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ANALYSIS OF VIBRATIONAL SPECTRA OF COPPER OCTAETHYL PORPHYRIN [CU (OEP)] BY USING U (2) ALGEBRAIC TECHNIQUE

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Abstract
The most interesting area of current research in Molecular physics is the study of the vibrational excited states of medium and large molecules using Lie algebra. The fundamental stretching vibrational energy levels of Copper Octaethyl Porphyrin [Cu (OEP)] for 28 vibrational bands are calculated by using *U*(2) algebraic technique. The model Hamiltonian so constructed appears to describe the vibrational energy levels accurately.
Keywords: Lie algebra, Vibrational spectra, Copper Octaethyl Porphyrin [Cu (OEP)]

I. INTRODUCTION

The algebraic methods have been found to be very much useful in the study of vibrational spectra of medium and large molecules using Lie algebra, especially after the development of quantum mechanics in the first part of 20th century. The interesting area of current research in molecular physics is to interpret the experimental data with the help of theoretical models. Two traditional approaches like Dunham like expansion of energy levels in terms of rotation-vibration quantum number and the solution of Schrödinger equation with potentials have been used so far in the analysis of experimental data. The new theoretical concept- Vibron model (based on Lie algebra) to study molecular spectra built in the last part of the 20th century [1, 2]. This new model seems to offer a concrete and complementary technique to the traditional approaches used in molecular spectroscopy. The algebraic model (Vibron model) originally developed for diatomic and tri-atomic molecules [3, 4]. *U*(4) and *U*(2) algebraic model been used so far in the analysis of experimental data. It is to be pointed out that the *U*(4) model becomes complicated when the number of atoms in a molecule increases more than four. The Vibron model has been applied successfully in describing the overtone frequencies of linear and bent X_2Y molecules [5]. Later, it extended to linear and quasi-linear tetratomic molecules [6] and could prove itself to be a competitive one to the traditional analysis. The main features and basic applications of these methods have been described by Iachello and Levine and Oss [7]. The brief review of the research work done in this field up to 2000 and its perspectives in the first part of 21st century has been presented by Iachello and Oss [8]. Lie algebraic approach was found to be successful in our study of vibrational frequencies of HCN, HCP, HCCF, HCCD [9], tetrahedral [10], octahedral [11] and Nickel Metallo-porphyrins [12]. The stretching vibrations of some polyatomic molecules like Octahedral, benzene, pyrrole, n-paraffin molecules, n-alkane molecules and polyethylene have been described using U(2) algebra. There is a renewed interest to study the vibrational excitations of Metalloporphyrins due to its importance not only in human life but also in scientific research.

In this paper, the vibrational frequencies of Copper Octaethyl Porphyrin for 28 stretching bands and their

locality parameter (ξ) are calculated by using U(2) algebraic mode Hamiltonian.

II. THEORY: AN ALGEBRAIC APPROACH

In constructing this model, we use the isomorphism of the Lie algebra of U(2) with that of the one-dimensional Morse oscillator[7].The eigen states of the one-dimensional Schrodinger equation, $h\psi = \epsilon\psi$, with a Morse potential

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

can be put into one to one correspondence with the representations of U(2) ⊃ O(2), characterized by the quantum numbers $|N, m\rangle$, with the provision that one takes only the positive branch of m, i.e. m = N, N-2, ……,1 or 0 for N= odd or even (N = integer). The Morse Hamiltonian (1) corresponds in the U (2) basis to a simple Hamiltonian, $h = \epsilon_0 + AC$, where C is the invariant operator of O (2), with eigen values (m^2-N^2).The eigen values of h are

$\epsilon = \epsilon_0 + A\,(m^2-N^2)$, (2)

m=N,N-2,……,1or 0 (N=integer).

Introducing the vibrational quantum number $\nu = (N-m)/2$, Eq (2) can be rewritten as

$\epsilon = \epsilon_0 - 4A\,(N\nu - \nu^2)$, (3)

ν = 0, 1,……,N/2 or N-1/2 (N = even or odd).

The values of ϵ_0, A, and N are given in terms of μ, D, and α by $\epsilon_0 = -D$, $-4AN = \hbar\alpha\,(2D/\mu)^{1/2}$, $4A = -\hbar^2\alpha^2/2\mu$. One can immediately verify that these are the eigen values of the Morse oscillator.

Now consider a molecule with n bonds. In the algebraic model [13], each bond i is replaced by an algebra (here $U_i(2)$), with Hamiltonian $h_i = \epsilon_{0i} + A_i C_i$, where C_i is the invariant operator of O_i (2) with eigen values $-4(N_i\nu_i - \nu_i^2)$. The bonds interact with a bond-bond interaction. Two types of interaction are usually considered [13], which we denote by C_{ij} and M_{ij}, are called Casimir and Majorana interactions respectively.

The algebraic model Hamiltonian we consider is thus

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij} \quad (4)$$

In the equation (4), C_i is an invariant operator with eigen values $4(\nu_i^2 - N_i\nu_i)$ and the operator C_{ij} is diagonal with matrix elements.

$$\langle N_i, \nu_i; N_j, \nu_j | C_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = 4[(\nu_i+\nu_j)^2 - (\nu_i+\nu_j)(N_i+N_j)] \quad (5)$$

while the operator M_{ij} has both diagonal and non-diagonal matrix element

$$\langle N_i, \nu_i; N_j, \nu_j | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = (N_i\nu_j + N_j\nu_i - 2\nu_i\nu_j)$$

$$\langle N_i, \nu_i+1; N_j, \nu_j -1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = -[\nu_j(\nu_i+1)(N_i-\nu_i)(N_j-\nu_j+1)]^{1/2}$$

$$\langle N_i, \nu_i -1; N_j, \nu_j +1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = -[\nu_i(\nu_j+1)(N_j-\nu_j)(N_i-\nu_i+1)]^{1/2} \quad (6)$$

Equation (6) is a generalization of the two-bond model of Ref. [7] to n bonds.

As an example of use of the algebraic method we analyze the stretching vibrations of different Metallo-porphyrins. 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 charact-erized by parameter A_{ij}. For the Majo-rana part we can have, the view of symmetry of the molecule, two possible types of couplings:

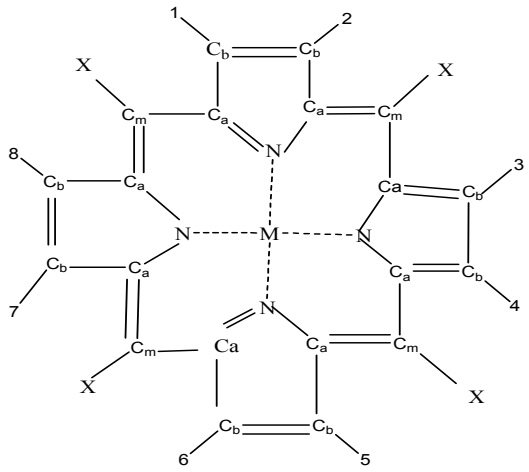

Figure 1. Structure of Metalloporphyrins

Different Porphyrins are obtained by specific substitution at X or 1 to 8 positions. Here in Cu (OEP) all X positions are C and 1to 8 positions are H (M-metal= Cu)

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

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

The symmetry-adapted operators of Metalloporphyrins with symmetry D_{4h} are those corresponding to these two couplings, that is,

$$S' = \sum_{i<j}^{n} c'_{ij} M_{ij}, \qquad S'' = \sum_{i<j}^{n} c''_{ij} M_{ij}, \quad (7)$$

With

$c'_{12}=c'_{23}=c'_{34}=c'_{45}= - - - - - =1,$

$c'_{13}=c'_{24}=c'_{35}=c'_{46}= - - - - - =0,$

$c''_{12}=c''_{23}=c''_{34}=c''_{45}= - - - - - =0,$

$c''_{13}=c''_{24}=c''_{35}=c''_{46}= - - - - - =1.$

The total Majorana operator S is the sum

$$S = S' + S'' \quad (8)$$

Diagonalization of S produces states that carry representations of S, the group of permutations of objects, while diagonalization of the other operators produces states that transform according to the representations A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1u} of D_{4h}.

Local to normal transition: The locality parameter (ξ)

The local-to-normal transition is governed by the dimensionless locality parameter (ξ). The local-to-normal transition can be studied [7] for polyatomic molecules, for which the Hamiltonian is

$H = H^{local} + \lambda_{12}M_{12}$

$= A_iC_i + A_{ij}C_{ij} + \lambda_{ij}M_{ij}$ (9)

For these molecules, the locality parameters [7] are

$\xi i = (2/\pi)\tan^{-1}[8\lambda_{ij}/(A_i+A_{ij})]$, (10)

i, j = 1, 2, 3, ------ corresponding to the two bonds. A global locality parameter for XYZ molecules can be defined as the geometric mean [7]

$$\xi=(|\xi_1\xi_2|)^{1/2} \qquad (11)$$

III. RESULTS & DISCUSSIONS

A comparison of the experimental and calculated frequencies of stretching vibrations of Copper Octaethyl Porphyrin using algebraic model are shown in table 1 respectively. Using established norms [7] the Vibron number N and other algebraic parameters A, A´, λ, λ´ are shown in table.2 for Cu (OEP).

Experimental data
References [15] provides the necessary experimental data for this study

Vibron number
The vibron number N [total number of bosons, label of the irreducible representation of U (2)] 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 parameters xe by means of

$$xe = 1/(N + 2) \qquad (12)$$

Equation (12) can be re-written as

$$N = (\omega e/\omega exe) - 2, \qquad (13)$$

ωe → spectroscopic constant.
Using the values of ωe and ωexe for the different diatomic bonds [14], from Eq. (12) we can have the value of N. Here from the figure 1, noticed that some of the bonds are equivalent. It may be noted here that during the calculation of the vibrational frequencies of Copper Octaethyl Porphyrin, the value of N is kept fixed and not used as free parameter.

Values of the fitting parameters
The fitting parameters A, A´, λ, λ´, N which are used in this study for the vibrational frequencies of Copper Octaethyl Porphyrin [Cu(OEP)] for 28 stretching vibrational bands are given in the following table 2.

Analysis of the Vibrational spectra

From the view of group theory, the molecule of Cu (OEP) takes a square planar structure with the D_{4h} symmetry point group. For the fundamental stretches of Metalloporphyrins, Cu (OEP), with D_{4h} symmetry, the symmetry species are A_{1g}, B_{1g}, A_{2g}, B_{2g}, and E_{1u}.The four identical stretching C_m-C oscillators describe the fundamental vibrational modes are given by A_{1g} (ν_1), B_{2g} (ν_{27}), E_u (ν_{36}) irreps, the eight identical stretching C_a-C_m oscillators describe the fundamental vibrational modes are given by A_{1g} (ν_3), B_{1g} (ν_{10}), A_{2g} (ν_{19}), B_{2g} (ν_{28}), E_u (ν_{37}), E_u (ν_{39}) irreps, the eight identical stretching C_b-H oscillators describe the fundamental vibrational modes are given by A_{1g} (ν_5), B_{1g} (ν_{14}), A_{2g} (ν_{23}), B_{2g} (ν_{31}), E_u (ν_{43}), E_u (ν_{45}) irreps, Locality parameters of this metallo-porphyrins is given in the results and discussions.With this definition, due to Child and Halonen [19], local-mode molecules are near to the ξ = 0 limit, normal mode molecules have ξ →1.
four identical stretching C_b-C_b oscillators describe the fundamental vibrational modes are given by A_{1g} (ν_2), B_{2g} (ν_{11}), E_u (ν_{38}) irreps and four identical Pyr half ring oscillators describe the fundamental vibrational modes are given by A_{1g} (ν_4), B_{1g} (ν_{12}), A_{2g} (ν_{22}), B_{2g} (ν_{30}) irreps. Here A_{1g} represents the symmetry irreps while B_{2g} represent antisymmetric irreps with respect to C_2 perpendicular to the principle axis, and E_u represents two dimensional antisymmetric irreps with respect to centre of inversion.

The locality parameter (ξ)
The locality parameter (ξ) for the 28 vibrational bands of Copper Octaethyl Porphyrin is 0.00341. Which shows the locality parameter (ξ) of Cu (OEP) is more close to the ξ=0 limit.

TABLE 1
Comparison between Experimental and Calculated frequencies of fundamental stretching vibrations of Copper Octaethyl Porphyrin [Cu (OEP)] (cm^{-1})

Block	Wilson Numbering	Species	$\upsilon^{(a)}_{exp}$ (cm^{-1})	υ_{Cal}(cm^{-1})	Δ(Exp-Cal) (cm^{-1})
C_m – C Stretch	ν_1	A_{1g}	-------	1236.8893	-------
	ν_{27}	B_{2g}	-------	1246.3943	-------
	ν_{36}	E_u	-------	1256.7254	-------
C_a-C_m Stretch	ν_3	A_{1g}	1503	1503.7694	-0.7694
	ν_{10}	B_{1g}	1637	1642.3432	-5.3432
	ν_{19}	A_{2g}	---------	1479.3932	---------
	ν_{28}	B_{2g}	---------	1475.9802	---------
	ν_{37}	E_u	---------	1482.7967	---------
	ν_{39}	E_u	---------	1471.1701	---------
C_b-H Stretch	ν_5	A_{1g}	1136	1135.7654	0.2346
	ν_{14}	B_{1g}	----------	1112.4687	---------
	ν_{23}	A_{2g}	----------	1177.1054	---------
	ν_{31}	B_{2g}	----------	1222.8056	---------
	ν_{43}	E_u	----------	1268.5132	---------
	ν_{45}	E_u	----------	1287.4508	---------
C_b-C_b Stretch	ν_2	A_{1g}	1592	1587.5509	4.4491
	ν_{11}	B_{1g}	1568	1568.2934	-0.2934
	ν_{38}	E_u	---------	1639.7732	-------
Pyr half ring	ν_4	A_{1g}	1378	1379.5509	-1.5509
	ν_{12}	B_{1g}	--------	1256.9387	---------
	ν_{22}	A_{2g}	--------	1189.0580	---------
	ν_{30}	B_{2g}	1160	1164.0384	-4.0384

(a) Experimental data from Ref [**15**]

TABLE 2
Values of the algebraic parameters used in the calculation of Cu (OEP)

Algebraic parameters	C_m – C	C_b – H		C_a – C_m	C_b – Cb	Pyr half ring			
N		140		44		140	140		140
A		-2.2173	-6.3023	-2.6258		-2.8825	-2.3863		
A´	-1.0182	-2.3841	-2.456		-1.223	-1.0923			
λ		0.0369		0.746		0.586	0.2581		0.0832
λ ´	0.1073		0.068		0.049		0.0981	0.1934	

All parameters are in cm^{-1}except N which is dimensionless.

IV. CONCLUSION

In this paper, we presented systematic analysis of the Vibrational spectral study of Copper Octaethyl Porphyrin in the algebraic framework making use of the one-dimensional Vibron model i.e. U (2) Vibron model. In this study, we reported the **RMS** deviation (i.e Δ (r.m.s)) and also the locality parameter (ξ) for Copper Octaethyl Porphyrin for 28 vibrational bands

In this study, we reported the vibrations of Copper Octaethyl Porphyrin are good accuracy with experimental data.

In the study of the vibrational spectra of Copper Octaethyl Porphyrin for 28 vibrational bands (table 1), we obtain the Δ (r.m.s) as 5.2839 cm^{-1} and the locality parameter (ξ) = 0.00341.

The locality parameter (ξ) of these Copper Octaethyl Porphyrin molecules are confirming the highly local behavior. Therefore, here the Hamiltonian is obviously the local mode Hamiltonian.
Hence, it may conclude that the algebraic local Hamiltonian gives good fit to the Copper Octaethyl Porphyrin. Therefore, the higher excited states and combinational bands of Copper Metalloporphyrins would be calculated using the algebraic local mode Hamiltonian with sufficient experimental data. The study of vibrational excitations of Metalloporphyrins has numerous importances not only in human life but also in scientific research.

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