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An $U(2)$ algebraic model to study the vibrational spectra of Nano molecules: An application to Fullerenes C_{60} and C_{70}

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ABSTRACT

Algebraic techniques are examined as a computational tool for the analysis and interpretation of experimental rovibrational spectral of small and medium-sized molecules. These techniques are based on the idea of dynamical symmetry, which in turn, is expressed through the language of unitary Lie algebras. Within this framework, any specific mechanism relevant for the correct characterization of the molecular dynamics and spectroscopy can accounted. Here every C-C bond of the molecule is replaced by a corresponding Lie algebra and finally the Hamiltonian is constructed considering the interacting Casimir and Majorana operators. The fundamental vibrational energy levels of the carbon C_{60} and C_{70} clusters are then calculated using this Hamiltonian to fit the experimental results.

Keywords: Lie algebra, vibrational spectra, C_{60} , C_{70} .

INTRODUCTION

Nanoscience is an interdisciplinary field that seeks to bring about nature nanotechnology. Focusing on the nanoscale intersection of fields such as Physics, Biology, Engineering, Chemistry, Computer Sciences and more, Nanoscience is rapidly expanding. The vibrational spectra of fullerenes have attracted a considerable attention as a probe of structural and dynamic properties of these carbon clusters and of their solid-state properties [1]. However, a complete assignment of the normal modes poses considerable problems particularly because the high symmetry of the clusters makes many normal modes inactive in the infrared and Raman spectra. Since the discovery of fullerenes in carbon soot, many spectroscopic techniques have been utilized to identify the cage-like carbon structures. These identification techniques include infrared spectroscopy (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS), ultraviolet-visible spectroscopy (UV-VIS), or a combination of these techniques [2-8]. To analyse these experimental data, there are many theoretical approaches for calculation of vibrational frequencies, which belong to quantum mechanical potential approach and Dunham expansion method [9-10].

Recently Lie algebraic model introduction [11-13] could proved itself to be a successful model in the study of vibrational spectra of small, medium size and polyatomic molecules [14]. The algebraic model is fully based on the dynamical symmetry and through the language of Lie algebra. For the triatomic, tetratomic, Tetrahedral and polyatomic Bio- molecules (i.e metalloporphyrins, Ni (OEP), Ni (TTP), Ni Porphyrin) we studied earlier [15-17] using algebraic model. Using the algebraic model in this study we have calculated the vibrational frequencies of fullerenes C60 & C70 for vibrational bands each using U (2) algebraic model Hamiltonian. In our study we used four fitting parameters which provide better comparisons between the experimental and theoretical calculations throughout the study.

II. ALGEBRAIC FRAMEWORK

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

$$G \equiv U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes \dots \quad (1)$$

For each oscillator i , states are characterized by representations of

$$\left| \begin{array}{cc} U_i(2) \supset O_i(2) \\ \downarrow \qquad \downarrow \\ N_i \qquad m_i \end{array} \right\rangle \quad (2)$$

We address here the explicit problem of the construction of the vibrational Hamiltonian operator for the fullerene molecule. 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

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i \neq j}^n A_{ij} C_{ij} + \sum_{i \neq j}^n \lambda_{ij} M_{ij} \quad (3)$$

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, $\sum_{i \neq j}^n A_{ij} C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms

of the operators C_{ij} . The third one, $\sum_{i \neq j}^n \lambda_{ij} M_{ij}$, 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

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

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.

II.1 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 (3). The Poschl-Teller Hamiltonian

$$H(p_s, s) = p_s^2 / 2\mu - D / \cosh^2(\alpha s) \tag{5}$$

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

$$H_i = \varepsilon_{0i} + A_i C_i, \tag{6}$$

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

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i (N_i \nu_i - \nu_i^2). \tag{7}$$

One can then proceed to couple the oscillators as done previously and repeat the same treatment.

II.2 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

$$S = \sum_{i < j}^n M_{ij} \tag{8}$$

is divided into subsets reflecting the symmetry of the molecule

$$S = S' + S'' + \dots \quad (9)$$

The operators S' , S'' , \dots are the symmetry-adapted operators.

II.3 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 [18] for polyatomic molecules, for which the Hamiltonian is

$$H = H^{\text{local}} + \lambda_{12}M_{12} = A_i C_i + A_{ij} C_{ij} + \lambda_{ij} M_{ij} \quad (10)$$

For these molecules, the locality parameters are

$$\xi_i = (2/\pi) \tan^{-1}[8\lambda_{ij}/(A_i + A_{ij})], \quad i, j = 1, 2, 3, \dots \quad (11)$$

corresponding to the two bonds. A global locality parameter for XYZ molecules can be defined as the geometric mean [18]

$$\xi = (\xi_1 \xi_2)^{1/2} \quad (12)$$

Locality parameters of this metalloporphyrins is given in the results and discussions

With this definition, due to Child and Halonen [18], local-mode molecules are near to the $\xi = 0$ limit, normal mode molecules have $\xi \rightarrow 1$.

RESULTS AND DISCUSSION

In the algebraic theory, we introduce the vibron number N which is directly related to the anharmonicity of the local 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. Equivalently it can be put in a one-to-one correspondence with the anharmonicity parameters x_e by means of

$$x_e = \frac{1}{N + 2} \quad (13)$$

We can rewrite the Equation (13) as

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad (i = 1, 2, \dots) \quad (14)$$

where, ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules of stretching interaction of the molecule considered [19]. Depending on the specific molecular structure N_i can vary between $\pm 20\%$ of the original value. The vibron number N between the diatomic molecules C-C is 140. 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.

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

$$E(v=1) = -4A (N-1) \quad (15)$$

Lastly, in the third step one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the 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 , 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 fullerene C_{60} & C_{70} molecules are presented in Table 1 & 2 and the corresponding algebraic parameters are presented in Table 3.

Table1. Comparisons between the experimental and Calculated fundamental vibrational frequencies of C_{60} & C_{70} (Cm^{-1})

<u>C_{60} molecule</u>				
Symmetry	Normal level	Exp ^(a)	Cal	$\Delta(\text{exp-Cal})$
A_{1g}	v_1	487	485.9303	-1.0697
	v_2	1473	1472.2039	0.7961
T_{1g}	v_3	561	562.3943	-1.3943
	v_4	824	826.3922	-2.3922
	v_5	1277	1277.2034	-0.2034
T_{2g}	v_6	555	550.2039	4.7961
	v_7	723	728.3049	-5.3049
	v_8	789	788.0293	0.9707
	v_9	1345	1346.3049	-1.3049
G_{1g}	v_{10}	480	484.3092	-4.3092
	v_{11}	565	564.8372	0.1628
	v_{12}	741	741.2345	-0.2345
	v_{13}	1073	1076.6573	-3.6573
	v_{14}	1309	1310.7748	-1.7748
	v_{15}	1507	1510.6253	-3.6253
H_g	v_{16}	261	266.3948	-5.3948
	v_{17}	429	430.8272	-1.8272
	v_{18}	705	704.2812	0.7188
	v_{19}	772	776.0893	-4.0893
	v_{20}	1105	1109.2034	-4.2034
	v_{21}	1251	1260.6592	-9.6592
	v_{22}	1426	1427.0983	-1.0983
A_u	v_{23}	1585	1587.2039	-2.2039
	v_{24}	947	948.3892	-1.3892
T_{1u}	v_{25}	527	528.2039	-1.2039
	v_{26}	577	577.9403	-0.9403
	v_{27}	1190	1191.2389	-1.2389
T_{2u}	v_{28}	1431	1432.2930	-1.2930
	v_{29}	336	339.4857	-3.4857
	v_{30}	709	708.3849	0.6151
	v_{31}	958	948.3049	9.6951
	v_{32}	1177	1182.2784	-5.2784
	v_{33}	1535	1536.2038	-1.2038

G _u	V ₃₄	351	352.3042	-1.3042
	V ₃₅	737	737.3048	-0.3048
	V ₃₆	751	751.2030	-0.2030
	V ₃₇	1308	1310.2933	-2.2933
	V ₃₈	1435	1438.2039	-3.2039
H _u	V ₃₉	400	399.9483	0.0517
	V ₄₀	530	535.4948	-5.4948
	V ₄₁	666	668.3049	-2.3049
	V ₄₂	728	732.2039	-4.2039
	V ₄₃	1220	1220.2039	-0.2039
	V ₄₄	1434	1437.3948	-3.3948
	V ₄₅	1576	1579.2039	-3.2039

 $\Delta(\text{r.m.s}) = 78.0888 \text{ cm}^{-1}$

Symmetry	Normal level	<u>C₇₀ molecules</u>		$\Delta(\text{exp-Calc})$	
		Exp ^(a)	Cal		
A ₁	V ₁	428	431.9302	-3.9302	
	V ₂	1472	1471.2735	0.7265	
A ₂	V ₃	629	630.3940	-1.3940	
	V ₄	936	940.3048	-4.3048	
	V ₅	1215	1210.2934	4.7066	
E ₁	V ₆	533	533.4758	-0.4758	
	V ₇	722	723.6785	-1.6785	
	V ₈	767	767.0920	-0.0920	
E ₂	V ₉	1350	1352.7839	-2.7839	
	V ₁₀	479	480.4637	-1.4637	
	V ₁₁	675	675.0493	-0.0493	
	V ₁₂	735	736.4072	-1.4072	
	V ₁₃	1055	1050.8373	4.1627	
	V ₁₄	1313	1313.7652	0.7652	
	V ₁₅	1516	1514.5869	1.4131	
	V ₁₆	245	245.7820	-0.7820	
	V ₁₇	408	410.2875	-2.2875	
	V ₁₈	714	715.8309	-1.8309	
A ₂ ''	V ₁₉	1169	1167.0392	1.9608	
	V ₂₀	1226	1226.5768	-0.5768	
	V ₂₁	1257	1260.6592	-3.6592	
	V ₂₂	1433	1429.0983	3.9170	
	V ₂₃	1574	1575.2039	-1.2039	
	A ₁ ''	V ₂₄	892	892.3049	-0.3049
		V ₂₅	507	504.5068	2.4932
	E ₁ ''	V ₂₆	573	577.3049	-4.3049
		V ₂₇	1177	1181.6099	-4.6099
		V ₂₈	1432	1432.2930	-0.2930
V ₂₉		438	439.3049	-1.3049	
V ₃₀		564	565.4054	-1.4054	
V ₃₁		1143	1145.5748	-2.5748	
V ₃₂		1463	1465.4950	-2.4950	
V ₃₃		318	316.2039	1.7961	
V ₃₄		704	706.9857	-2.9857	
V ₃₅		896	900.6574	-4.6574	
V ₃₆		1206	1210.0398	-6.0398	
V ₃₇		1568	1570.3049	-2.3049	

E _{v2}	V ₃₈	1577	1580.7812	-3.7812
	V ₃₉	304	309.7856	-5.7856
	V ₄₀	701	705.8517	-4.8517
	V ₄₁	920	923.7869	-3.7869
	V ₄₂	1156	1160.6530	-4.6530
	V ₄₃	1517	1520.6652	-3.6652
	V ₄₄	383	384.7854	-1.7854
	V ₄₅	728	728.6755	-0.6755
				----- Δ(r.m.s) = 68.2436 cm ⁻¹

^(a) Experimental data has taken from the reference[20]

The fitting parameters used in the study of vibrational spectra of fullerene C₆₀ & C₇₀ is given in Table 2.

Table 2

	<u>Vibron number</u>	<u>Algebraic parameters</u>		
	N	A	λ	λ
C ₆₀	140	-1.2039	0.0739	-0.4932
C ₇₀	140	0.8493	0.0348	0.5903

All values in cm⁻¹ except N, which is dimensionless.

CONCLUSION

We have presented here a vibrational analysis of the stretching/bending modes of Bio molecules (i.e Nickel Porphyrins) and Nano molecules (Fullerenes C₆₀, C₇₀) in terms of one-dimensional Vibron model i.e U(2) algebraic model. The Nano-molecules C₆₀ and C₇₀ are I_h and D_{5h} point group symmetry respectively.

In this study the vibrational frequencies of Nano molecules C₆₀ and C₇₀ for 7 vibrational bands, we obtain the RMS deviation i.e Δ(r.m.s) = 78.0888 cm⁻¹, 68.243cm⁻¹, and the locality parameters are ξ₁ = 0.0124, ξ₂= 0.0097 respectively.

Using improved set of algebraic parameters, the RMS deviation we reported in this study for Bio and Nano molecule is lying near about the experimental accuracy. Using only four algebraic parameters, the RMS deviation we reported in this study for Nano molecule are better fit.

The above two points confirm that in four parameters fit, the set of algebraic parameters we reported in this study of local to normal transition provide the best fit to the spectra of Nano molecules.

We hope that this work will be stimulate further research in analysis of vibrational spectra of other Nano molecules like fullerenes and protein molecules where the algebraic approach has not been applied so far. The research work concern is in progress in case of complex Nano systems.

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