

Overtone spectra of porphyrins and its substituted forms: an algebraic approach

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ABSTRACT

We introduce an algebraic model to vibrations of polyatomic Bio-molecules and present, as an example, the vibrational analysis of C_m-H , C_m-C , C_m-D , C_b-C_b , pyrrol breathing and C_b-C , stretching modes of Metalloporphyrins and its substituted forms. The excited energy levels of C_b-C , pyrrol breathing stretching modes of Ni(OEP) and Ni(OEP)- d_4 are calculated by using U(2) algebraic mode Hamiltonian. The higher excited energy levels of C_m-H , C_m-C , C_m-D and C_b-C_b vibrational modes of Porphyrin and its substituted forms are predicted upto second overtone. It shows that the energy levels are clustering at the higher overtones. The results obtained by this method are accuracy with experimental data.

Keywords: Algebraic Model; Vibrational Spectra; Energy Levels; Metalloporphyrins

1. INTRODUCTION

Recently measurement of highly-excited overtone-combination spectra of molecules have renewed in a theoretical description and understanding of the observed spectral properties. Two approaches have been mostly used so far in an analysis of experimental data: 1) the familiar Dunham like expansion of energy levels in terms of rotations-vibrations quantum numbers and 2) the solution of Schrodinger equation with potentials obtained either by appropriately modifying ab-initio calculations or by more phenomenological methods. In this article, we begin a systematic analysis of overtone-combination spectra of molecules in terms of novel ap-

proach: 3) Vibron model [1-4]. This model is a formulation of the molecular spectral problem in terms of elements of Lie algebra and it contains the same physical information of the Dunham and potential approach. However, by making use of the powerful methods of group theory, one is able to obtain the desired results in a much faster and straightforward way.

In recent years, these polyatomic bio-molecules (*i.e.* Metalloporphyrins) have numerous importances in the field of Chemical Physics. In case of polyatomic bio-molecules the parameters play major role in the Vibron model. Of course, we have explicitly described with few parameters, the vibrational bands of the triatomic linear molecules HCN, OCS, HCP [5-7] and tetraatomic molecules HCCF, HCCD by using an algebraic approach [8]. We have also reported the vibrational bands of tetrahedral molecules CCl_4 , $SnBr_4$ and Propadiene [9-11] and polyatomic bio-molecules like Nickel Octaethyl porphyrin, Nickel porphyrin molecules using U (2) Vibron model respectively [12-18]. The advantage of the algebraic approach, as compared to that of Dunham or phonological potential models, is that typically it requires few parameters to obtain the same level of accuracy. It also provides a simultaneous description of bending and stretching modes [19-25].

In Section 2, review the theory of algebraic model to polyatomic molecules is described. In Section 3, the calculation procedure of Vibron number and the fitting algebraic parameters corresponding to various Porphyrins and its substitute form molecule results are discussed. Finally, the conclusions are presented in Section 4.

2. THEORY: AN ALGEBRAIC APPROACH

A complete description of the theoretical foundations

needed to formulate the algebraic model for a vibrating molecule. We apply the one-dimensional algebraic model, consisting of a formal replacement of the interatomic, bond coordinates with unitary algebras. To say it in different words, the second-quantization picture suited to describe anharmonic vibrational modes, is specialized through an extended use of Lie group theory and dynamical symmetries. By means of this formalism, one can attain algebraic expressions for eigenvalues and eigenvectors of even complex Hamiltonian operators, including intermode coupling terms as well expectation values of any operator of interest (such as electric dipole and quadrupole interactions). Algebraic model are not ab-initio methods, as the Hamiltonian operator depends on a certain number of a priori undetermined parameters. As a consequence, algebraic techniques can be more convincingly compared with semi-empirical approaches making use of expansions over power and products of vibrational quantum numbers, such as a Dunham-like series. However, two noticeable advantages of algebraic expansions over conventional ones are that 1) algebraic modes lead to a (local) Hamiltonian formulation of the physical problem at issue (thus permitting a direct calculation of eigenvectors in this same local basis) and 2) algebraic expansions are intrinsically anharmonic at their zero-order approximation. This fact allows one to reduce drastically the number of arbitrary parameters in comparison to harmonic series, especially when facing medium-or large- size molecules. However, it should also be noticed that, as a possible drawback of purely local Hamiltonian formulations (either algebraic or not) compared with traditional perturbative approaches, the actual eigenvectors of the physical system. Yet, for very local situations, the aforementioned disadvantage is not a serious one. A further point of import here is found in the ease of accounting for proper symmetry adaptation of vibrational wave functions. This can be a great help in the systematic study of highly excited overtones of not-so-small molecules, such as the present one. Last but not least, the local mode picture of a molecule is enhanced from the very beginning within the algebraic framework. This is an aspect perfectly lined up with the current tendencies of privileging local over normal mode pictures in the description of most topical situations.

2.1. Hamiltonian Operators

We address here the explicit problem of the construction of the vibrational Hamiltonian operator for the Metalloporphyrin molecules. According to the general algebraic description for one-dimensional degrees of freedom, a dynamically-symmetric Hamiltonian operator for n -interacting (not necessarily equivalent) oscillators can be written as

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i < j}^n A_{ij} C_{ij} + \sum_{i < j}^n \lambda_{ij} M_{ij} \quad (1)$$

In this expression, one finds three different classes of effective contributions. The first one, $\sum_{i=1}^n A_i C_i$ is devoted to the description of n independent, anharmonic sequences of vibrational levels (associated with n independent, local oscillator) in terms of the operators C_i . The second one, $\sum_{i < j}^n A_{ij} C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij} . The third one, $\sum_{i < j}^n \lambda_{ij} M_{ij}$, describes anharmonic, non-diagonal interactions involving pairs of local oscillators in terms of the operators M_{ij} . The C_i , C_{ij} operators are invariant (Casimir) operators of certain Lie algebras, whilst the M_{ij} are invariant (Majorana) operators associated with coupling schemes involving algebras naturally arising from a systematic study of the algebraic formulation of the one-dimensional model for n interacting oscillators. We work in the local (uncoupled oscillators) vibrational basis written as

$$|v\rangle \equiv |v_1 v_2 v_3 \dots v_n\rangle$$

In which the aforementioned operators have the following matrix elements

$$\langle v | C_i | v \rangle = -4v_i(N_i - v_i)$$

$$\langle v | C_{ij} | v \rangle = -4(v_i + v_j)(N_i + N_j - v_i - v_j)$$

$$\langle v' | M_{ij} | v \rangle = (v_i N_i + v_j N_j - 2v_i v_j) \delta_{v'_i v_i} \delta_{v'_j v_j}$$

$$\langle v' | M_{ij} | v \rangle = -[(v_i + 1)(N_i - v_i)v_j(N_j - v_j + 1)]^{1/2} \delta_{v'_i - 1 v_i} \delta_{v'_j + 1 v_j}$$

$$\langle v' | M_{ij} | v \rangle = -[(v_j + 1)(N_j - v_j)v_i(N_i - v_i + 1)]^{1/2} \delta_{v'_i + 1 v_i} \delta_{v'_j - 1 v_j}$$

We note, in particular, that the expressions above depend on the numbers N_i (Vibron numbers). Such numbers have to be seen as predetermined parameters of well-defined physical meaning, as they relate to the intrinsic anharmonicity of a single, uncoupled oscillator through the simple relation. We report in **Table 4** & **Table 5** the values of the Vibron numbers used in the present study.

The general Hamiltonian operator (1) can be adapted to describe the internal, vibrational degrees of freedom of any polyatomic molecule in two distinct steps. First, we associate three mutually perpendicular one-dimensional anharmonic oscillators to each atom. This procedure eventually leads to a redundant picture of the whole molecule, as it will include spurious (*i.e.* translational/rotational) degrees of freedom. However, it is possible to remove easily such spurious modes through

different techniques. One is thus left with a Hamiltonian operator dealing only with true vibrations. Such modes are given in terms of coupled oscillators in the local basis (3). The coupling is induced by the Majorana operators. A sensible use of these operators is such that the correct symmetries of vibrational wave functions are properly taken into account. As a second step, the algebraic parameters A_i , A_{ij} , λ_{ij} of **Eq.1** need to be calibrated to reproduce the observed spectrum. Let us clarify the actual meaning of these two steps by considering explicitly the C_m -H/ C_m -D/ C_m -N stretches manifold of the Nickel Metalloporphyrin molecule.

We limit ourselves to in-plane C_m -H/ C_m -D/ C_m -N stretching motions *i.e.*, without including possible coupling terms with ring deformation. So, we can write for these remaining four degrees of freedom the Hamiltonian operator,

$$H_{CH} = \sum_{i=1}^4 A_i C_i + \sum_{i<j}^4 A'_{ij} C_{ij} + \sum_{i<j}^4 \lambda_{ij} M_{ij}$$

The algebraic theory of polyatomic molecules consists in the separate quantization of rotations and vibrations in terms of vector coordinates r_1, r_2, r_3, \dots quantized through the algebra

$$G \equiv U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes \dots$$

For the stretching vibrations of polyatomic molecules correspond to the quantization of anharmonic Morse oscillators, with classical Hamiltonian

$$H(p_s, s) = p_s^2/2\mu + D[1 - \exp(-\beta s)]^2 \quad (2)$$

For each oscillator i , states are characterized by representations of

$$\left. \begin{array}{cc} U_i(2) & \supset & O_i(2) \\ \downarrow & & \downarrow \\ N_i & & m_i \end{array} \right\} \quad (3)$$

With $m_i = N_i, N_i - 2, \dots, 1$ or 0 (N_i - odd or even). The Morse Hamiltonian (2) can be written, in the algebraic approach, simply as

$$H_i = \varepsilon_{0i} + A_i C_i, \quad (4)$$

where C_i is the invariant operator of $O_i(2)$, with eigenvalues

$$\varepsilon_i = \varepsilon_{0i} + A_i (m_i^2 - N_i^2).$$

Introducing the vibrational quantum number $v_i = (N_i - m_i)/2$, [26] one has

$$\varepsilon_i = \varepsilon_{0i} - 4A_i (N_i v_i - v_i^2). \quad (5)$$

For non-interacting oscillators the total Hamiltonian is

$$H = \sum_i H_i,$$

With eigenvalues

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i (N_i v_i - v_i^2). \quad (6)$$

2.2. Hamiltonian for Stretching Vibrations

The interaction potential can be written as

$$V(s_i, s_j) = k_{ij} [1 - \exp(-\alpha_i s_i)][1 - \exp(-\alpha_j s_j)], \quad (7)$$

which reduces to the usual harmonic force field when the displacements are small

$$V(s_i, s_j) \approx k_{ij} s_i s_j.$$

Interaction of the type **Eq.7** can be taken into account in the algebraic approach by introducing two terms [26]. One of these terms is the Casimir operator, C_{ij} , of the combined $O_i(2) \otimes O_j(2)$ algebra. The matrix elements of this operator in the basis **Eq.3** are given by

$$\langle N_i, v_i, N_j, v_j | C_{ij} | N_i, v_i, N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \quad (8)$$

The operator C_{ij} is diagonal and the vibrational quantum numbers v_i have been used instead of m_i . In practical calculations, it is sometime convenient to subtract from C_{ij} a contribution that can be absorbed in the Casimir operators of the individual modes i and j , thus considering an operator C'_{ij} whose matrix elements are

$$\langle N_i, v_i, N_j, v_j | C'_{ij} | N_i, v_i, N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] + [(N_i + N_j)/N_i]4(N_i v_i - v_i^2) + [(N_i + N_j)/N_j]4(N_j v_j - v_j^2). \quad (9)$$

The second term is the Majorana operator, M_{ij} . This operator has both diagonal and off-diagonal matrix elements

$$\begin{aligned} \langle N_i, v_i, N_j, v_j | M_{ij} | N_i, v_i, N_j, v_j \rangle &= (N_i v_j + N_j v_i - 2v_i v_j) \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i, N_j, v_j \rangle &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i, N_j, v_j \rangle &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2} \end{aligned} \quad (10)$$

The Majorana operators M_{ij} annihilates one quantum of vibration in bond i and create one in bond j , or vice versa.

The total Hamiltonian for n stretching vibrations is

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij} \quad (11)$$

If $\lambda_{ij} = 0$ the vibrations have local behavior. As the λ_{ij} increase, one goes more and more into normal vibrations.

2.3. Symmetry- Adapted Operators

In polyatomic molecules, the geometric point group symmetry of the molecule plays an important role. States must transform according to representations of the point symmetry group. In the absence of the Majorana operators M_{ij} , states are degenerate. The introduction of the Majorana operators has two effects: 1) it splits the degeneracies of figure and 2) in addition it generates states with the appropriate transformation properties under the point group. In order to achieve this result the λ_{ij} must be chosen in an appropriate way that reflects the geometric symmetry of the molecule. The total Majorana operator

$$S = \sum_{i < j}^n M_{ij} \quad (12)$$

is divided into subsets reflecting the symmetry of the molecule

$$S = S' + S'' + \dots \quad (13)$$

The operators S' , S'' , \dots are the symmetry-adapted operators. The construction of the symmetry-adapted operators of any molecule become clear in the following sections where the cases of Porphyrins (D_{4h}) discussed.

2.4. Hamiltonian for Bending Vibrations

We emphasize once more that the quantization scheme of bending vibrations in $U(2)$ is rather different from $U(4)$ and implies a complete separation between rotations and vibrations. If this separation applies, one can quantize each bending oscillator i by means of an algebra $U_i(2)$ as in **Eq.2**. The Poschl-Teller Hamiltonian

$$H(p_s, s) = p_s^2/2\mu - D/\cosh^2(as) \quad (14)$$

Where we have absorbed the $\lambda(\lambda - 1)$ part into D , can be written, in the algebraic approach, as

$$H_i = \varepsilon_{0i} + A_i C_i, \quad (15)$$

This Hamiltonian is identical to that of stretching vibration (**Eq.3**). The only difference is that the coefficients A_i in front of C_i are related to the parameters of the potential, D and α , in a way that is different for Morse and Poschl-Teller potentials. The energy eigenvalues of uncoupled Poschl-Teller oscillators are, however, still given by

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i (N_i v_i - v_i^2). \quad (16)$$

One can then proceed to couple the oscillators as done previously and repeat the same treatment of **Eqs.2, 3, and 4**.

2.5. The Metalloporphyrin Molecule

The construction of the symmetry-adapted operators and of the Hamiltonian operator of polyatomic molecule illustrated using the example of Metalloporphyrin. In order to do the construction, draw a figure corresponding to the geometric structure of the molecule (**Figure 1**). Number of degree of freedom we wish to describe.

By inspection of the figure, one can see that two types of interactions in Metalloporphyrin:

- 1) First-neighbor couplings (Adjacent interactions)
- 2) Second-neighbor couplings (Opposite interactions)

With D_{4h} symmetry here, the operators (on the basis of the considerations mentioned above) are

$$S = \sum_{i < j}^n M_{ij}, S' = \sum_{i < j}^n c'_{ij} M_{ij}, S'' = \sum_{i < j}^n c''_{ij} M_{ij}.$$

$$c'_{12} = c'_{23} = c'_{34} = c'_{45} = \dots = 1, c'_{13} = c'_{24} = c'_{35} = c'_{46}$$

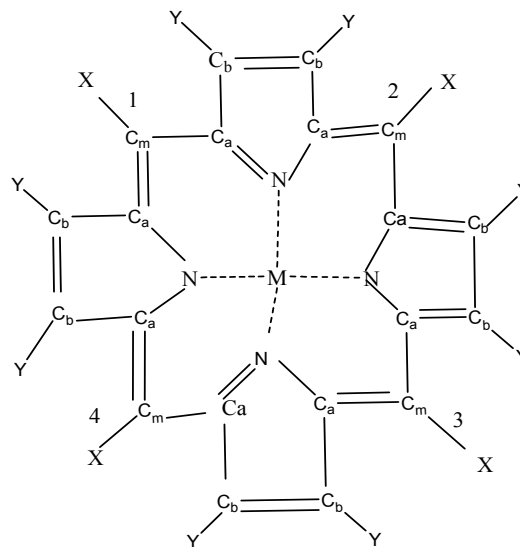


Figure 1. The structure of Metalloporphyrin.

Ni (OEP)	→ X = H,	Y = Ethyl,
Ni (OEP)-d ₄	→ X = D,	Y = Ethyl.
Ni (TPP)	→ X = Phenyl,	Y = H,
Cu (TMP)	→ X = Mesityl,	Y = H.
Ni Por	→ X = H,	Y = H.

$$= \dots = 0, \\ c''_{12} = c''_{23} = c''_{34} = c''_{45} = \dots = 0, c''_{13} = c''_{24} = c''_{35} \\ = c''_{46} = \dots = 1, \quad (17)$$

Diagonalization of S' produces states that carry representations transform according to the representations A_{1g} , B_{1g} , A_{2g} , B_{2g} , and E_{1u} of D_{4h} . The S' operator is thus the "symmetry adapter" operator. This result, which, at first sight, appears to be surprising, can be easily verified by computing the characters of the representations carried by the eigenstates of S' in the usual way. Here, in this case the value of n is either 4 ($j = 4, i = 3$) or 8 ($j = 8, i = 7$).

3. RESULTS AND DISCUSSIONS

We have used $U(2)$ algebraic model to study vibrational spectra of the Porphyrin and its substituted form molecules. The fitting algebraic parameters are A , A' , λ , λ' and N (Vibron number). The values of Vibron number (N) can be determined by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, (i = 1, 2, \dots) \quad (18)$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules [27]. This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than $\pm 20\%$ of the original value (**Eq.18**). The Vibron number N between

the diatomic molecule C-C, C-H and C-D are 140, 44 and 59 respectively. From the figure 1, it is noticed that some of the bonds are equivalent. It may be noted that during the calculation of the vibrational frequencies of Porphyrins and substituted forms, the value of N is kept fixed and not used as free parameter.

The second step is to obtain a starting guess for the parameter A . As such, the expression for the single-oscillator fundamental mode as

$$E (\nu = 1) = -4 A (N - 1). \quad (19)$$

In the present case we have three different energies, corresponding to symmetric and antisymmetric combinations of the different local modes. A possible strategy is to use the center of gravity of these modes, so the guess for

$$\bar{A} = \frac{\bar{E}}{4(1-N)} \quad (20)$$

The third step is to obtain an initial guess for λ . Its role is to split the initially degenerate local modes, placed here at the common value E used in **Eq.19**. Such an estimate is obtained by considering the simple matrix structure, we can find

$$\lambda = \frac{|E_{Eu} - E_{A1g}|}{2N} \quad (21)$$

$$\& \lambda' = \frac{|E_{B2g} - E_{A1g}|}{4N} \quad (22)$$

Finally a numerical fitting procedure is to be carried to adjust (in a least-square sense, for example) the parameters A and λ starting from values **Eq.20** and **Eq.21**, and A' (whose initial guess can be zero).

Using the **Eqs.20, 21** and **22**, A , λ and λ' are calculated [4,5-7,27] using the available data points. We have taken $\lambda'' = 0$ (In this case, the next nearest neighbor couplings are omitted). As one can see from **Table 1** & **Table 2**, the agreement with experiment is good and thus we think that the parameter set of **Table 4** & **Table 5** can be used reliably to compute energies of highly excited overtones. We note that in **Table 2** & **Table 3**, there are many predicted overtones that have not been studied experimentally. We have explicit calculations up to the second overtone (energy up to $\approx 10000 \text{ cm}^{-1}$).

We have used the algebraic Hamiltonian to study the highly excited vibrational levels of the molecule Ni (TPP), Cu (OEP), Mg (OEP), Cu (TPP), Cu (TMP), Ni Porphyrin, Ni (OEP) and its substitution form Ni (OEP)-d₄. Eight bands are studied, which can be labeled the C_m-H, C_b-C_b and only for Ni (OEP)-d₄ the bands labeled are C_m-D, C_b-C_b respectively. The highly excited vibrational levels, calculated by using the algebraic Hamiltonian **Eq.11**, are shown in **Figures 2, 3, 4**, and **5** (The detail calculated vibrational energy levels are listed

in **Tables 3**). **Figures 2** and **3** gives the levels corresponding to the C_m-H, C_b-C_b of Ni (TPP). **Figures 4** and **5** gives the levels corresponding to the C_m-H, C_b-C_b of Cu (TPP). **Figures 6** and **7** gives the levels corresponding to the C_m-H, C_b-C_b of Cu (TMP). **Figures 8** and **9** gives the levels corresponding to the C_m-D, C_b-C_b of Ni (OEP)-d₄. When the quantum number ν increases in a fixed band, the numbers of energy levels increase rapidly. Usually, the degeneracy or quanti-degeneracy of energy levels is called clustering. It may be seen from **Figures 2, 3, 4, 5, 6, 7, 8** and **9** that the vibrational energy levels of Porphyrin and its substituted form make up clusters.

4. CONCLUSIONS

In this paper, we have presented a systematic analysis of vibrational spectra of Porphyrin and its substituted forms in the algebraic framework making use of the one-dimensional Vibron model *i.e.* U (2) Vibron model.

Using the U (2) algebraic model Hamiltonian, the stretching frequencies of C_b-C and Pyrrol breathing up to Second overtone ($\nu = 2$), the combinational bands of Nickel Octaethyl Porphyrin [Ni(OEP)] and its substituted form Ni(OEP)-d₄ molecules are given in **Table 2**. However, due to lack of sufficient data base, we could not compare the calculated vibrational frequencies with that of observed data of Nickel Metalloporphyrin and its substituted forms at higher overtones. This study is useful to the experimentalist to analyze the predicted vibrational frequencies with the observed data. The model presented here describes the splitting of local stretching/bending modes due to residual interbond interactions. The splitting pattern determines the nature of interaction (Parameter λ λ'). Once we get the parameter, we predict the splitting pattern of overtones. It is worth to point out that most applications of previous algebraic models available in literature [28-33] are restricted to vibrations of Bio-molecules.

The importance of the method is that it allows one to do a global analysis of all molecular species in terms of few algebraic parameters. In turn provides a way to make assignments of unknown levels or to check assignments of known levels. The study of vibrational excitations of these bio-molecules (proteins) has numerous importance not only in human life but also in scientific research.

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Table 1. Comparison between the Observed and Calculated frequencies of the fundamental vibrations of Porphyrin and its substitution forms.

Sym	E _{Obs} (cm ⁻¹)	E _{Calc} (cm ⁻¹)	Δ (Obs-Calc) (cm ⁻¹)	E _{Obs} (cm ⁻¹)	E _{Calc} (cm ⁻¹)	Δ (Obs-Calc)(cm ⁻¹)
Ni (OEP) Molecule			Ni Porphyrin Molecule			
C _m -H vibrational mode						
A _{1g} (ν ₁)	3041	3041.9321	-0.9321	3042	3042.0322	-0.0322
B _{2g} (ν ₂₇)	3041	3040.8903	+0.1103	3041	3041.0420	-0.0420
E _{1u} (ν ₃₆)	3040	3040.0189	-0.0189	3041	3041.4001	-0.4001
C _b -C _b vibrational mode						
B _{1g} (ν ₂)	1602	1602.0445	-0.0445	1579	1579.0590	-0.0590
A _{1g} (ν ₁₁)	1577	1577.9601	-0.9601	1509	1509.0589	-0.0589
E _{1u} (ν ₃₈)	1604	1604.2822	-0.2822	1547	1548.9754	-1.9754
Cu (OEP) Molecule			Mg (OEP) Molecule			
C _m -H vibrational mode						
A _{1g} (ν ₁)	3041	3042.3001	-1.3001	3041	3039.3000	+1.7000
B _{2g} (ν ₂₇)	3052.3226	3052.3207
E _{1u} (ν ₃₆)	3062.2923	3062.2910
C _b -C _b vibrational mode						
B _{1g} (ν ₂)	1592	1594.6856	-2.6856	1596.8243
A _{1g} (ν ₁₁)	1568	1575.6450	-7.6450	1578	1578.0634	-0.0634
E _{1u} (ν ₃₈)	1613.7239	1615.58
Ni (TPP) Molecule			Cu (TPP) Molecule			
C _m -C vibrational mode						
A _{1g} (ν ₁)	1235	1234.4200	+0.5800	1234	1235.6438	-1.6438
B _{2g} (ν ₂₇)	1269	1270.6832	-1.6832	1245.0709
E _{1u} (ν ₃₆)	1306.9467	1271.1534
C _b -C _b vibrational mode						
B _{1g} (ν ₂)	1572	1571.9300	+0.0700	1530	1532.5800	-2.5200
A _{1g} (ν ₁₁)	1504	1504.6540	-0.6540	1524.7402
E _{1u} (ν ₃₈)	1639.2243	1626.8234
Ni (OEP)-d₄			Cu (TMP)			
C _m -D vibrational mode			C _m -C vibrational mode			
A _{1g} (ν ₁)	3041	3038.6800	+2.3200	1235	1236.8843	-1.8843
B _{2g} (ν ₂₇)	3041	3040.4000	+0.6000	1246.3940
E _{1u} (ν ₃₆)	3041	3042.1219	-1.1219	1256	1256.7238	-0.7238
C _b -C _b vibrational mode						
B _{1g} (ν ₂)	1602	1602.0484	-0.0484	1567	1567.5587	-0.5587
A _{1g} (ν ₁₁)	1576	1577.9629	-1.9629	1495	1495.2902	-0.2902
E _{1u} (ν ₃₈)	1604	1604.2889	-0.2889	1639.7793

Table 2. Comparison between the Observed and Calculated frequencies of C_b-C stretching vibrations of Nickel Octaethyl Porphyrin [Ni(OEP)] and its substituted form *i.e* Ni(OEP)-d₄.

<i>n</i> species	E _{Obs} (cm ⁻¹)	E _{Calc} (cm ⁻¹)	(Obs-Calc) (cm ⁻¹)	E _{Obs} (cm ⁻¹)	E _{Calc} (cm ⁻¹)	Δ(Obs-Calc)(cm ⁻¹)
Ni(OEP) Molecule						
Ni(OEP)-d₄ Molecule						
C _b -C vibrational mode						
A _{1g} (ν ₅)	1025	1043.3471	-18.3471	1026	1024.1729	1.8271
B _{1g} (ν ₁₄)	1151	1134.4480	16.5520	1187	1168.2545	18.7455
A _{2g} (ν ₂₃)	1022	1045.5548	-23.5548	1029	1026.7901	2.2099
B _{2g} (ν ₃₁)	1019	1010.5280	8.4720	999	1006.2923	-7.2923
E _u (ν ₄₃)	1159.4680		1165.7804	
E _u (ν ₄₅)	994.4080		978.6798	
First Overtone						
A _{1g} (ν ₅ +ν ₆)	1831	1837.3438	-6.3438	1828	1823.6649	4.3351
E _u		1981.8380			1924.4935	
B _{1g}		2039.4881			1948.6704	
A _{2g}		2040.7594			2019.2772	
E _u		2089.0281			2088.5504	
E _u		2126.0643			2189.3792	
A _{1g} (ν ₂₂ +ν ₂₃)	2135	2145.5906	-10.5906	2216	2246.3847	-30.3847
E _u		2190.3683			2289.3098	
E _u		2261.3456			2293.3070	
B _{1g}		2289.6720			2309.3572	
E _u		2324.6758			2365.8686	
E _u		2356.7683			2371.8268	
E _u		2454.6856			2398.7437	
E _u		2488.9103			2404.7578	
A _{1g} (ν ₂₈ +ν ₃₁)	2494	2490.1380	3.8610	2460	2452.6969	7.3031
B _{1g}		2497.4836			2479.8699	
Second Overtone						
A _{1g}		2502.3920			2529.2334	
E _u		2519.2033			2530.8538	
A _{2g} (ν ₃ +ν ₂₃)	2541	2537.2890	3.7110	2539	2541.9693	-2.9693
A _{2g} (ν ₁₄ +ν ₂₉)	2568	2569.3040	-1.3040	2607	2609.5773	-2.5773
E _u		2582.2093			2601.3572	
A _{1g} (ν ₁₉ +ν ₂₃)	2614	2606.4803	7.5197	2604	2599.9575	4.0425
B _{1g} (ν ₃ +ν ₁₄)	2670	2689.3094	-19.3094	2710	2703.3547	6.6453
E _u		2730.3802			2734.8643	
A _{1g}		2772.9689			2767.8346	
E _u		2826.3283			2798.3468	
Pyr breathing vibrational mode						
A _{1g} (ν ₆)	806	804.1759	1.8241	802	801.6378	0.3622
B _{1g} (ν ₁₅)	761	751.2534	9.7466	758	759.7356	-1.7356
E _u (ν ₄₇)	765.7932			783.3495	
First Overtone						
A _{1g}		1496.0304			1398.7654	
E _u		1524.7395			1404.8475	
E _u		1548.6704			1439.8364	
B _{1g} (ν ₆ +ν ₁₆)	1557	1559.2772	-2.2772	1481	1476.8364	4.1636
E _u		1668.5904			1558.8239	

E_u		1782.3804			1702.7529	
$A_{1g}(v_5+v_6)$	1831	1864.0326	-33.0326	1828	1825.4704	2.5296
E_u		1893.4056			1870.7354	
E_u		1899.0328			1892.7253	
Second Overtone						
$A_{2g}(v_6+v_{21})$	2109	2131.9844	-22.9844	2114	2103.7364	10.2636
$B_{1g}(v_6+v_{20})$	2144	2148.4379	-4.4379	2148	2152.7856	-4.7856
$A_{1g}(v_4+v_6)$	2184	2231.9844	-47.9844	2189	2190.4356	-1.4356
E_u		2260.5412			2237.2455	
E_u		2339.6766			2290.5472	
A_{1g}		2310.9441			2367.3864	
E_u		2363.5840			2443.9763	
E_u		2417.2044			2489.8322	
E_u		2481.1734			2547.3453	
B_{1g}		2542.5424			2601.3643	
$A_{2g}(v_5+v_{19})$	2626	2616.8038	9.1962	2628	2629.7439	-1.7439
E_u		2683.3023			2668.5233	

Observed values taken from the reference [34-36]

Table 3. Calculated excited vibrational frequencies of C_m -H stretching vibrations of Porphyrins & its substituted forms (Cm^{-1}).

	Sym	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	
		Ni (OEP)		Ni Porphyrin		Cu (OEP)		Mg (OEP)		
n = 1	$A_{1g}(v_1)$	3041	3041	3041.93	3042	3042.03	3041	3042.30	3041	3042.30
	$B_{2g}(v_{27})$	3041	3041	3040.89	3041	3041.04	3052.32	3052.32
	$E_{1u}(v_{36})$	3040	3040	3040.01	3041	3041.40	3062.29	3062.29
n = 2	E_{1u}			5941.47		5951.92		5945.15		5922.78
	B_{1g}			5942.44		5951.37		5946.23		5923.63
	A_{2g}			5944.38		5951.73		5947.14		5924.36
	E_{1u}			5945.16		5952.00		5948.14		5924.89
	E_{1u}			5946.84		5953.35		5986.70		5924.65
	E_{1u}			5947.29		5953.72		5994.28		5925.15
	E_{1u}			5948.07		5954.35		6007.48		5925.94
n = 3	A_{1g}			8707.29		8730.98		8708.54		8676.16
	E_{1u}			8708.52		8731.73		8709.53		8676.95
	E_{1u}			8708.97		8731.97		8709.90		8677.24
	E_{1u}			8709.75		8732.33		8712.60		8679.38
	B_{1g}			8712.30		8731.90		8713.53		8680.12
	E_{1u}			8713.45		8732.96		8812.42		8681.44
	E_{1u}			8715.91		8735.95		8853.97		8683.71
	A_{1g}			8716.09		8735.02		8858.35		8683.79
	E_{1u}			8703.35		8737.94		8874.75		8684.60
	E_{1u}			8717.14		8737.94		8899.68		8685.87
	B_{1g}			8712.13		8738.08		8904.67		8691.29
E_{1u}			8719.56		8738.93		8921.42		8695.86	
Calculated excited vibrational frequencies of C_b - C_b stretching vibrations of Porphyrins & its substituted forms										
	Sym	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	E_{Obs}	E_{Calc}	

	Ni (OEP)		Ni Por		Cu (OEP)		Mg (OEP)		
n = 1	B _{1g} (ν ₂)	1602	1602.04	1579	1579.05	1592	1594.68		1596.82
	A _{1g} (ν ₁₁)	1577	1577.96	1509	1509.05	1568	1575.64	1578	1578.06
	E _{1u} (ν ₃₈)	1604	1604.28	1547	1548.97		1613.72		1615.58
n = 2	A _{2g}		3143.88		3021.25		3138.57		3137.07
	E _{1u}		3159.17		3033.88		3157.61		3142.67
	B _{2g}		3170.90		3061.13		3164.55		3144.71
	E _{1u}		3183.36		3161.24		3176.65		3148.27
	E _{1u}		3192.04		3081.13		3190.09		3174.59
	E _{1u}		3200.82		3231.24		3195.69		3181.43
	E _{1u}		3216.12		3068.45		3215.85		3193.35
n = 3	A _{1g}		4696.54		4539.77		4688.79		4689.66
	E _{1u}		4720.62		4559.73		4707.83		4695.26
	E _{1u}		4729.40		4567.02		4714.77		4697.30
	E _{1u}		4744.70		4579.69		4766.28		4712.45
	B _{1g}		4794.54		4621.02		4783.99		4717.66
	E _{1u}		4816.94		4639.59		4869.11		4820.98
	E _{1u}		4865.10		4679.51		4878.12		4827.54
	A _{1g}		4868.71		4682.52		4894.87		4839.74
	E _{1u}		4817.61		5183.77		4925.89		4862.25
	E _{1u}		4889.18		4699.48		4927.63		4867.88
	B _{1g}		4762.34		4889.77		4933.51		4872.57
	E _{1u}		4895.60				4939.95		4874.32

Calculated excited vibrational frequencies of C _m -C & C _m -D stretching vibrations of Porphyrins & its substituted forms									
Sym	E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		(C _m - D)
	Ni (TPP)		Cu (TPP)		Cu (TMP)		Ni (OEP)-d ₄		
n = 1	A _{1g} (ν ₁)	1235	1234.42	1234	1235.64	1235	1236.88	3041	3038.68
	B _{2g} (ν ₂₇)	1269	1270.68		1245.07		1246.39	3041	3040.40
	E _{1u} (ν ₃₆)		1306.94		1271.15	1256	1256.72	3041	3042.12
n = 2	E _{1u}		2459.13		2417.34		2464.18		5952.05
	B _{1g}		2495.39		2427.57		2474.51		5953.77
	A _{2g}		2508.62		2436.20		2475.39		5953.91
	E _{1u}		2531.65		2452.85		2484.84		5955.49
	E _{1u}		2777.49		2459.33		2524.26		6007.76
	E _{1u}		2835.59		2470.61		2535.23		6017.93
	E _{1u}		2936.67		2445.64		2554.31		6035.62
n = 3	A _{1g}		3674.12		3545.08		3681.89		8774.90
	E _{1u}		3713.46		3554.51		3692.22		8776.62
	E _{1u}		3710.38		3557.95		3695.99		8777.25
	E _{1u}		3821.69		3583.47		3702.55		8778.34
	B _{1g}		4321.98		3633.87		3723.94		8781.91
	E _{1u}		3855.42		3669.38		3804.16		8888.28
	E _{1u}		4470.02		3675.60		3832.11		8914.19
A _{1g}		4788.38		3687.14		3892.19		8969.91	

	E _{1u}	4812.25	3704.90	3902.71	8979.66				
	E _{1u}	4947.56	3708.45	3922.24	8997.77				
	B _{1g}	5138.57	3617.35	3952.28	9025.63				
	E _{1u}	5187.30	3718.93	3958.29	9031.21				
Calculated excited vibrational frequencies of C _b -C _b stretching vibrations of Porphyrins & its substituted forms									
Sym	E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		E _{Obs} E _{Calc}		
	Ni (TPP)		Cu (TPP)		Cu (TMP)		Ni (OEP)-d ₄		
n = 1	A _{1g} (ν ₁)	1572	1571.93	1530	1532.58	1567	1567.55	1602	1602.04
	B _{2g} (ν ₂₇)	1504	1504.65		1524.74	1495	1495.29	1576	1577.96
	E _{1u} (ν ₃₆)		1639.22		1626.82		1639.77	1604	1604.28
	E _{1u}		3035.20		3018.75		3201.84		3143.88
	B _{1g}		3062.66		3027.25		3229.30		3159.17
	A _{2g}		3065.00		3034.43		3231.64		3170.90
	E _{1u}		3090.13		3042.27		3256.77		3183.36
	E _{1u}		3169.76		3120.83		3346.37		3192.04
	E _{1u}		3194.32		3139.46		3372.75		3200.82
	E _{1u}		3237.05		3171.88		3418.64		3216.12
n = 3	A _{1g}		4543.99		4471.00		4782.85		4696.54
	E _{1u}		4571.45		4478.84		4810.31		4720.62
	E _{1u}		4581.48		4481.70		4820.34		4729.40
	E _{1u}		4598.92		4502.90		4837.78		4744.70
	B _{1g}		4655.78		4678.74		4894.64		4794.54
	E _{1u}		4817.83		4726.22		5076.98		4816.94
	E _{1u}		4880.41		4828.30		5144.19		4865.10
	A _{1g}		5014.97		4846.17		5288.72		4868.71
	E _{1u}		5038.52		4879.35		5314.01		4817.61
	E _{1u}		5082.26		4930.39		5360.99		4889.18
	B _{1g}		5149.54		4940.60		5433.26		4762.34
	E _{1u}		5163.00		4945.56		5447.71		4895.60

Table 4. Values ^(a) of Algebraic Parameters Used in the calculation of C_m-H, C_m-D Stretching Modes of Porphyrins and its substituted forms.

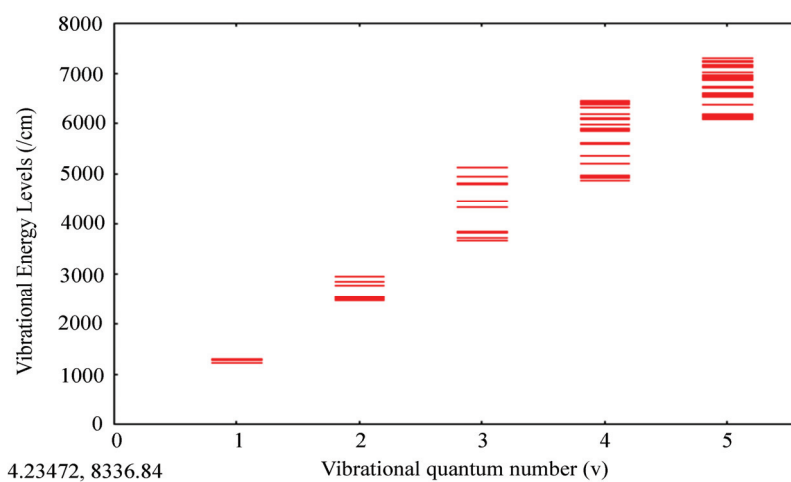
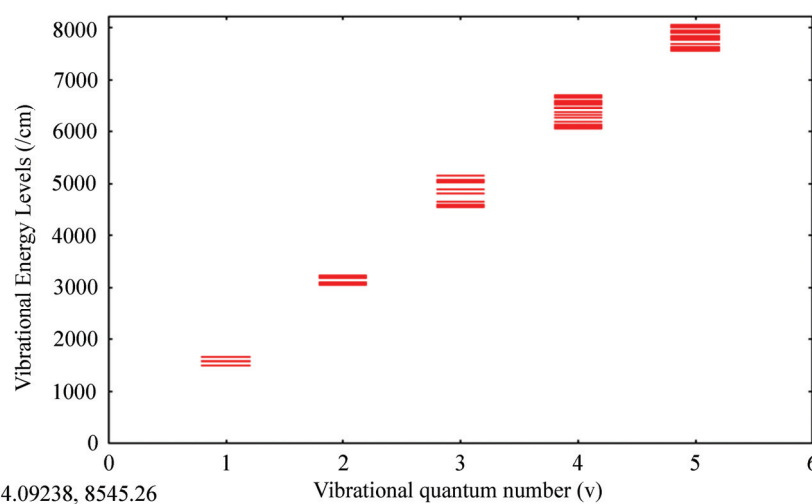
	Ni(OEP)	Cu(OEP)	Mg(OEP)	Ni(TPP)	Cu(TPP)	Cu(TMP)	Ni Por	Ni(OEP)-d ₄ (C _m -D)
<i>N</i>	44	44	44	44	44	44	44	59
<i>A</i>	-17.6802	-17.6820	-17.614	-2.213	-7.1740	-2.2173	-17.65	-13.043
<i>A'</i>	-0.24	-0.25	-0.28	-0.9985	-0.4302	-1.0182	-1.3108	-0.2782
<i>λ</i>	0.014	0.01136	0.009	0.1295	0.1072	0.0369	0.0113	0.0146
<i>λ'</i>	0.011	0.012	0.012	0.5685	0.2018	0.1073	0.0021	0.2361

^(a) All values in cm⁻¹ except N, which is dimensionless.

Table 5. Values ^(a) of Algebraic Parameters Used in the calculation of C_b-C_b Stretching Modes of Porphyrins and its substituted forms.

Ni(OEP)	Cu(OEP)	Mg(OEP)	Ni(TPP)	Cu(TPP)	Cu(TMP)	Ni Por	Ni(OEP)-d ₄
<i>N</i>	140	140	140	140	140	140	140
<i>A</i>	-2.83	-2.825	-2.835	-2.7205	-2.7502	-2.8825	-2.691
<i>A'</i>	-1.223	-1.286	-0.452	-1.986	1.0921	-1.223	-3.216
<i>λ</i>	0.086	0.068	0.067	0.2403	0.028	0.2581	0.0713
<i>λ'</i>	0.047	0.092	0.020	0.0981	0.1823	0.0981	0.047

^(a) All values in cm⁻¹ except *N*, which is dimensionless.

**Figure 2.** C_m-H band vibrational energy level of Ni(TPP).**Figure 3.** C_b-C_b band vibrational energy level of Ni(TPP).

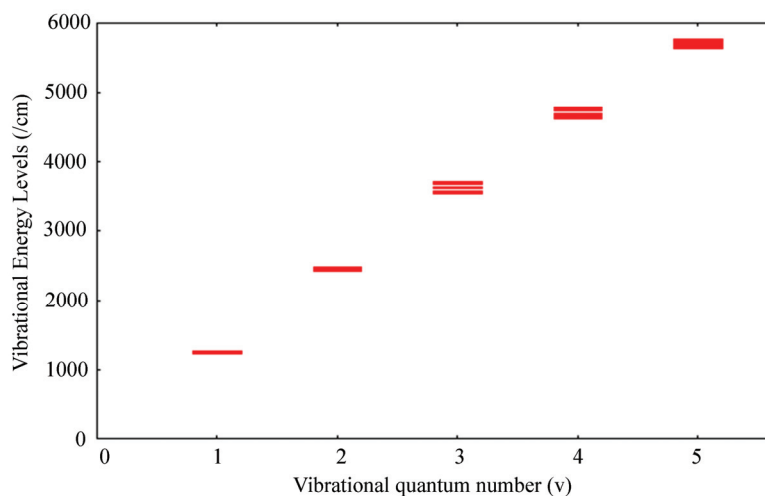


Figure 4. C_m-H band vibrational energy level of Cu(TPP).

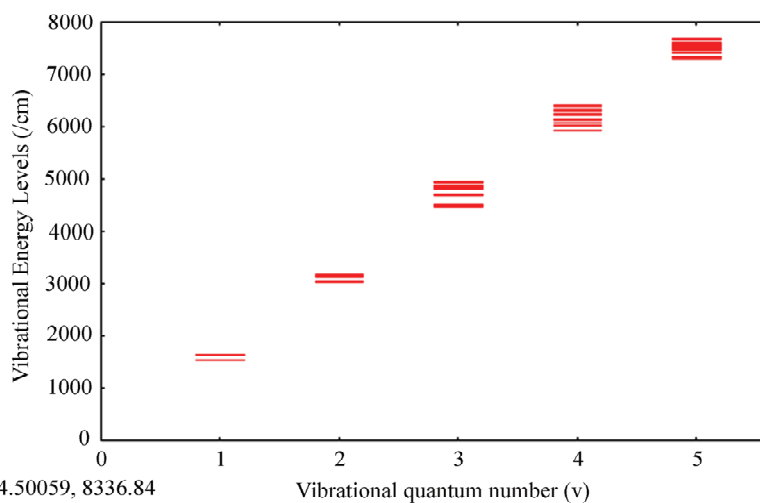


Figure 5. C_b-C_b band vibrational energy level of Cu(TPP).

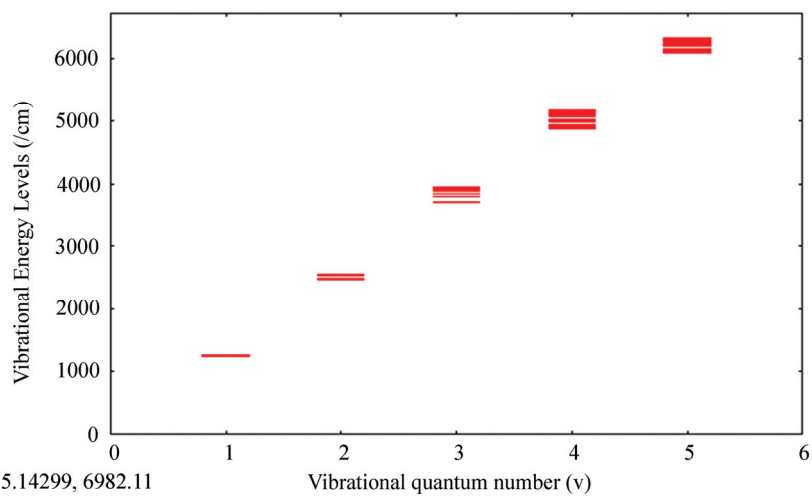


Figure 6. C_m-H band vibrational energy level of Cu(TMP).

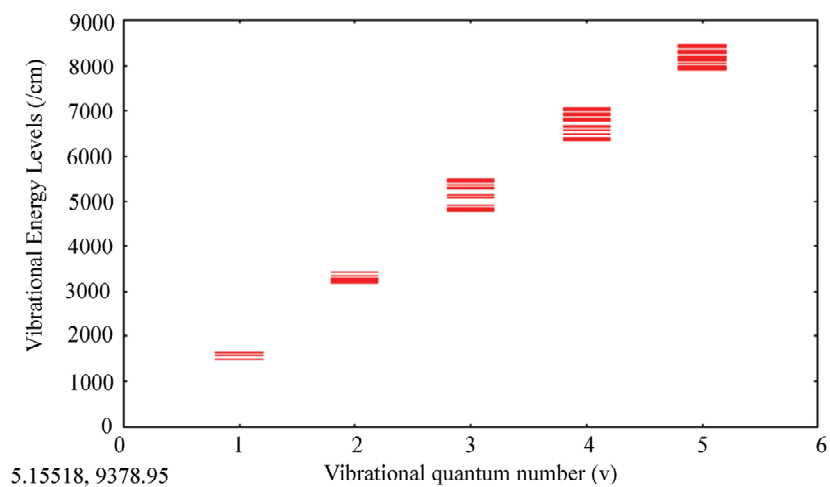


Figure 7. C_b-C_b band vibrational energy level of Cu(TMP).

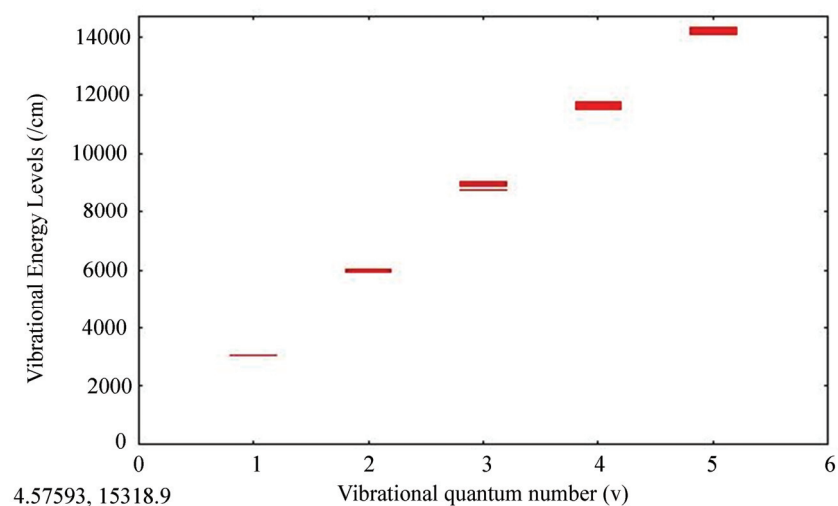


Figure 8. C_m-H band vibrational energy level of Ni(OEP)- d_4 .

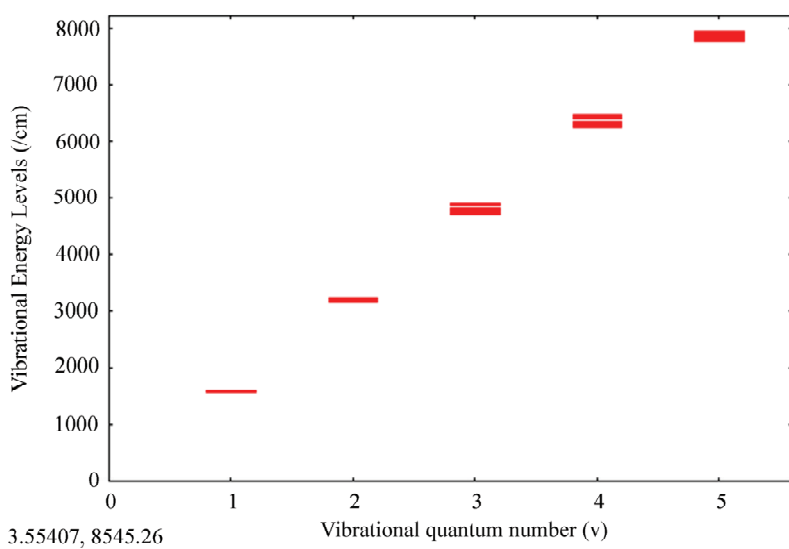


Figure 9. C_b-C_b band vibrational energy level of Ni(OEP)- d_4 .

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