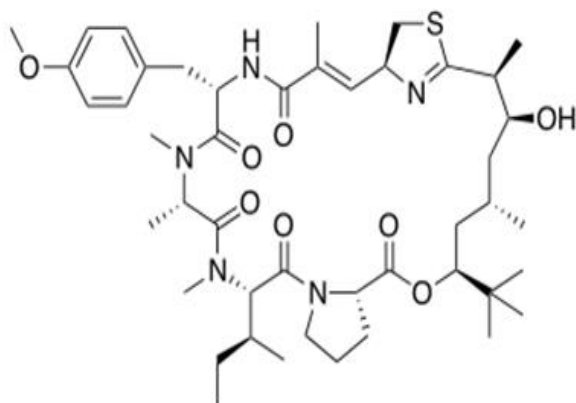


# Kalkitoxin Time-Resolved Absorption and Resonance FT-IR and Raman Biospectroscopy and Density Functional Theory (DFT) Investigation of Vibronic-Mode Coupling Structure in Vibrational Spectra Analysis

## Abstract

Kalkitoxin, a lipopeptide derived from the cyanobacterium *Lyngbya majuscula*, induces NMDA receptor mediated neuronal necrosis, blocks voltage-dependent sodium channels, and induces cellular hypoxia by inhibiting the electron transport chain (ETC) complex. Parameters such as FT-IR and Raman vibrational wavelengths and intensities for single crystal Kalkitoxin 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 Kalkitoxin 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.



Molecular structure of Kalkitoxin [1-42].

## Open Access

## Review Article

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

## Introduction

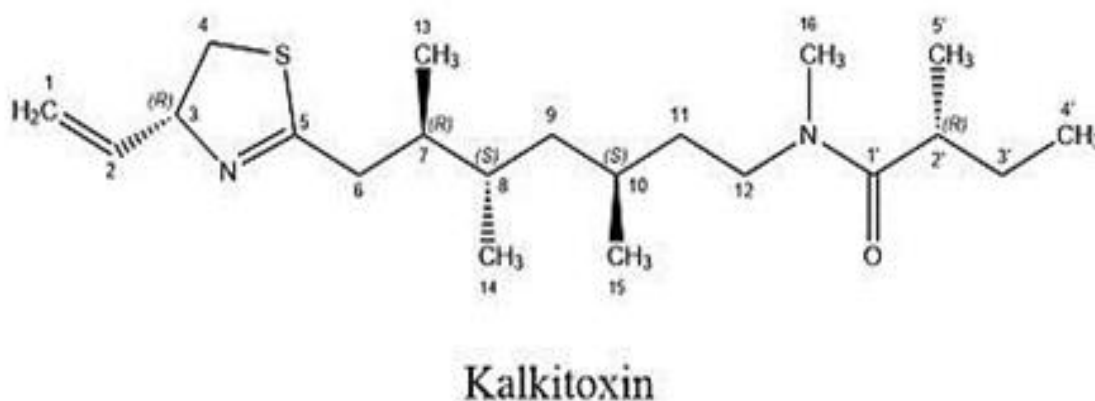
Kalkitoxin, a lipopeptide derived from the cyanobacterium *Lyngbya majuscula*, induces NMDA receptor mediated neuronal necrosis, blocks voltage-dependent sodium channels, and induces cellular hypoxia by inhibiting the electron transport chain (ETC) complex. Density Functional Theory (DFT) is one of the 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 wave numbers, 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 [17-324].

## Details of Calculations

All calculations of molecular orbital in the base of ab are performed by Gaussian 09. In calculation process, the structure of Kalkitoxin molecule (Figure 1) is optimized and FT-IR and Raman wave numbers 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 wave numbers 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 424 (K).



**Figure x1:** Section of the Kalkitoxin [43–93].

## Vibration Analysis

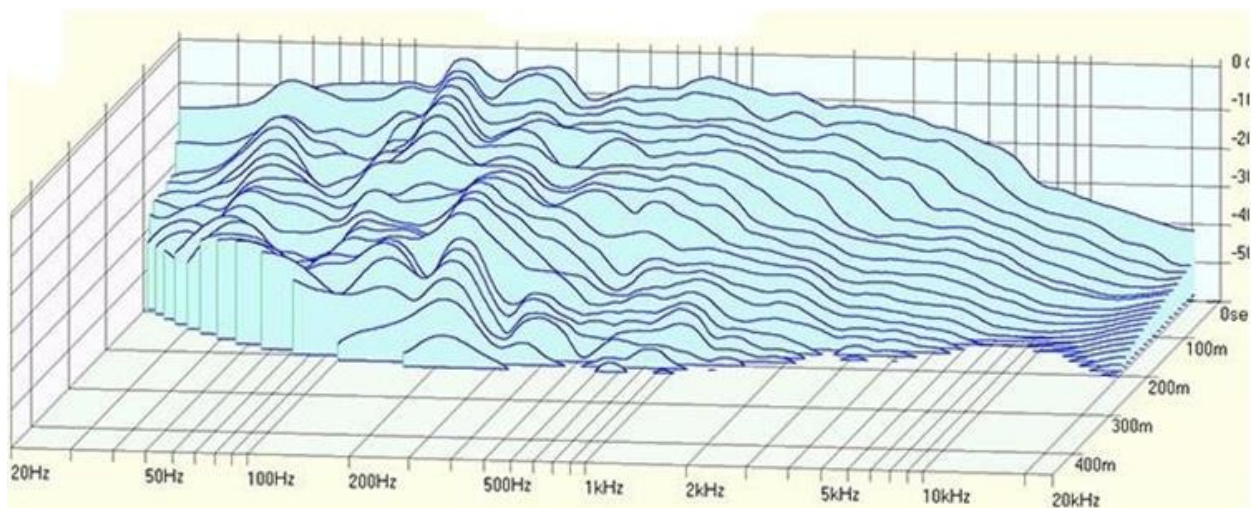
Analysis of vibrational spectrum of Kalkitoxin is performed based on theoretical simulation and FT-IR empirical spectrum and Raman empirical spectrum using density functional theory in levels of F/6-31G\*, HF/6-31++G\*\*, MP2/6-31G, MP2/6-31++G\*\*, BLYP/6-31G, BLYP/6-31++G\*\*, B3LYP/6-31G and B3LYP6-31-HEG\*\*. 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 3235-3485  $\text{cm}^{-1}$ . Weak Raman bands are at 3224  $\text{cm}^{-1}$  and 3237  $\text{cm}^{-1}$ . C-C stretching mode is a strong Raman mode at 1234  $\text{cm}^{-1}$ . Raman weak band is seen at 1708  $\text{cm}^{-1}$ , too. Bending mode of C-H is emerged as a weak mode at 1433  $\text{cm}^{-1}$  and 1235  $\text{cm}^{-1}$  and a strong band at 1326  $\text{cm}^{-1}$  in Raman spectrum. Raman is considerably active in the range of 1235-1485  $\text{cm}^{-1}$  which 1238  $\text{cm}^{-1}$  indicates this issue. C-H skew-symmetric stretching mode of methylene group is expected at 3220  $\text{cm}^{-1}$  and its symmetric mode is expected at 3034  $\text{cm}^{-1}$ . Skew-symmetric stretching mode of  $\text{CH}_2$  in Kalkitoxin has a mode in mid-range of Raman spectrum at 3135-3255  $\text{cm}^{-1}$ . When this mode is symmetric, it is at 3130  $\text{cm}^{-1}$  and is sharp. The calculated wave numbers of higher modes are at 3098  $\text{cm}^{-1}$  and 3128  $\text{cm}^{-1}$  for symmetric and

skew-symmetric stretching mode of methylene, respectively.

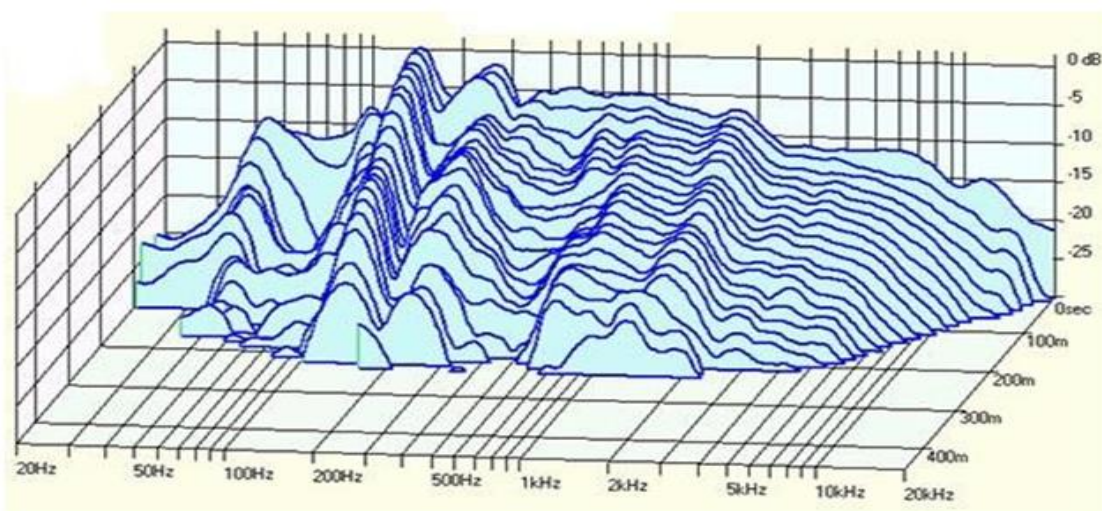
Scissoring vibrations of  $\text{CH}_2$  are usually seen at the range of 15620-1616  $\text{cm}^{-1}$  which often includes mid-range bands. Weak bands at 1575  $\text{cm}^{-1}$  are scissoring modes of  $\text{CH}_2$  in Raman spectrum. Moving vibrations of methylene are usually seen at 1494  $\text{cm}^{-1}$ . For the investigated chemical in the current study, these vibrations are at 1374  $\text{cm}^{-1}$  were calculated using density functional theory. Twisting and rocking vibrations of  $\text{CH}_2$  are seen in Raman spectrum at 950  $\text{cm}^{-1}$  and 1224  $\text{cm}^{-1}$ , respectively, which are in good accordance with the results at 934  $\text{cm}^{-1}$  and 1199  $\text{cm}^{-1}$ , respectively. In a non-ionized carboxyl group ( $\text{COOH}$ ), stretching vibrations of carbonyl [ $\text{C}=\text{O}$ ] are mainly observed at the range of 1875-1923  $\text{cm}^{-1}$ . If dimer is considered as an intact constituent, two stretching vibrations of carbonyl for symmetric stretching are at 1775-1820  $\text{cm}^{-1}$  in Raman spectrum. In the current paper, stretching vibration of carbonyl mode is at 1832  $\text{cm}^{-1}$  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 1392  $\text{cm}^{-1}$  which is due to in-plain metamorphosis mode. Out-of-plain mode of O-H group is a very strong mode of peak at 1084  $\text{cm}^{-1}$  of Raman spectrum. The stretching mode of C-O (H) emerges as a mid-band of Raman spectrum at

$1281\text{ cm}^{-1}$ . Lattice vibrations are usually seen at the range of  $0\text{--}585\text{ cm}^{-1}$ . These modes are induced by rotary and transferring vibrations of molecules and vibrations and are including Hydrogen bond. Bands with low wave numbers 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 wave numbers involving two-bands O-H, O dimer at  $125\text{ cm}^{-1}$ ,  $228\text{ cm}^{-1}$  and  $284\text{ cm}^{-1}$  are attributed to a rotary moving of two molecules involving in-plane rotation of molecules against each other.



(a)



(b)

**Figure 2:** 3D Simulation of (a) FT-IR spectrum and (b) Raman spectrum of Kalkitoxin.



## 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 wave numbers and intensities in single crystal of Kalkitoxin. 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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