# A Comparative Study of Vibrational Spectra of Fullerene C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub> and C<sub>84</sub> using U(2) Lie Algebra

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The vibrational energy levels of spheroidal carbon cluster  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$  and  $C_{84}$  are calculated considering the local Hamiltonian of Morse potential using U(2) algebra. Here, each 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 stretching modes of vibration of fullerenes  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$  and  $C_{84}$  are then calculated using this Hamiltonian to fit the results of semi empirical PM3 molecular modelling technique for  $C_{60}$ ,  $C_{80}$ , density functional theory (DFT) for  $C_{70}$  and semi empirical QCFF/PI program for  $C_{84}$ .

## 1. Introduction

The algebraic model [1,2] attracted a wider scientific community in recent years for the interpretation of experimental analysis and rotational-vibrational spectra of small and mediumsized molecules. The model is based on the idea of dynamical symmetry, which is expressed through the language of Lie algebras. Applying algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rotationalvibrational degrees of freedom of the physical system. This frame work can account any specific mechanism relevant for the correct characterization of the molecular dynamics and spectroscopy. The proposed algebraic models are formulated such that they contain the same physical information for both ab initio theories (based on the solution of the Schrödinger equation) and semi empirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). It should be noted here that the algebraic approaches to complex spectra have already been proven useful in other fields of physics.

It has been proved that the algebraic models are successful models in the study of the vibrational spectra of small and medium-sized molecules. Some small and large molecules can be studied by using the U(4) and U(2) algebraic models. But, the U(4) model becomes complicated when the number of atoms in a molecule increases more than four. On the other hand, the U(2) model introduced by Wulfman and Levine [3] is found to be successful explaining the stretching vibrations of in polyatomic molecules such as tetrahedral, Icosahedral, benzene-like octahedral, and molecules. The brief review and the research work done with the algebraic models up to the year 2000 and its outlook and perception in the first decade of the 21<sup>st</sup> century was presented by Iachello and Oss [4]. Recently, it is found that Lie algebraic method [5, 6] is extremely successful and accurate in vibrational frequencies calculating the of polyatomic molecules compare to the other methods such as Dunham expansion and potential approach method reported earlier [4]. So far no extensive experimental study of the vibrational spectra of C<sub>80</sub> and C<sub>84</sub> is reported, but only the quantum mechanical approach of PM3 (Parametric Method 3) method for C<sub>80</sub> and semi empirical QCFF/PI program [13] for C<sub>84</sub> have come forward to analyze the vibrational spectra of fullerenes  $C_{80}$ [7] and  $C_{84}$  [13] with its different energy bands. However, there are sufficient experimental studies of vibrational spectra of fullerenes  $C_{60}$  [7, 14],  $C_{70}$ [12]. By using the one-dimensional U(2) algebraic model, in this study we have calculated the stretching vibrational energies of fullerenes  $C_{60}$ ,  $C_{70}$ , C<sub>80</sub> and C<sub>84</sub>, which is an excellent alternative mathematical treatment for determination of energy bands of fullerenes C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub> and C<sub>84</sub> and make the comparison in spectroscopic point of view.

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### 2. The Algebraic Theory

It is necessary to begin with a brief review of the theory of the algebraic model. Recently, the algebraic method has been introduced as a computational tool for the analysis and interpretation of experimental rotational-vibrational spectra of large and medium-size molecules .This method has been used extensively in chemical physics and molecular physics. This method is based on the idea of dynamic symmetry, which, in turn, is expressed through the language of Lie algebras. By applying Lie algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rotational-vibrational degrees of freedom of the physical system [8]. The algebraic methods are formulated in such a way that they contain the same physical information of both ab initio theories (based on the solution of the Schrödinger equation) and of semi empirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). However, by employing the powerful method of group theory, the results can be obtained in a more rapid and straightforward way [9]. In Lie algebraic approaches, U(4) and U(2) algebraic models have been extensively used. The U(4)model deals with the rotation and the vibration simultaneously, but it becomes quite complicated when the number of atoms in a molecule are more than four. The U(2) model has been particularly successful in explaining stretching vibrations of polyatomic molecules such as benzene-like and Octahedral, Icosahedral molecules. Thus, here we use the U(2) algebraic model to study the vibrational energy level of fullerenes C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub> and  $C_{84}$  .

To introduce the U(2) algebraic model, we use the isomorphism of the Lie algebra of U(2) with that of the one-dimensional Morse oscillator. The eigenstates of the one-dimensional Schrödinger equation, with a Morse potential

$$h(p.x) = p_2 / 2\mu + D[1 - \exp(-\alpha x)]^2$$
(1)

which can be put into one to one correspondence with the representations of  $U(2) \supset O(2)$ , characterized by 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 in Eqn.1 corresponds in the U(2) basis to a simple Hamiltonian,  $h = \overline{C}_0 + AC$ , where *C* is the invariant operator. The eigenvalues of *h* are  $\overline{C} = \overline{C}_0 + A(m^2 - N^2)$ , where

$$m = N, N - 2, \dots 1 \text{ or } 0 \quad (N = \text{Integer})$$
 (2)

Introducing the vibrational quantum number, v = (N - m)/2, Eqn.2 can be rewritten as,

$$\overline{C} = \overline{C}_0 - 4A(Nv - v^2, \text{ where, } v = 0, 1, \dots N/2 \text{ or}$$

$$\frac{N-1}{2} \text{ (where } N = \text{even or odd)}$$
(3)

The value of  $C_0$ , A and N are given in terms of  $\mu$ , D and  $\alpha$ , respectively, by using the following relations

$$C_0 = -D, \quad -4AN = h\alpha(2D/\mu)^{1/2},$$
  
 $4A = -h^2\alpha^2/2\mu$ 

One can verify that these are the eigenvalues of the Morse oscillator.

For a Icosahedral molecule like  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$ and  $C_{84}$ , we introduce nU(2) Lie algebra to describe *n* stretching bonds (C-C). The two possible chains [10] of molecular dynamical groups in Icosahedral molecule are

$$U_1(2) \otimes \dots \otimes U_n(2) \supset O_1(2) \otimes \dots \otimes O_n(2) \supset O(2)$$
$$U_1(2) \otimes \dots \otimes U_n(2) \supset U(2) \supset O(2)$$

which correspond to local and normal coupling, respectively. The coupling to final O(2) group in the first chain is carried out through different intermediate couplings  $O_{ij}(2)$  and the second chain arises from all the possible couplings of  $U_i(2)$ groups to obtain a total U(2) group, which in turn contains the final O(2) group. For these two situations, the Hamiltonian operator can be diagonalized analytically. The common algebraic model Hamiltonian, in the case of stretching for Icosahedral molecules, can be considered as [5]

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

In Eqn. 4,  $C_i$  is an invariant operator with eigenvalues  $4(v_i^2 - N_1v_i)$  and the operator  $C_{ij}$  is diagonal with matrix elements.

$$\langle N_{i}, v_{i}; N_{j}, v_{j} | C_{ij} | N_{i}, v_{i}; N_{j}, v_{j} \rangle = 4[(v_{i} + v_{j})^{2} - (v_{i} + v_{j})(N_{i} + N_{j})]$$
 (5)

While, the operator  $M_{ij}$  has both diagonal and nondiagonal matrix element

$$\langle N_{i}, v_{i}; N_{j}, v_{j} | M_{ij} | N_{i}, v_{i}; N_{j}, v_{j} \rangle = \langle N_{i}v_{j} + N_{j}v_{i} - 2v_{i}v_{j} \rangle$$

$$\langle N_{i}, v_{i} + 1; N_{j}, v_{j} - 1 | M_{ij} | N_{i}, v_{i}; N_{j}, v_{j} \rangle = -[v_{j}(v_{i} + 1)(N_{i} - v_{i})(N_{j} - v_{j} + 1)]^{1/2}$$

$$\langle N_{i}, v_{i} - 1; N_{j} + 1 | M_{ij} | N_{i}, v_{i}; N_{j}, v_{j} \rangle = -[v_{i}(v_{j} + 1)(N_{j} - v_{j})(N_{i} - v_{i} + 1)]^{1/2}$$

$$(6)$$

Eqn. 6 is a generalization of the two-bond model to n bonds [9], where i take values from 1 to n for the calculation of stretching vibrational energy level. The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain, where below each group we have used quantum numbers characterizing the eigenvalues of the corresponding invariant operator. N is the number of bosons related to stretching physical modes. The quantum numbers  $v_i$  correspond to the number of quanta in each oscillator, while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i \tag{7}$$

For a particular polyad, the total vibrational quantum number is always conserved. The inclusion of  $M_{ij}$  in the local Hamiltonian operator cannot affect the conservation rule. In Eqn. 5,  $C_i$  is an invariant operator of uncoupled bond with eigenvalues  $4(v_i^2 - N_i v_i)$  and the operator  $C_{ij}$  for coupled bonds are diagonal with matrix elements.

### 3. Result and Discussion

In this work, we use four algebraic parameters i.e.,  $A, A', \lambda, \lambda'$ , and the vibron number N to study the vibrational spectra of the C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub> and C<sub>84</sub> molecules.

The value of N (vibron number) can be determined by the relation

$$N = \frac{\omega_e}{\omega_e x_e} - 1 \tag{8}$$

Where,  $\omega_e$  and  $\omega_e x_e$  are the spectroscopic constants [11] of stretching interaction of the molecules considered. This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such

an estimate, however, which should not be larger than  $\pm 20\%$  of the original value Eqn.8. It may be noted that during the calculation of the vibrational frequencies of fullerenes C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub> and C<sub>84</sub>, the value of *N* is kept fixed and not used as free parameter.

To obtain a starting guess for the parameter A, we use the expression for the single-oscillator fundamental mode, which is given as

$$E(\nu = 1) = -4A(N - 1) \tag{9}$$

Using Eqn. 9,  $\overline{A}$  can be obtained as

$$\overline{A} = \frac{\overline{E}}{4(1-N)} \tag{10}$$

To obtain an initial guess for the parameter,  $\lambda$ , whose role is to split the initially degenerate local modes, we consider the following relations:

$$\lambda = \frac{\left|E_1 - E_2\right|}{2N} \tag{11}$$

and

$$\lambda' = \frac{\left|E_1 - E_2\right|}{6N} \tag{12}$$

To have better results, a numerical fitting procedure (in a least-square sense) is required to obtain the parameters,  $A, A', \lambda$ , and  $\lambda'$ , starting from the values as given by Eqns. 10-12. Initial guess for A' may be taken as zero.

The fitting parameters along with the simulated and calculated energies of fullerenes  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$ , and  $C_{84}$  are given in Tables 1-8.

Vibron number	Stretching parameters		
Ν	Α	λ	λ'
140	-1.468	0.3285	-0.0404

# Table 1: Fitting parameters<sup>\*</sup> of fullerene $C_{60}$

\*  $A, \lambda, \lambda'$  all are in cm<sup>-1</sup> whereas N is dimensionless

Normal level	I Ref.[7]	<i>II</i> This Study	$\Delta(I-II)$	Percentage of deviation $\frac{\Delta  I - II }{I} \times 100\%$
v <sub>1</sub>	816.34	816.84	-0.50	0.061%
<i>V</i> <sub>2</sub>	850.21	850.77	-0.56	0.065%
V <sub>3</sub>	908.84	908.83	0.01	0.001%
$v_4$	912.56	913.24	-0.68	0.074%
V <sub>5</sub>	940.96	941.76	-0.80	0.085%
V <sub>6</sub>	1124.37	1121.30	3.07	0.273%
V <sub>7</sub>	1245.80	1247.22	-1.42	0.113%
$v_8$	1290.04	1285.58	4.46	0.345%
$v_9$	1337.55	1334.78	2.77	0.207%

Table 2: Simulated and calculated energies  $(cm^{-1})$  of fullerene  $C_{60}$ 

 $\Delta(rms) = 2.125 \text{ cm}^{-1}$ 

Tabl	e 3:	Fitting	parameters	of	fullerene	C <sub>70</sub>
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Vibron number	Stretching parameters			
Ν	Α	λ	λ'	
140	-0.570	0.875	-0.167	

 $A, \lambda, \lambda'$  all are in cm<sup>-1</sup> whereas N is dimensionless

Normal level	<i>I</i> Ref.[12]	<i>II</i> This Study	$\Delta (I - II)$	Percentage of deviation $\frac{\Delta  I - II }{\Delta X} \times 100\%$
V,	318.00	317.10	0.90	0.283%
<i>v</i> <sub>2</sub>	458.80	457.38	1.42	0.309%
v <sub>3</sub>	563.90	562.10	1.80	0.319%
$\mathcal{V}_4$	703.80	700.32	3.48	0.494%
V <sub>5</sub>	895.80	907.90	-12.10	1.350%
V <sub>6</sub>	1142.90	1156.82	-13.92	1.217%
V 7	1205.60	1190.42	15.18	1.259%
V 8	1320.80	1331.6	-10.80	0.817%
$V_9$	1462.40	1469.02	-6.62	0.452%

Table 4: Simulated and calculated energies  $(cm^{-1})$  of fullerene  $C_{70}$ 

 $\Delta(rms) = 9.124 \text{ cm}^{-1}$ 

Table 5: Fitting	parameters*	of fullerene	$C_{so}$

Vibron number	Stretching parameters		
Ν	Α	λ	$\lambda'$
140	-2.197	0.3428	-0.0808

\*  $A, \lambda, \lambda'$  all are in cm<sup>-1</sup> whereas N is dimensionless

Table 6: Simulated and calculated energies  $(cm^{-1})$  of fullerene  $C_{80}$ 

Normal level	I Ref.[7]	<i>II</i> This Study	$\Delta (I - II)$	Percentage of deviation $\frac{\Delta  I - II }{I} \times 100\%$
$v_1$	1222.54	1222.00	0.54	0.044%
V 2	1294.61	1289.87	4.74	0.366%
V <sub>3</sub>	1319.49	1317.98	1.51	0.114%
$v_4$	1352.29	1346.09	6.20	0.458%
V <sub>5</sub>	1382.42	1374.20	8.22	0.594%
V <sub>6</sub>	1421.10	1430.42	- 9.32	0.655%
V 7	1457.36	1458.53	- 1.17	0.080%
V <sub>8</sub>	1494.73	1486.64	8.09	0.541%
$\mathcal{V}_9$	1516.96	1514.75	2.21	0.145%

 $<sup>\</sup>Delta(rms) = 5.672 \text{ cm}^{-1}$ 

Vibron number	Stretching parameters		
Ν	Α	λ	$\lambda'$
140	-0.624	0.678	-0.159

Table 7: Fitting parameters<sup>\*</sup> of fullerene  $C_{84}$ 

 $^{\circ}A, \lambda, \lambda'$  all are in cm<sup>-1</sup> whereas N is dimensionless

Normal level	<i>I</i> Ref.[13]	<i>II</i> This Study	$\Delta(I-II)$	Percentage of deviation $\frac{\Delta  I - II }{I} \times 100\%$
$v_1$	346	347.00	-1.00	0.289%
v <sub>2</sub>	480	480.56	-0.56	0.116%
v <sub>3</sub>	536	536.84	-0.84	0.156%
$v_{4}$	722	719.96	2.04	0.282%
v <sub>5</sub>	826	818.24	7.76	0.939%
v <sub>6</sub>	896	888.80	7.20	0.803%
<i>v</i> <sub>7</sub>	1060	1064.36	-4.36	0.411%
v <sub>8</sub>	1328	1331.48	-3.48	0.262%
v <sub>9</sub>	1445	1444.04	0.96	0.066%

Table 8: Simulated and calculated energies (cm<sup>-1</sup>) of fullerene  $C_{84}$ 

 $\Delta(rms) = 4.086 \, {\rm cm}^{-1}$ 

#### 4. Conclusion

The algebraic model presented here is a model of coupled one dimensional Morse oscillators describing the C-C stretching vibrations of the molecule C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub>, and C<sub>84</sub>. By making use of this algebraic model, one can avoid the complicated integrations in the solution of coupled differential Schrödinger equations. For the C-C stretching inter-bond interactions, this model can be used in a simple and straightforward way and reliable calculation of the stretching bonds can be explained in terms of the above fitting parameters. In this paper, we presented only a few modes of vibrations of C<sub>60</sub>, C<sub>70</sub>, C<sub>80</sub>, and C<sub>84</sub>, which are in good agreement with the results of computer simulated semi empirical PM3 molecular modelling technique [7], DFT [12] and QCFF/PI program [13].

It is hoped that with further advancement of U(2) model, the higher order modes of vibrations

of  $C_{60}$ ,  $C_{70}$ ,  $C_{80}$ , and  $C_{84}$  also can be explained with good accuracy considering the bent vibrations of the molecules along with the stretch vibrations.

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