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***Corresponding author**

Alizera Heidari,
Faculty of Chemistry,
California South University, 14731 Comet
St. Irvine, CA 92604, USA

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Research Article

Maitotoxin 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: A Spectroscopic Study on an Anti-Cancer Drug

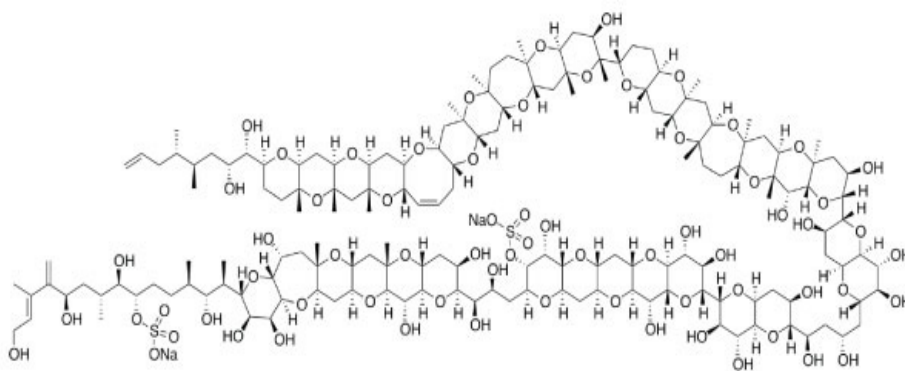
Alireza Heidari^{1*}, Jennifer Esposito¹, Angela Caissutti²

¹ Faculty of Chemistry, California South University, 14731 Comet St. Irvine, CA 92604, USA

² American International Standards Institute, Irvine, CA 3800, USA

Graphical Abstract

Maitotoxin (or MTX) is an extremely potent toxin produced by *Gambier discus toxicus*, a dinoflagellate species. Maitotoxin is so potent that it has been demonstrated that an intraperitoneal injection of 130 ng/kg was lethal in mice. Maitotoxin was named from the ciguateric fish *Ctenochaetus striatus*—called “maito” in Tahiti—from which maitotoxin was isolated for the first time. It was later shown that maitotoxin is actually produced by the dinoflagellate *Gambier discus toxicus*. Parameters such as FT-IR and Raman vibrational wavelengths and intensities for single crystal Maitotoxin 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 Maitotoxin 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 Maitotoxin (1-4)

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



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Introduction

Maitotoxin (or MTX) is an extremely potent toxin produced by Gambier discus toxics, a din flagellate species. Maitotoxin is so potent that it has been demonstrated that an intraperitoneal injection of 130ng/kg was lethal in mice. Maitotoxin was named from the ciguateric fish *Ctenochaetus striatus*—called "maito" in Tahiti—from which maitotoxin was isolated for the first time. It was later shown that maitotoxin is actually produced by the din flagellate *Gambier discus toxicus*. 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 [17–363].

Details of Calculations

All calculations of molecular orbital in the base of ab are performed by Gaussian 09. In calculation process, the structure of Maitotoxin molecule (Figure 1) 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 525 (K).

Vibration Analysis

Analysis of vibrational spectrum of Maitotoxin 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 3220–3470 cm^{-1} . Weak Raman bands are at 3209 cm^{-1} and 3222 cm^{-1} . C–C stretching mode is a strong Raman mode at 1219 cm^{-1} . Raman weak band is seen at 1693 cm^{-1} , too. Bending mode of C–H is emerged as a weak mode at 1418 cm^{-1} and 1217 cm^{-1} and a strong band at 1301 cm^{-1} in Raman spectrum. Raman is considerably active in the range of 1220–1470 cm^{-1} which 1213 cm^{-1} indicates this issue.

C–H skew–symmetric stretching mode of methylene group is expected at 3205 cm^{-1} and its symmetric mode is expected at 3019 cm^{-1} . Skew–symmetric stretching mode of CH_2 in Maitotoxin has a mode in mid–range of Raman spectrum at 3120–3240 cm^{-1} . When this mode is symmetric, it is at 3115 cm^{-1} and is sharp. The calculated wavenumbers of higher modes are at 3083 cm^{-1} and 3113 cm^{-1} for symmetric and skew–symmetric stretching mode of methylene, respectively.

Scissoring vibrations of CH_2 are usually seen at the range of 1547–1601 cm^{-1} which often includes mid–range bands. Weak bands at 1560 cm^{-1} are scissoring modes of CH_2 in Raman spectrum. Moving vibrations of methylene are usually seen at 1489 cm^{-1} . For the investigated chemical in the current study, these vibrations are at 1359 cm^{-1} were calculated using density functional theory. Twisting and rocking vibrations of CH_2 are seen in Raman spectrum at 935 cm^{-1} and 1209 cm^{-1} , respectively, which are in good accordance with the results at 919 cm^{-1} and 1184 cm^{-1} , respectively.

In a non–ionized carboxyl group (COOH), stretching vibrations of carbonyl [C=O] are mainly observed at the range of 1860–1918 cm^{-1} . If dimer is considered as an intact constituent, two stretching vibrations of carbonyl for symmetric stretching are at 1760–1805 cm^{-1} in Raman spectrum. In the current paper, stretching vibration of carbonyl mode is at 1817 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 1387 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 1069 cm^{-1} of Raman spectrum. The stretching mode of C–O (H) emerges as a mid–band of Raman spectrum at 1267 cm^{-1} .

Lattice vibrations are usually seen at the range of 0–570 cm^{-1} . These modes are induced by rotary and transferring vibrations

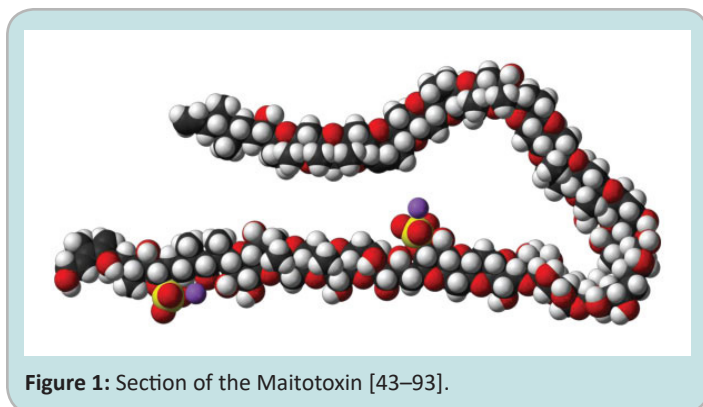


Figure 1: Section of the Maitotoxin [43–93].

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 108 cm^{-1} , 213 cm^{-1} and 269 cm^{-1} are attributed to a rotary moving of two molecules involving in-plain rotation of molecules against each other.

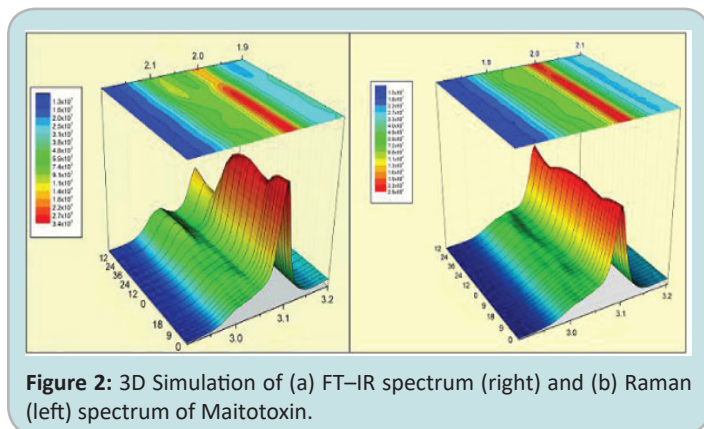


Figure 2: 3D Simulation of (a) FT-IR spectrum (right) and (b) Raman (left) spectrum of Maitotoxin.

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 B3LYP/6-31-HEG** levels were used to obtain vibrational wavenumbers and intensities in single crystal of Maitotoxin. 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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