Analysis of vibrational spectra of nano-bio molecules: Application to metalloporphrins

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In this paper, we have applied the Lie algebraic model to nano-bio molecules to determine the vibrational spectra of different stretching and bending vibrational modes. The determined vibrational energy levels by the Lie algebraic model are compared with the experimental data. The results from the theoretical model are consistent with the experimental data. The vibrational energy levels are clustering in the excited states.

Keywords: Lie algebraic model, vibrational spectra, vibrational modes, metalloporphyrins

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1. Introduction

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

The logical scheme of the vibron model is parallel to that of the Dunham and the potential approaches. Consider, for example, the vibrational spectra of bent triatomic molecules. The familiar term value expansion is

$$\begin{aligned} &E(\nu_1,\nu_2,\nu_3)\\ &= E_0+\sum_{i=1}^{3}\omega_i(\nu_i+1/2)\\ &\quad+\sum_{i\le j}^{3}X_{ij}(\nu_i+1/2)(\nu_j+1/2)\\ &\quad+\sum_{i\le j\le k}^{3}Y_{ijk}(\nu_i+1/2)(\nu_j+1/2)(\nu_k+1/2)+\cdots. \end{aligned} \quad (1)$$

This expansion has 3 parameters when stopped at linear terms, 9 when stopped at quadratic terms, 19 when stoped at cubic terms. The typical root-mean-square (rms) deviations of the expansion stopped at quadratic terms for bent triatomic with ~40 known levels are of the order of 10 cm^{-1}. The inclusion of cubic terms brings this deviation down to 1 cm^{-1} and further improvements can be obtained by additional terms.

In the potential approach, one first chooses a set of coordinates. For bent triatomics, for example, an appropriate set is the bond (r_1 and r_2) and angle (θ) displacements from the equilibrium configuration. One then expands the potential into these coordinates (or functions of coordinates)

$$V(r_1,r_2,r_3)=V_0+\sum_{m,n,k=2}a_{mnk}r_1^m r_2^n\theta^k, \quad (2)$$

and solves the Schrodinger equation with the potential V. The expansion has 6 parameters when stopped at quadratic terms, 16 parameters when stopped at cubic terms. The results also depend on the form of the kinetic energy. If the values a_{mnk} are taken from *ab-initio* calculations, the typical rms deviations are of the order of 50 cm^{-1}, but quite often, small modifications[5] of the *ab-initio* values provide accurate results within a few cm^{-1}.

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In the vibron model, one again chooses first a set of coordinates, for example, the bond coordinates r_1 and r_2. One then replaces the coordinates (and associated momenta) by Lie algebraic structures and expands the Hamiltonian in terms of the elements of these algebras. Denoting generically by G_1 and G_2 the algebraic structures associated with r_1 and r_2, one has

$$H = E_0 + \sum_{\alpha i} A_{\alpha i} G_{\alpha i} + \sum_{\alpha i,\beta j} A_{\alpha i,\beta j} G_{\alpha i} G_{\beta j} + \cdots, \quad i,j = 1,2. \tag{3}$$

The explicit form of the expansion is discussed, the expansion for bent triatomic has 6 parameters when stopped at the lowest order, 16 when stopped at the next order. If the bonds are identical, as in XY_2 molecules, the numbers of parameters are reduced further to 4 and 11, respectively.

In recent years, polyatomic nano-bio molecules (i.e., metalloporphyrins) have held numerous importances in the field of chemical physics. In the case of polyatomic bio-molecules, the parameters play a major role in the vibron model. Of course, we have explicitly described with fewer parameters the vibrational bands of the triatomic linear molecules HCN, OCS[5,6] and tetratomic molecules HCCF, HCCD by using an algebraic approach.[7] We have also reported the vibrational bands of tetrahedral molecules CCl_4, $SnBr_4$[8–11] and polyatomic bio-molecules nickel octaethyl porphyrin, nickel porphyrin molecules using $U(2)$ vibron model respectively.[12–16] The advantage of the algebraic approach, as compared to that of the Dunham or phonological potential models, is that typically it requires fewer parameters to obtain the same level of accuracy. It also provides a simultaneous description of bending and stretching modes.

We consider in this paper the vibrational modes of polyatomic nao-bio molecules, i.e., metalloporphyrins and their substituted forms. In Section 2, we briefly review the theory of the vibron model of vibrations of polyatomic molecules. In Section 3, we describe the stretching vibrations and infrared intensity transitions of different metalloporphyrins and their substitute forms. Conclusions are presented in Section 4.

2. Vibron model of vibrations of polyatomic molecules

A general algebraic model of rotation–vibration spectra of molecules was introduced in Refs. [1]–[4] and applied to the study of tri-atomic[17,18] and tetra-atomic[19,20] molecules. In this model, rotations and vibrations are treated simultaneously. For this reason, it becomes impractical when the number of atoms exceeds four. However, if rotations and vibrations are separated, it is possible to construct a simpler version of the vibron model, which can be used for the vibrational analysis of large molecules. This model, which we call the one-dimensional vibron model,[21–25] starts from the observation[26–28] that the eigenstates of a one-dimensional Schrodinger equation with a Morse potential

$$h(p,x) = p^2/2\mu + D[1-\exp(-\alpha x)]^2 \tag{4}$$

can be put into one to one correspondence with the representations of the algebra $U(2) \supset O(2)$, characterized by the quantum numbers $|N,m\rangle$, with the proviso that one takes only the positive branch of m, i.e. $m = N, N-2, \ldots, 1$ or 0 for $N =$ odd or even ($N =$ integer) (the negative branch describes the mirror image of the potential $x \to -x$). The Morse Hamiltonian (4) can be written, in the algebraic approach, simply as, $h = \epsilon_0 + AC$, where C is the invariant operator of $O(2)$, with eigenvalues $m^2 - N^2$. The eigenvalues of h are

$$\epsilon = \epsilon_0 + A(m^2 - N^2), \quad m = N, N-2, \ldots, 1 \text{ or } 0, \ (N = \text{odd or even}). \tag{5}$$

By introducing the usual vibrational quantum number $v = (N-m)/2$, equation (5) can be rewritten as

$$\epsilon = \epsilon_0 - 4A(Nv - v^2), \quad v = 0, 1, \ldots, N/2 \text{ or } (N-1)/2, \ (N = \text{even or odd}). \tag{6}$$

One can immediately verify that these are the eigenvalues of the Morse oscillator. Potentials that deviate from the Morse oscillator can be described by an expansion in terms of the Morse functions

$$V(x) = \sum_{s=1}^{k} D_s [f(x)]^s, \quad f(x) = [1-\exp(-\alpha x)]^2. \tag{7}$$

In the algebraic approach, this corresponds to an expansion of the type

$$h = \varepsilon_0 + \sum_{s=1}^{k} A^{(s)} C^s, \tag{8}$$

with eigenvalues

$$\varepsilon = \varepsilon_0 + \sum_{s=1}^{k} A^{(s)} [-4(Nv - v^2)]^s. \tag{9}$$

For stretching vibrations, a representation of the potential in terms of the lower-order Morse oscillator is usually rather accurate, we therefore study the stretching vibrations with only the lowest-order term in Eq. (4), $s = 1$. If the model is used for the bending vibrations where the coordinate of x in Eq. (4) is the bending angle θ, the representation in terms of a single Morse oscillator may not be sufficient and one has to include higher-order terms.

Consider now a molecule with n bonds. In the vibron model,[19–23] each bond i is replaced by an algebra G_i. For one-dimensional problems, $G_i = U_i(2)$. Each bond has Hamiltonian

$$h_i = \varepsilon_{0i} + A_i C_i, \tag{10}$$

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

$$\varepsilon_i = \varepsilon_{0i} + A_i[-4(N_i v_i - v_i^2)]. \tag{11}$$

The bond interacts with a bond–bond interaction. The interaction potential can be written as

$$V(x_i, x_j) = k'_{ij}[1 - \exp(-\alpha_i x_i)][1 - \exp(-\alpha_j x_j)], \tag{12}$$

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

$$V(x_i, x_j) \approx k'_{ij}\alpha_i\beta_j x_i x_j = k_{ij} x_i x_j. \tag{13}$$

In the algebraic approach, the interaction of the type can be taken into account by introducing two terms, called Casimir and Majorana interactions, respectively. If these are added, the total Hamiltonian becomes

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij}. \tag{14}$$

The operators C_{ij} are diagonal with matrix elements given by

$$\begin{aligned} &\langle N_i, v_i; N_j, v_j | C_{ij} N_i, v_i; N_j, v_j \rangle \\ &= 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)], \end{aligned} \tag{15}$$

where we have subtracted (relative) the last two terms, since they can be reabsorbed in C_i and C_j. The operators M_{ij} have both diagonal and non-diagonal matrix elements

$$\begin{aligned} &\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= (N_i v_j + N_j v_i - 2 v_i v_j), \\ &\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}, \\ &\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}. \end{aligned} \tag{16}$$

The physical meaning of this apparently complex result can be understood by an example of four identical oscillators. Let us start from the local basis states $|v_a v_b v_c v_d\rangle = |1,0,0,0\rangle, |0,1,0,0\rangle, |0,0,1,0\rangle, |0,0,0,1\rangle$. In manifest agreement, the Majorana operator has the effect of mixing these states, so we obtain

$$\begin{aligned} \langle 1,0,0,0|M_{12}|0,1,0,0\rangle &= \langle 0,1,0,0|M_{21}|0,1,0,0,0\rangle \\ &= -\sqrt{N_1 N_2}, \\ \langle 1,0,0,0|M_{13}|0,0,1,0\rangle &= \langle 0,0,1,0|M_{31}|0,1,0,0,0\rangle \\ &= -\sqrt{N_1 N_3}, \\ \langle 1,0,0,0|M_{14}|0,0,0,1\rangle &= \langle 0,0,0,1|M_{41}|0,1,0,0,0\rangle \\ &= -\sqrt{N_4 N_1}, \\ \langle 0,1,0,0|M_{23}|0,0,1,0\rangle &= \langle 0,0,1,0|M_{32}|0,0,1,0,0\rangle \\ &= -\sqrt{N_2 N_3}, \\ \langle 0,1,0,0|M_{24}|0,0,0,1\rangle &= \langle 0,0,0,1|M_{42}|0,0,1,0,0\rangle \\ &= -\sqrt{N_2 N_4}, \\ \langle 0,0,1,0|M_{34}|0,0,0,1\rangle &= \langle 0,0,0,1|M_{43}|0,0,0,1,0\rangle \\ &= -\sqrt{N_3 N_4}. \end{aligned} \tag{17}$$

If we start from the Hamiltonian operator (13), in which we formally replace C_{ij} with M_{ij}, the eigenvalue problem for the first four local modes is expressed in terms of the Hamiltonian matrix

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) \\ +3(\lambda + \lambda')N & -\lambda N & -\lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) \\ & +3(\lambda + \lambda')N & -\lambda N & -\lambda N \\ -\lambda N & -\lambda N & -4A(N-1) - 4A'(2N-1) \\ & & +3(\lambda + \lambda')N & -\lambda N \\ -\lambda N & -\lambda N & -\lambda N & -4A(N-1) - 4A'(2N-1) \\ & & & +3(\lambda + \lambda')N \end{pmatrix}, \tag{18}$$

where we put $A_1 = A_2 = A_3 = A_4 \equiv A$, $A_{12} = A_{23} = A_{34} = A_{41} \equiv A'$, $N_1 = N_2 = N_3 = N_4 \equiv N$. The corresponding secular determinant shows that the four local modes $|1,0,0,0\rangle$, $|0,1,0,0\rangle$, $|0,0,1,0\rangle$, $|0,0,0,1\rangle$ initially with the same energy $\varepsilon_0 = -4A(N-1) - 4A'(2N-1)$ are now mixed, shifted, and split under the action of M_{ij}. The sign of λ, λ' determines which of these combinations has the highest energy. This simple example can readily be generalized to an entire manifold of levels founded on the local basis of four anharmonic modes. The matrix elements of M_{ij} [Eq. (14)] are such that the Hamiltonian matrix is in the diagonal form, thus leading to the block structure shown in Fig. 1. Specifically, we observe that each block contains states with the same value of $v_a + v_b + v_c + v_d$, which is a conserved quantity for both chains. The inclusion of M_{ij} in the local Hamiltonian operator cannot affect the $v_a + v_b + v_c + v_d$ conservation rule. We will see how this specific feature has far-reaching consequences for both computational and physical aspects for these kinds of problems.

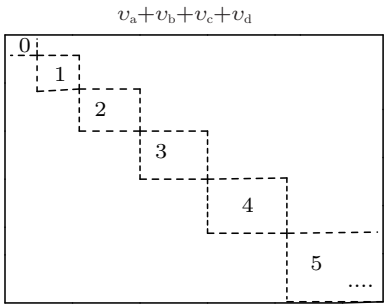


Fig. 1. Block structure of the Hamiltonian matrix caused by the Majorana operator.

Finally, we mention the possibility of assigning a measure of locality (or, equivalently, of normality) to a given situation by means of the dimensionless parameter

$$\xi \equiv 2/\pi \tan^{-1}[8(\lambda+\lambda')/(A+A')],$$

which is obviously a very small quantity in local or quasilocal molecules, while for normal cases, ξ is close to 1.[29]

The eigenvalues of Eq. (13) can be easily evaluated and provide a description of n coupled anharmonic vibrators. The couplings in Eq. (13) are only of the first order, in the sense that the operators M_{ij} annihilate one quantum of vibration in bond j and create one in bond i (or vice-verse). In the same way in which one can improve the description of each bond by considering higher powers in the C operators, one can also improve the description of the couplings by considering higher-order terms in the M operators. We have derived explicit formulas for couplings in which two quanta are annihilated and one is created, for example,

$$\langle N_i, \nu_i \pm 2; N_j, \nu_j \mp 1 \,|M_{ij}^{!}|\, N_i, \nu_i; N_j, \nu_j \,\rangle, \qquad (19)$$

and one can generate, in a relatively simple fashion, others, if needed. For applications to the problem described here, these higher-order couplings are not needed and we therefore omit them henceforth.

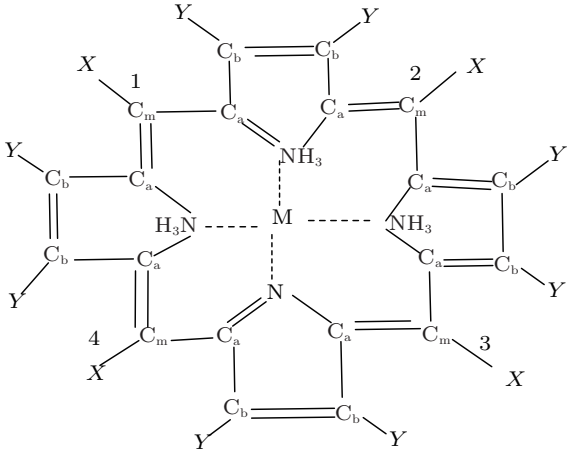
2.1. Sample vibrational analysis: stretching vibrations of metalloporphyrins

As an example of the use of the algebraic method, we analyze the stretching vibrations of different metalloporphyrins. We number the bonds as shown in Fig. 2. Each bond i is characterized by its vibron number N_i and parameter A_i. The Casimir part of the interbond interactions is characterized by parameter A_{ij}. For the Majorana part, we can have (due to the symmetry of the molecule) two possible types of couplings:

(I) first neighbor couplings, [for example (12), (23), . . .],

(II) second neighbor couplings, [for example (13), (24),. . .].

Figure 2 shows the planar D_{4h} structure of a metalloporphyrin. The simplest porphyrin, porphin (Por), has $105(3\times 37-6)$ normal vibrations, which are classified as shown in Table 2 (see Tables 1 and 2).



Ni(OEP)	→	$X=$H,	$Y=$ Ethy1,
Ni(OEP)−d_4	→	$X=$D,	$Y=$ Ethy1,
Ni(TPP)	→	$X=$Pheny1,	$Y=$ H,
Cu(TMP)	→	$X=$Mesity1,	$Y=$ H,
Ni Por	→	$X=$H,	$Y=$ H,

Fig. 2. Structure of metalloporphrins.

Table 1. The character table of D_{4h} point group symmetry.

D_{4h}	E	$2C_4$	C_2	$2C_2$	$2C_2$	I	$2S_4$	ρ_h	$2\rho_v$	$2\rho_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$X^2+Y^2+Z^2$
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1		X^2–Y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1		XY
E_g	2	0	–2	0	0	2	0	–2	0	0	(R_x, R_y)	(XZ,YZ)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{1u}	1	1	1	–1	–1	–1	–1	–1	1	1	Z	
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1		
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1		
E_u	2	0	–2	0	0	–2	0	2	0	0	(X,Y)	

Table 2. Classification of normal vibrations of a metalloporphyrin of D_{4h} symmetry.

In-plane vibrations		Out-of-plane vibrations	
A_{1g}	9	A_{1u}	3
A_{2g}	8	A_{2u}	6
B_{1g}	9	B_{1u}	5
B_{2g}	9	B_{2u}	4
E_u	18	E_g	8

In this paper, we have considered only the in-plane vibrations of metalloporphyrins of vibrational bands (stretching vibrations) using the $U(2)$ vibron model. The symmetry species in the higher overtones of metalloporphyrins (i.e., for D_{4h} point group) are shown in Table 4 (see Tables 3 and 4).

Table 3. Symmetry correlation for deformed metalloporphyrins.

	Ruffling D_{2d}	Planar D_{4h}	Domed C_{4v}
	A_1	A_{1g}	A_1
	A_2	A_{2g}	A_2
	B_1	B_{1g}	B_1
	B_2	B_{2g}	B_2
	E	E	E
	B_1	A_{1u}	A_2
	B_2	A_{2u}	A_1
	A_1	B_{1u}	B_2
	A_2	B_{2u}	B_1
	E	E	E
IR[a)]	B_2, E A	$_{2u}$, E_u	A_1, E
Raman	A_1, B_1, B_2, E	A_{1g}, B_{1g}, B_{2g}, E_g	A_1, B_1, B_2, E
RR[b)]	A_2	A_{2g}	A_2

[a)] Active species for each method; [b)] RR implies the species which is inactive in an ordinary Raman but active under resonance conditions.

Table 4. Symmetry species of the overtones and combination modes for point group D_{4h}.

	A_{1g}	B_{1g}	A_{2g}	B_{2g}
A_{1g}	A_{1g}	B_{1g}	A_{2g}	B_{2g}
B_{1g}		A_{1g}	B_{2g}	A_{2g}
A_{2g}			$A_{1g}B_{1g}$	
B_{2g}				A_{1g}

3. Results and discussion

We begin our analysis from molecules with the maximal symmetry, D_{4h}, Ni(OEP) and Ni(OEP)-d_4. On account of this symmetry, we must have

$$\begin{aligned} &N_i = N_{\rm H},\ \ A_i = A_{\rm H},\ \ \text{for Ni(OEP)},\\ &N_i = N_{\rm D},\ \ A_i = A_{\rm D},\ \ \text{for Ni(OEP)-d}_4, \end{aligned} \tag{20}$$

i.e., all the bonds are equivalent. Also we have

$$\begin{aligned} &A_{ij} = A'_{\rm HH},\ \ \text{for Ni(OEP)},\\ &A_{ij} = A'_{\rm DD},\ \ \text{for Ni(OEP)-d}_4. \end{aligned} \tag{21}$$

The Majorana couplings, on the basis again of the symmetry, must satisfy

$$\begin{aligned} &\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{41} = \lambda_{\rm HH},\ \ \text{or}\ \ \lambda_{\rm DD},\\ &\lambda_{13} = \lambda_{24} = \lambda_{\rm HH},\ \ \text{or}\ \ \lambda_{\rm DD}. \end{aligned} \tag{22}$$

One can thus describe all the stretching vibrations of Ni(OEP) or Ni(OEP)-d_4 in terms of five parameters ($N_{\rm H}$, $A_{\rm H}$, $A_{\rm HH}$, $\lambda_{\rm HH}$, $\lambda_{\rm HH}$) or ($N_{\rm D}$, $A_{\rm D}$, $A_{\rm DD}$, $\lambda_{\rm DD}$, $\lambda_{\rm DD}$). The vibron numbers $N_{\rm H}$ or $N_{\rm D}$ can be taken from the known anharmonicities of the free C–H or C–D bonds using Eq. (6).

The number N is related to the total number of bound states supported by the potential well. Equivalently it can be put in a one-to-one correspondence with the anharmonicity parameter $x_{\rm e}$ by means of

$$x_{\rm e} = \frac{1}{N+2}.$$

We can rewrite the above equation as

$$N_i = \frac{\omega_{\rm e}}{\omega_{\rm e}x_{\rm e}} - 1,\ \ (i = 1, 2, \ldots).$$

Now, for a blood cell molecule, we can have the values of $\omega_{\rm e}$ and $\omega_{\rm e}x_{\rm e}$ for the distinct bonds (say CH, CC, CD, etc) from the study of Nakamoto[30] and that of Huber and Herzberg.[31] Using the values of $\omega_{\rm e}$ and $\omega_{\rm e}x_{\rm e}$ for the bond CH/CC, we can have an initial guess for the value of the vibron number N.

Depending on the specific molecular structure, N_i can vary between $\pm 20\%$ of the original value. The vibron number N for the diatomic molecules C–H and C–C are 44 and 140, respectively. Since the bonds are equivalent, the value of N is kept fixed. This is equivalent to change the single-bond anharmonicity according to the specific molecular environment, in which it can be slightly different.

The values are shown in Tables 5 and 6. The data used to determine the parameters are shown in Table 7. We have used the Wilson numbering for the spices of stretching vibrations in these tables. It would be very interesting to see whether or not our calculations predict the states correctly. We have explicit calculations up to the fourth overtone (energy up to 15000 $\rm cm^{-1}$).

An important feature of the algebraic model discussed here is that it not only provides a description of the vibrational modes, but also gives a simple solution to a crucial problem in the description of the polyatomic molecules, namely, the construction of states that transform accordingly to the irreducible representations of the appropriate point group. For the fundamental stretches of metalloporphyrins, with the D_{4h} symmetry, the symmetry species are A_{1g}, B_{1g}, A_{2g}, B_{2g}, and E_{1u}. The construction of these symmetry adapted states is an extremely difficult task, as discussed, for example, in Ref. [32]. In the

Table 5. Algebraic parameters used in the calculation of C_m–H, C_m–D stretching modes of metalloporphyrins. All values are in units of cm^{-1} except N which is dimensionless.

	Ni(OEP)	Cu(OEP)	Mg(OEP)	Ni(TPP)	Cu(TPP)	Cu(TMP)	Ni Por	Ni(OEP)–d_4 (C_m–D)
N	44	44	44	44	44	44	44	59
A	–17.6802	–17.6820	–17.614	–2.213	–7.1740	–2.2173	–17.65	–13.043
A'	–0.24	–0.25	–0.28	–0.9985	–0.4302	–1.0182	–1.3108	–0.2782
λ	0.014	0.01136	0.009	0.1295	0.1072	0.0369	0.0113	0.0146
λ'	0.011	0.012	0.012	0.5685	0.2018	0.1073	0.0021	0.2361

Table 6. Algebraic parameters used in the calculation of C_b–C_b stretching modes of metalloporphyrins. All values are in units of cm^{-1} except N which is dimensionless.

	Ni(OEP)	Cu(OEP)	Mg(OEP)	Ni(TPP)	Cu(TPP)	Cu(TMP)	Ni Por	Ni(OEP)–d_4
N	140	140	140	140	140	140	140	140
A	-2.83	-2.825	-2.835	-2.7205	-2.7502	-2.8825	-2.691	-2.83
A'	-1.223	-1.286	-0.452	-1.986	1.0921	-1.223	-3.216	-1.223
λ	0.086	0.068	0.067	0.2403	0.028	0.2581	0.0713	0.086
λ'	0.047	0.092	0.020	0.0981	0.1823	0.0981	0.25	0.047

Table 7. Comparison between the observed and calculated frequencies of the fundamental stretching vibrations in different metalloporphyrins and their substitution forms. Observed values taken from Refs. [33]–[35].

	Ni(OEP)			Ni porphyrin		
Sym	Obs	Calc	Obs – Calc	Obs	Calc	Obs – Calc
			C_m–H vibrational mode			
$A_{1g}(\nu_1)$	3041	3041.93	–0.93	3042	3042.03	–0.03
$B_{2g}(\nu_{27})$	3041	3040.89	+0.11	3041	3041.04	–0.04
$E_{1u}(\nu_{36})$	3040	3040.01	–0.01	3041	3041.40	–0.40
			C_b–C_b vibrational mode			
$B_{1g}(\nu_2)$	1602	1602.04	–0.04	1579	1579.05	–0.05
$A_{1g}(\nu_{11})$	1577	1577.96	–0.96	1509	1509.05	–0.05
$E_{1u}(\nu_{38})$	1604	1604.28	–0.28	1547	1548.97	–1.97
	Cu(OEP)			Mg(OEP)		
Sym	Obs	Calc	Obs – Calc	Obs	Calc	Obs – Calc
			C_m–H vibrational mode			
$A_{1g}(\nu_1)$	3041	3042.30	–1.30	3041	3039.30	+1.70
$B_{2g}(\nu_{27})$	···	3052.32	···	···	3052.32	···
$E_{1u}(\nu_{36})$	···	3062.29	···	···	3062.29	···
			C_b–C_b vibrational mode			
$B_{1g}(\nu_2)$	1592	1594.68	–2.68	···	1596.82	···
$A_{1g}(\nu_{11})$	1568	1575.64	–7.64	1578	1578.06	–0.06
$E_{1u}(\nu_{38})$	···	1613.72	···	···	1615.58	···
	Ni(TPP)			Cu(TPP)		
Sym	Obs	Calc	Obs – Calc	Obs	Calc	Obs – Calc
			C_m–C vibrational mode			
$A_{1g}(\nu_1)$	1235	1234.42	+0.58	1234	1235.64	–1.64
$B_{2g}(\nu_{27})$	1269	1270.68	–1.68	···	1245.07	···
$E_{1u}(\nu_{36})$	···	1306.94	···	···	1271.15	···
			C_b–C_b vibrational mode			
$B_{1g}(\nu_2)$	1572	1571.93	+0.07	1530	1532.58	–2.52
$A_{1g}(\nu_{11})$	1504	1504.65	–0.65	···	1524.74	···
$E_{1u}(\nu_{38})$	···	1639.22	···	···	1626.82	···
	Ni(OEP)–d_4			Cu(TMP)		
Sym	Obs	Calc	Obs – Calc	Obs	Calc	Obs – Calc
	C_m–D vibrational mode			C_m–C vibrational mode		
$A_{1g}(\nu_1)$	3041	3038.68	+2.32	1235	1236.88	–1.88
$B_{2g}(\nu_{27})$	3041	3040.40	+0.60	···	1246.39	···
$E_{1u}(\nu_{36})$	3041	3042.12	–1.12	1256	1256.72	–0.72
			C_b–C_b vibrational mode			
$B_{1g}(\nu_2)$	1602	1602.04	–0.04	1567	1567.55	–0.55
$A_{1g}(\nu_{11})$	1576	1577.96	–1.96	1495	1495.29	–0.29
$E_{1u}(\nu_{38})$	1604	1604.28	–0.28	——	1639.77	···

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

$$S = \sum_{i<j}^{n} M_{ij}, \quad S' = \sum_{i<j}^{n} c'_{ij} M_{ij}, \quad S'' = \sum_{i<j}^{n} c''_{ij} M_{ij}, \tag{23}$$

$$\begin{aligned} &c'_{12} = c'_{23} = c'_{34} = c'_{45} = \cdots = 1, \\ &c'_{13} = c'_{24} = c'_{35} = c'_{46} = \cdots = 0, \\ &c''_{12} = c''_{23} = c''_{34} = c''_{45} = \cdots = 0, \\ &c''_{13} = c''_{24} = c''_{35} = c''_{46} = \cdots = 1. \end{aligned} \tag{24}$$

Diagonalization of S produces states that carry representations which transform according to the representations A_{1g}, B_{1g}, A_{2g}, B_{2g}, and E_{1u} of D_{4h}. The S' (or 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.

When written in terms of the operators S and

$$C = \sum_{i}^{n} C_i, \quad C' = \sum_{i}^{n} C_{ij}, \tag{25}$$

the Hamiltonian of Ni(OEP) is

$$H = A_{\mathrm{H}} C + A'_{\mathrm{HH}} C' + \lambda_{\mathrm{HH}} S' + \lambda'_{\mathrm{HH}} S''. \tag{26}$$

For Ni(OEP)-d_4, the index H is replaced by D in the case of C_m–H. The diagonalization of this Hamiltonian (which also has the same D_{4h} symmetry) automatically produces the states of the appropriate species.

We have used the algebraic Hamiltonian to study the highly excited vibrational levels of the molecules Ni(TPP) and Cu(TPP). Eight bands are studied, which can be labeled as C_m–H, C_b–C_b, and for Ni(OEP)-d_4, the bands labeled are C_m–D and C_b–C_b, respectively. The highly excited vibrational levels, calculated by using the algebraic Hamiltonian (25), are shown in Figs. 3–6. Figures 3 and 4 give the levels corresponding to C_m–H and C_b–C_b of Ni(TPP). Figures 5 and 6 give the levels corresponding to C_m–H and C_b–C_b of Cu(TPP). When the quantum number v increases in a fixed band, the number of energy levels increases rapidly. Usually, the degeneracy or quantidegeneracy of energy levels is called clustering. It may be seen from Figs. 3–6 that the vibrational energy levels of different metalloporphyrin and its substituted form make-up clusters.

The algebraic method allows one to also compute the intensities of infrared (IR) and Raman (R) transitions. We consider here explicitly the infrared transitions. The transition operator (dipole) is constructed from the bond operators

$$T = \sum_{i=1}^{n} \alpha_i t_i.$$

We model the matrix elements of the bond operators, t_i ,

$$\langle N_i, v_i | t_i | N_i, v_i \rangle = \mathrm{e}^{-\beta_i |v_i - v'_i|}.$$

Since by diagonalizing the Hamiltonian (2.11), we have already constructed the wave functions, we can calculate without further assumptions the infrared transitions. For in plane transitions and with the choice of axis in Fig. 1, we have two components of T, i.e., T_x and T_y. The intensity transitions are

$$R_{vv'} = |\langle v | T_x | v' \rangle|^2 + |\langle v | T_y | v' \rangle|^2.$$

For transitions from the lowest states $v' = 0$, the absorption intensities are given by

$$I_{vv'} = \nu_{vv'} R_{vv'},$$

where ν is the frequency of the absorbed radiation.

For nickel octaethyl porphyrin and its substituted forms, we have two types of bonds considered, C_m–H and C_m–D, characterized by the parameters. For both molecules, the transition operator has the symmetry and explicit form (for Ni(OEP))

$$\begin{aligned} T_x &= \alpha_{\mathrm{H}} \frac{\sqrt{3}}{2} (t_1 + t_2 - t_3 - t_4), \\ T_y &= \alpha_{\mathrm{H}} \frac{1}{2} (t_1 + t_4 - t_2 - t_3). \end{aligned}$$

For Ni(OEP)–d_4 molecule, α_{H} is replaced by α_{D} and β_{H} by β_{D}.

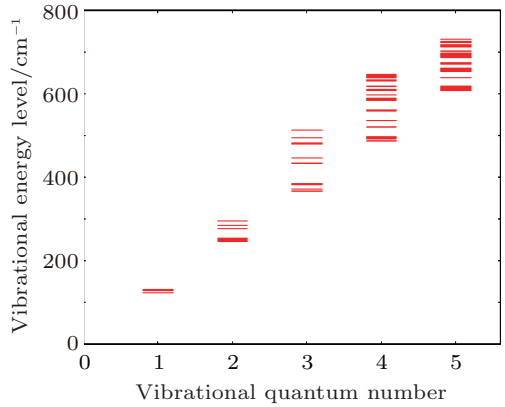


Fig. 3. (color online) C_m–H band vibrational energy level of Ni(TPP).

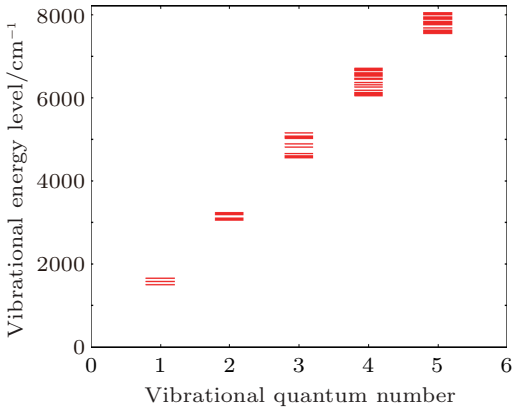


Fig. 4. (color online) C_b–C_b band vibrational energy level of Ni(TPP).

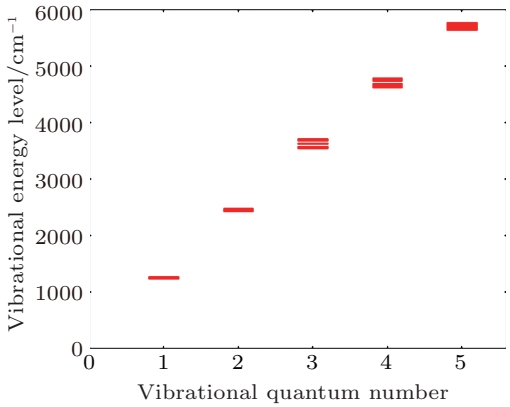


Fig. 5. (color online) C_m–H band vibrational energy level of Cu(TPP).

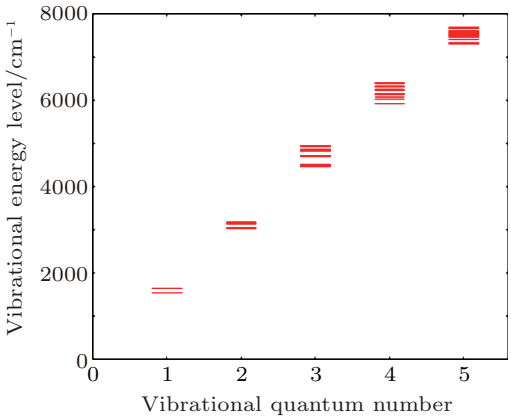


Fig. 6. (color online) C_b–C_b band vibrational energy level of Cu(TPP).

4. Conclusion

We have presented here a vibrational analysis of the stretching modes of eight forms of metalloporphyrin molecules in terms of the one-dimensional vibron model. The parameters of C_m–H, C_b–C_b, and C_m–D bonds have been determined by a fit to the known states of metalloporphyrins, while the interactions between different bonds have been estimated. The calculation provides a complete analysis of some of the stretching modes of metalloporphyrins (we have also calculate the remaining modes).

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

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