

Research Article

Spectroscopic Studies of Distorted Structure Systems in the Vibron Model: Application to Porphyrin and Its Isotopomers

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Received 7 July 2011; Accepted 13 August 2011

Academic Editor: Veronica Vaida

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We have introduced an algebraic technique to biomolecules (porphyrins) family to determine the vibrational spectra. We present an algebraic model of vibrations of polyatomic biomolecules, as an example, the vibrational analysis of stretching modes of nickel octaethylporphyrin (Ni(OEP)) and its isotopomers. The algebraic technique obtained the results are compared with experimental data; the results are showing good accuracy. Some reassignments of energy levels that predict location of energy states not yet observed.

1. Introduction

For the last few years, theoretical studies of highly excited vibrational states of polyatomic molecules have been one of the most interesting topics for theoreticians and experimentalists because of the development of new laser spectroscopic techniques. The measurements of highly-excited overtone-combination spectra of molecules have renewed in a theoretical description and understanding of the observed spectral properties. Two approaches have mostly been 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 paper, we begin a systematic analysis of overtone-combination spectra and intensities of molecules in terms of novel approach: (3) vibron model [1–4]. An algebraic model of boson realization is proposed to study the vibrational spectra of a tetrahedral molecule [5]. The analytical expression for the vibrational transition probability is obtained by using an algebraic approach [6]. We study the dynamical

entanglement of vibrations in small molecules by employing algebraic models [7]. 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. Potential energy surfaces also play an important role in studying theoretical chemistry. The expression of the potential energy surface containing information about the bending motion of triatomic molecules is derived by using the semiclassical limit of the algebraic Hamiltonian with the dynamical symmetry group $U_1(4) \otimes U_2(4)$ [8, 9]. In recent years, these polyatomic biomolecules (i.e., metalloporphyrins) have huge importance in the field of chemical physics. In case of polyatomic biomolecules the parameters play major role in the vibron model. The vibrational excitations of linear triatomic molecules, HCN, OCS, and bent triatomic molecules, that is, H₂O, including both bending/stretching vibrations, and tetra-atomic molecules HCCF, HCCD are studied in the framework of the $U(4)$ algebra [10–14]. We have also reported the vibrational bands of tetrahedral molecules CCl₄, SnBr₄ [15, 16] and polyatomic

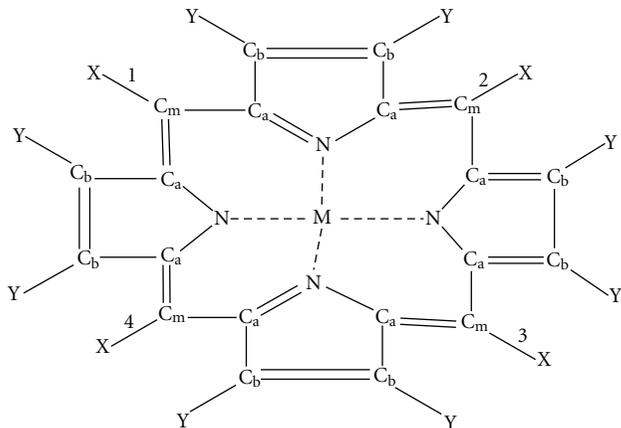
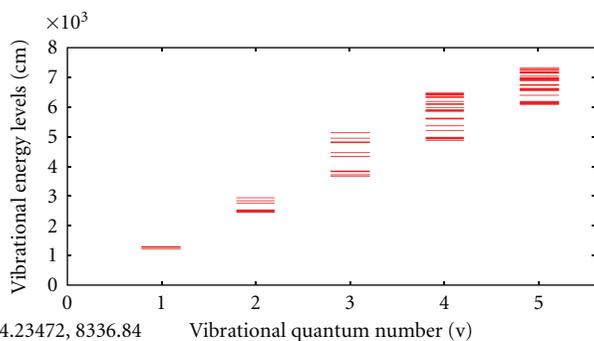


FIGURE 1: The structure of metalloporphyrins.

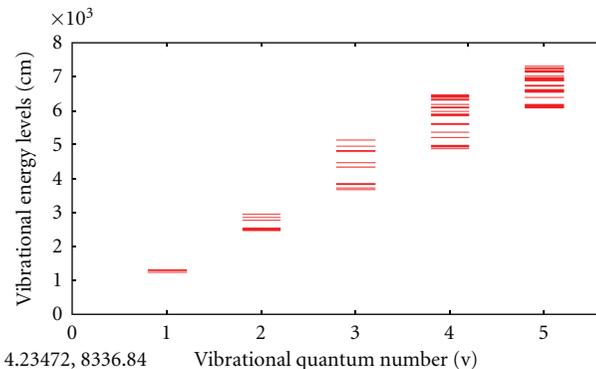
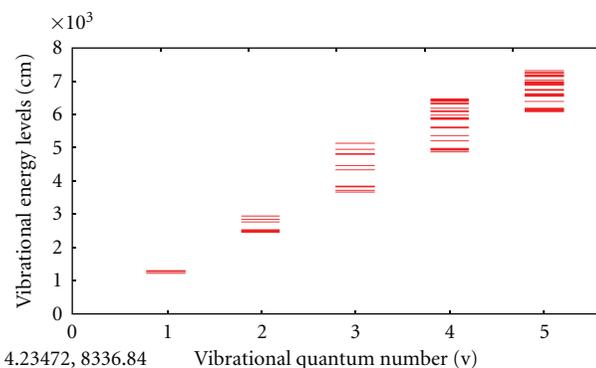
FIGURE 2: C_m -H band vibrational energy level of Ni (OEP)- ^{15}N .

biomolecules nickel octaethylporphyrin, nickel porphyrin molecules using $U(2)$ vibron model, respectively [17–23]. The advantage of the algebraic approach, as compared to that of 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 biomolecules that is, metalloporphyrins and their isotopomers. In Section 2, we briefly review the theory of vibron model of vibrations of polyatomic molecules. In Section 3, we describe the stretching vibrations 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 and applied to the study of triatomic and tetra-atomic [24–26] 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

FIGURE 3: C_m -H band vibrational energy level of Ni (OEP)-meso- d_4 .FIGURE 4: C_m -H band vibrational energy level of Ni (OEP)-meso- d_4 .

of the vibron model, which can be used for vibrational analysis of large molecules. This model, which we call the one-dimensional vibron model, starts from the observation of the eigenstates of a one-dimensional Schrodinger equation with a Morse potential,

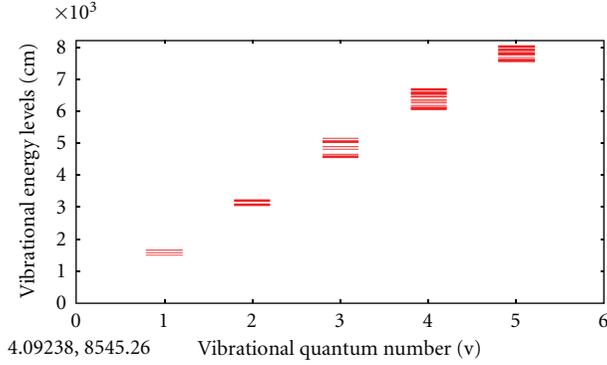
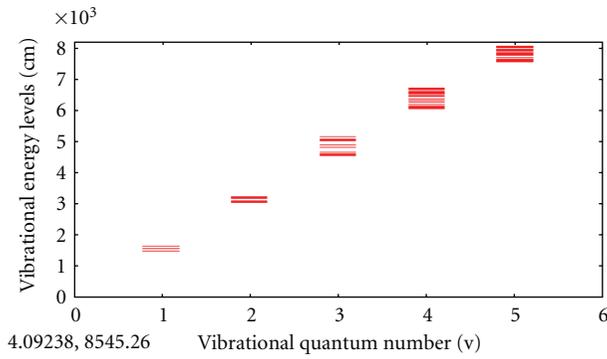
$$h(p, x) = \frac{p^2}{2\mu} + D[1 - \exp(-ax)]^2. \quad (1)$$

In the algebraic approach, 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

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i < j} A_{ij} C_{ij} + \sum_{i < j} \lambda_{ij} M_{ij}. \quad (2)$$

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

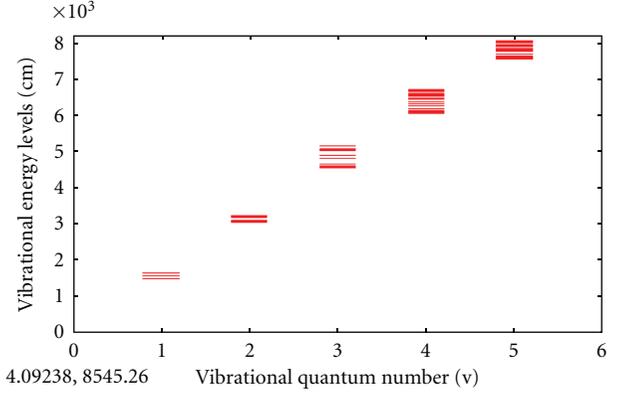
$$\begin{aligned} & \langle N_i, \nu_i; N_j, \nu_j | C_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\ & = 4 \left[(\nu_i + \nu_j)^2 - (\nu_i + \nu_j)(N_i + N_j) \right], \end{aligned} \quad (3)$$

FIGURE 5: C_m-H band vibrational energy level of Ni (OEP)-¹⁵N.FIGURE 6: C_m-H band vibrational energy level of Ni (OEP)-meso-d₄.

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

$$\begin{aligned}
 & \langle N_i, \nu_i; N_j, \nu_j | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\
 &= (N_i \nu_j + N_j \nu_i - 2 \nu_i \nu_j), \\
 & \langle N_i, \nu_i + 1; N_j, \nu_j - 1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\
 &= -[\nu_j(\nu_i + 1)(N_i - \nu_i)(N_j - \nu_j + 1)]^{1/2}, \\
 & \langle N_i, \nu_i - 1; N_j, \nu_j + 1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle \\
 &= -[\nu_i(\nu_j + 1)(N_i - \nu_i)(N_j - \nu_j + 1)]^{1/2}.
 \end{aligned} \tag{4}$$

The eigenvalues of (2) can be easily evaluated and provide a description of n coupled anharmonic vibrators. The couplings in (2) are only 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 versa). 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

FIGURE 7: C_m-H band vibrational energy level of Ni (OEP)-meso-d₄.

explicit formulas for couplings in which two quanta are annihilated and one is created, for example,

$$\langle N_i, \nu_i \pm 2; N_j, \nu_j \mp 1 | M_{ij}^{\dagger} | N_i, \nu_i; N_j, \nu_j \rangle, \tag{5}$$

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.

3. Results and Discussions

3.1. Sample Vibrational Analysis: Stretching Vibrations of Metalloporphyrins and Their Isotopomers. As an example of use of the algebraic method, we analyze the stretching vibrations of different metalloporphyrins. We number the bonds as shown in Figure 1. 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, the view of symmetry of the molecule, two possible types of couplings.

In the algebraic theory, we introduce the vibron number N which is directly related to the anharmonicity of the local C-H/C-C stretching bonds. The number N (total number of bosons, label of the irreducible representation of $U(4)$) is related to the total number of bound states supported by the potential well.

The vibron number can be calculated by the relation $N_i = (\omega_e/\omega_e x_e) - 1$ ($i = 1, 2, \dots$), where, ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules of stretching interaction of the molecule considered. Depending on the specific molecular structure N_i can vary between $\pm 20\%$ of the original value. The vibron numbers N between 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.

Secondly, the energy expression for the single oscillator in fundamental mode is

$$E(v = 1) = -4A(N - 1). \tag{6}$$

Lastly, in the third step, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the

TABLE 1: Comparison between the observed and calculated frequencies of the fundamental stretching vibrations.

Sym	Ni (OEP)- ¹⁵ N			Ni (OEP)-meso-d ₄			Ni (OEP)-methylene-d ₁₆		
	$E_{\text{obs}}^{(a)}$	E_{Calc}	Δ	$E_{\text{obs}}^{(a)}$	E_{Calc}	Δ	$E_{\text{obs}}^{(a)}$	E_{Calc}	Δ
C _m -H vibrational mode									
$A_{1g} (\nu_1)$	3041	3041.93	-0.93	2263	2258.49	4.51	3044	3042.03	1.97
$B_{2g} (\nu_{27})$	3041	3040.89	+0.11	2261	2265.38	-4.38	3041	3040.20	0.80
$E_{1u} (\nu_{36})$	3041	3040.01	0.99	2262	2262.30	-0.30	3041	3040.92	0.18
C _b -C _b vibrational mode									
$B_{1g} (\nu_2)$	1604	1604.04	-0.04	1598	1597.05	0.05	1597	1597.35	-0.35
$A_{1g} (\nu_{11})$	1578	1577.96	-0.04	1578	1580.50	-2.50	1567	1568.89	-1.89
$E_{1u} (\nu_{38})$	1588	1590.00	-2.00	1586	1587.97	-1.97	1579	1579.05	-0.05

^(a) Observed values taken from [27–29].

TABLE 2: Values^(b) of algebraic parameters used in the calculation of C_m-H, C_b-C_b stretching modes of porphyrins and their isotopomers.

	C _m -H vibrational mode			C _b -C _b vibrational mode		
	Ni (OEP)- ¹⁵ N	Ni (OEP)-meso-d ₄	Ni (OEP)-methylene-d ₁₆	Ni (OEP)- ¹⁵ N	Ni (OEP)-meso-d ₄	Ni (OEP)-methylene-d ₁₆
N	44	44	44	140	140	140
A	-17.6802	-17.6820	-17.614	-2.83	-2.835	-2.825
A'	-0.24	-0.25	-0.28	-1.223	-1.286	-0.452
λ	0.014	0.01136	0.009	0.086	0.068	0.067
λ'	0.011	0.012	0.5685	0.047	0.092	0.020

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

role of which is to degenerate the local modes. The value of these parameters can be calculated by considering the matrix structure of the molecules. By using a numerical fitting procedure (in a least square sense), one can adjust the values of the parameters N , A , A' , λ , λ' , and A' (whose initial value can be taken as zero) to fit the experimental results. The complete calculation data in stretching and bending modes of porphyrin and its isotopomer molecules are presented in Table 1, and the corresponding algebraic parameters are presented in Table 2.

One can thus describe all stretching vibrations of Ni (OEP)-¹⁵N, Ni (OEP)-meso-d₄, Ni (OEP)-methylene-d₁₆ in terms of five parameters (N , A , A' , λ , λ'). We have used in these tables Wilson numbering for the species of stretching vibrations. It would be very interesting to see whether or not our calculations predict states at the correct. We have explicit calculations up to the fourth overtone (energy up to ≈ 15000 cm⁻¹).

We have used the algebraic Hamiltonian to study the highly excited vibrational levels of the moleculeless Ni (OEP)-¹⁵N, Ni (OEP)-meso-d₄, and Ni (OEP)-methylene-d₁₆. The highly excited vibrational levels, calculated by using the algebraic Hamiltonian (2), are shown Figures 2, 3, 4, 5, 6, and 7. When the quantum number ν 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 in Figures 2, 3, 4, 5, and 6, that the vibrational energy levels of porphyrins and their isotopomers make up clusters at excited states.

4. Conclusions

We have presented here a vibrational analysis of the stretching modes of porphyrin and its isotopomers in terms of one-dimensional vibron model. The parameters of C_m-H, C_b-C_b bonds have been determined by a fit to the known states of metalloporphyrins, while the interactions between different have been estimated. The calculation provides complete analysis of some of the stretching modes of metalloporphyrins (we have the calculation also for 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 few parameters. In turn it provides a way to make assignments of unknown levels or to check assignments of known levels.

Acknowledgments

The author Dr. S. R. Karumuri would like to thank Professor Thomson G Spiro and Professor Stefano Oss for providing the necessary literature for this study. The author Srinivasa Rao Karumuri also would like to thank the Department of Science and Technology, New Delhi, India, for providing the financial assistance for this study.

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