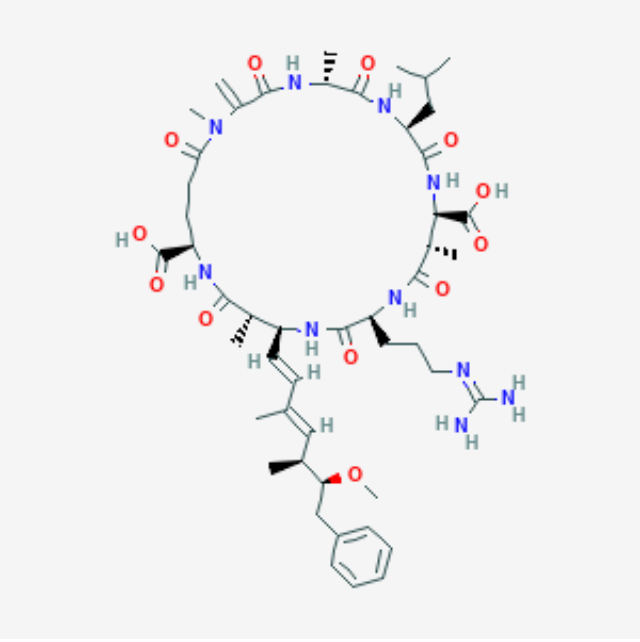

Figure1. Section of the microcystin-LR [43–93].

VIBRATION ANALYSIS

Analysis of the vibrational spectrum of microcystin–LR was 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 were separately investigated.

C–H stretching vibrations in single replacement of benzene cycles are usually seen in band range of 3210-3460 cm^{-1}. Weak Raman bands are at 3199 cm^{-1} and 3212 cm^{-1}. C–C stretching mode is a strong Raman mode at 2009 cm^{-1}. Raman weak band is seen at 1683 cm^{-1}, too. Bending mode of C–H is emerged as a weak mode at 1408 cm^{-1} and 1207 cm^{-1} and a strong band at 1291 cm^{-1} in Raman spectrum. Raman is considerably active in the range of 1210–1460 cm^{-1} which 1203 cm^{-1} indicates this issue.

C–H skew-symmetric stretching mode of methylene group is expected at 3195 cm^{-1} and its symmetric mode is expected at 3009 cm^{-1}. Skew-symmetric stretching mode of CH_2 in microcystin-LR has a mode in mid–range of Raman spectrum at 3110–3230 cm^{-1}. When this mode is symmetric, it is at 3105 cm^{-1} and is sharp. The calculated wavenumbers of higher modes are at 3073 cm^{-1} and 3103 cm^{-1} for symmetric and skew-symmetric stretching mode of methylene, respectively.

Scissoring vibrations of CH_2 are usually seen at the range of 1537–1591 cm^{-1} which often includes mid-range bands. Weak bands at 1550 cm^{-1} are scissoring modes of CH_2 in the Raman spectrum. Moving vibrations of methylene are usually seen at 1479 cm^{-1}. For the investigated chemical in the current study, these vibrations at 1349 cm^{-1} were calculated using density functional theory. Twisting and rocking vibrations of CH_2 were seen in Raman spectrum at 925 cm^{-1} and 1199 cm^{-1}, respectively, which were in good accordance with the results at 999 cm^{-1} and 1174 cm^{-1}, respectively.

In a non-ionized carboxyl group (COOH), stretching vibrations of carbonyl [C=O] are mainly observed at the range of 1850–1898 cm^{-1}. If dimer is considered as an intact constituent, two stretching vibrations of carbonyl for symmetric stretching are at 1750–1795 cm^{-1} in Raman spectrum. In the current paper, stretching vibration of carbonyl mode was at 1807 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 the hydrogen bond, stretching band of O–H is of a strong Raman peak at 1377 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 1059 cm^{-1} of Raman spectrum. The stretching mode of C–O (H) emerges as a mid-band of Raman spectrum at 1257 cm^{-1}.

Lattice vibrations are usually seen at the range of 0–700 cm^{-1}. These modes are induced by rotary and transferring vibrations of molecules and vibrations include hydrogen bond. Bands with low wavenumbers of hydrogen bond vibrations in FT-IR and Raman spectrum (Figure 2) are frequently weak, wide 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 98 cm^{-1}, 203 cm^{-1} and 259 cm^{-1} are attributed to a rotary moving of two molecules involving in-plain rotation of molecules against each other.

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 a single crystal of microcystin–LR. Investigation and consideration of vibrational spectrum confirmed 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 were obtained from calculations of density functional theory was in good accordance with recorded empirical values which indicated successful simulation of the problem. The obtained results indicated that the results obtained from theoretical calculations were valid through comparing with empirical recorded results.

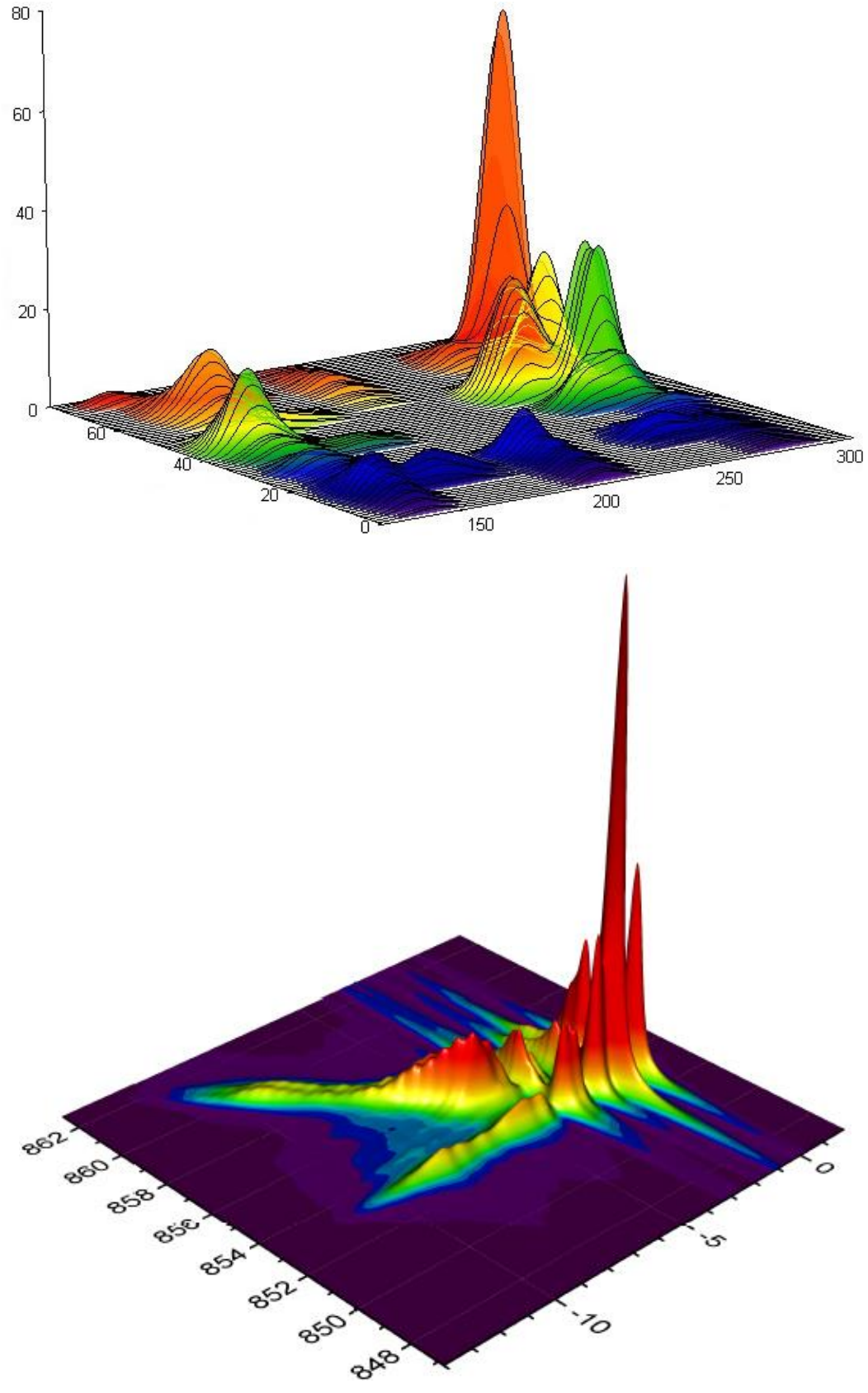

Figure 2. 3D simulation of (a) FT-IR spectrum and (b) Raman spectrum of microcystin–LR.

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