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## **$U(2)$ LIE ALGEBRAIC STUDY OF VIBRATIONAL SPECTRA OF FULLERENE $C_{80}$ AND ITS EPOXIDE $C_{80}-O$**

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Using the Lie algebraic method, the stretching vibrational energies of fullerene  $C_{80}$  & its epoxide  $C_{80}-O$  are calculated in the one-dimensional  $U(2)$  framework. By constructing the model Hamiltonian with the help of Casimir and Majorana invariant operators in this framework, we calculated the local mode vibrational energy levels of fullerene  $C_{80}$  &  $C_{80}-O$ .

### 1. Introduction

In the theoretical, as well as experimental, background, the study of excited vibrational states of polyatomic molecules has been one of the most interesting advanced topics in the field of molecular spectra due to the development and the introduction of new laser techniques in the recent past. In 1979, the introduction of the algebraic approach to molecular spectra by Levine and Wulfman fetched a revolutionary change in the theoretical field (the algebraic approach to a Morse oscillator) to study the vibrational states of molecules [1]. Two years later, in 1981, a new theoretical concept known as the Vibron model (based on  $U(4)$  Lie algebra) to study the molecular spectra was introduced by Iachello [2]. This new model seems to offer a specific complementary technique to the traditional approaches used in molecular spectroscopy. The Vibron model was originally developed for diatomic and triatomic molecules [3], and, thus,  $U(4)$  Lie algebra can be used to calculate the stretching

and vibrational excitations of polyatomic molecules. But  $U(4)$  model becomes complicated, when the number of atoms in a molecule increases more than four. On the other hand,  $U(2)$  model introduced in [1] is found to be successful in explaining the stretching vibrations of polyatomic molecules such as tetrahedral, octahedral, and benzene-like 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-st century was presented by Iachello and Oss [4]. Recently, it was found that the Lie algebraic method [5, 6] was extremely successful and accurate in calculating the vibrational frequencies of polyatomic molecules compare to the other methods such as Dunham expansion and potential approach method reported earlier [4].

After the introduction of Lie algebras at the end of the nineteenth century by S. Lie, they become much more familiar and popularized in the recent past in the field of physics. Such Lie algebra is the unitary algebra  $U(n+1)$ . Hence, one can formulate quantum mechanics in  $n$  dimensions in terms of the unitary algebra  $U(n+1)$ .

Till date, no extensive experimental study of the vibrational spectra of  $C_{80}$  &  $C_{80}-O$  are reported, but is the only quantum mechanical approach of PM3 method (Parametric Method 3) which comes forward to analyze the vibrational spectra of fullerenes  $C_{80}$  &  $C_{80}-O$  with their different energy bands [7, 13]. By using the one-dimensional  $U(2)$  algebraic model, which is an excel-

lent alternative mathematical treatment for the determination of the energy bands of fullerenes  $C_{80}$  &  $C_{80-O}$  from the spectroscopic point of view, we will calculate the stretching vibrational energies of fullerenes  $C_{80}$  &  $C_{80-O}$ .

## 2. Review of the Theory

It is necessary to begin with a brief review of the theory of the algebraic model. Recently, an algebraic method has been introduced as a computational tool for the analysis and the interpretation of experimental ro-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 dynamical symmetry, which, in turn, is expressed through the language of Lie algebras.

In connection with molecular spectroscopy, dynamical symmetries explored in this work constitute a big step forward over a conventional use of symmetry arguments, especially those concerning the description and the classification of energy spectra denoting specific degeneracy patterns. The dynamical symmetries contain, within themselves, both the degeneracy aspects of a physical system and the complete machinery for describing the transitions among different states. All these tasks can be solved in the extremely compact and convenient framework of Lie groups and Lie algebras. The use of dynamical symmetry, a very powerful technique related to the dynamical group leads to a conveniently simple form of the second-quantized Hamiltonian operator.

Thus, we obtain an effective Hamiltonian operator by applying Lie algebraic techniques that conveniently describes the ro-vibrational degrees of freedom of a 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 semiempirical 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 was particularly successful in explaining the stretching vibrations of polyatomic molecules such as benzene-like and octahedral molecules. Here, we use the

$U(2)$  algebraic model to study the higher excited vibrations of fullerenes  $C_{80}$  &  $C_{80-O}$ .

For introducing the  $U(2)$  algebraic model, we use the isomorphism of the Lie algebra of  $U(2)$  with that of the one-dimensional Morse oscillator [9].

The eigenstates of the one-dimensional Schrodinger equation with a Morse potential are

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

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

The eigenvalues of  $h$  are

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

where  $m = N, N - 2, \dots, 1$  or  $0$  ( $N = \text{Integer}$ ), and  $A$  is the normalization constant. Introducing the vibrational quantum number  $\nu = (N - m)/2$ , Eq. (1) can be written as

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

where  $\nu = 0, 1, \dots, N/2$ , or  $(N - 1)/2$  (where  $N = \text{odd}$  or even). The value of  $\epsilon_0$ ,  $A$  and  $N$  are given in terms of  $\mu$ ,  $D$ , and  $\alpha$  by using the relations

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

where  $D$  is the dissociation energy and  $\mu$  is the reduced mass. Now, one can verify that these are the eigenvalues of the Morse oscillator.

Now consider a molecule with  $n$  bonds. In the algebraic model, each bond  $i$  is replaced by an algebra with the Hamiltonian  $h_i = \epsilon_{0i} + A_i C_i$ , where  $C_i$  is the invariant operator with eigenvalues  $-4(N_i\nu_i - \nu_i^2)$ . The bonds interact through a bond-bond interaction. Two types of interaction are usually considered in terms of two operators  $C_{ij}$  and  $M_{ij}$ , called invariant or Casimir and Majorana operators, respectively, where the Casimir operator has only the diagonal matrix element, whereas the Majorana operators have both diagonal and non-diagonal matrix elements [Eq. (5) & Eq. (6)].

Thus, the algebraic model Hamiltonian we consider has the following form [5]:

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

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

$$\begin{aligned} \langle N_i, \nu_i; N_j, \nu_j | C_{ij} | N_i, \nu_i; N_j, \nu_j \rangle &= 4[(\nu_i + \nu_j)^2 - \\ &- (\nu_i + \nu_j)(N_i + N_j)] - \left(\frac{N_i + N_j}{N_i}\right) 4[\nu_i^2 - \nu_i N_i] - \\ &- \left(\frac{N_i + N_j}{N_j}\right) 4[\nu_j^2 - \nu_j N_j], \end{aligned} \quad (5)$$

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

$$\langle N_i, \nu_i; N_j, \nu_j | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle =$$

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

Equation (6) is a generalization of the two-bond model to  $n$  bonds [9]. The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain [10]

$$\begin{array}{ccccccc} U^{(1)}(2) \otimes U^{(2)}(2) \otimes U^{(3)}(2) \supset SO^{(1)}(2) \otimes SO^{(2)}(2) \otimes SO^{(3)}(2) \supset SO(2) \\ \downarrow \quad \quad \downarrow \\ | [N_1], \quad [N_2], \quad [N_3]; \quad \nu_1, \quad \nu_2, \quad \nu_3; \quad V \rangle, \end{array}$$

where, below each group, we have indicated the eigenvalues that label their irreducible representations.

The quantum numbers  $\nu_i$  correspond to the number of quanta in each oscillator while  $V$  is the total vibrational quantum number given by

$$V = \sum_{i=1}^n \nu_i. \quad (7)$$

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 Eq. (4),  $C_i$  is an invariant operator of an uncoupled bond with eigenvalues  $-4(N_i\nu_i - \nu_i^2)$ , and the operators  $C_{ij}$  for coupled bonds are diagonal with matrix elements [Eq. (5) and Eq. (6)].

### 3. Results and Discussion

In this work, we use the algebraic parameters  $A, A', \lambda, \lambda'$ , and  $N$  (the vibron number) to study the vibrational spectra of the  $C_{80}$  &  $C_{80}-O$  molecules. After considering the common coupled and uncoupled bond-bond interaction in the molecular configuration in the case of  $C_{80}$  &  $C_{80}-O$  and considering the Majorana couplings of the

molecules, the number of algebraic parameters is reduced to four.

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

$$N_i = \frac{\omega_e}{\omega_e \chi_e} - 1, \quad (i = 1, 2, \dots), \quad (8)$$

where  $\omega_e$  and  $\omega_e \chi_e$  are the spectroscopic constants [11] of polyatomic molecules (e.g.,  $C_{80}$  &  $C_{80}-O$ ) of the stretching interaction of a molecule considered and represented as

$$x_e = \frac{1}{N + 1} \quad \text{and} \quad \omega_e = -4A(N + 1).$$

This numerical value must be seen as an initial guess [12]; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than  $\pm 20\%$  of the original value [Eq. (8)]. It may be noted that, during the calculation of the vibrational frequencies of fullerenes  $C_{80}$  &  $C_{80}-O$ , the value of  $N$  is kept fixed and not used as a 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

$$E(\nu = 1) = -4A(N - 1). \quad (9)$$

Using Eq. (9),  $\bar{A}$  can be obtained as

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

where  $\bar{A}$  and  $\bar{E}$  are the average values of the algebraic parameters  $A$  and  $E$ .

$$\left( \begin{array}{cc} -4A(N-1) - 4A'(2N-1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) + \lambda N \end{array} \right).$$

We easily find that

$$\lambda = \frac{|E_3 - E_1|}{2N} \tag{11}$$

and

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

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 given by Eq. (10), Eq. (11) and Eq. (12). The initial guess for  $A'$  may be taken as zero.

The fitting parameters used in the study of the vibrational spectra of fullerene  $C_{80}$ -O are given in Table 1.

The fitting parameters used in the study of vibrational spectra of fullerene  $C_{80}$  are given in Table 3.

**Table 1. Fitting parameters\* of fullerene  $C_{80}$ -O**

Vibron number	Stretching parameters			
	$N$	$A$	$\lambda$	$\lambda'$
140		-1.640	0.49	0.07

\* $A, \lambda, \lambda'$  all are in  $\text{cm}^{-1}$ , whereas  $N$  is dimensionless

**Table 2. Experimental and calculated energies ( $\text{cm}^{-1}$ ) of fullerene  $C_{80}$ -O**

Normal level	I	II	$\Delta(\text{I-II})$	Percentage of error $\frac{ \text{I-II} }{\text{I}} \times 100\%$
	Ref. [13]	Calculated		
$\nu_1$	911.19	912.20	-1.01	0.110%
$\nu_2$	969.49	971.00	-1.51	0.155%
$\nu_3$	1048.32	1049.40	-1.08	0.103%
$\nu_4$	1165.79	1167.00	-1.21	0.103%
$\nu_5$	1205.06	1206.20	-1.14	0.094%
$\nu_6$	1266.00	1265.00	+1.00	0.078%
$\nu_7$	1300.17	1304.20	-4.03	0.309%
$\nu_8$	1338.21	1343.40	-5.19	0.387%

$\Delta(\text{rms}) = 2.534 \text{ cm}^{-1}$

To obtain the initial guess for  $\lambda$ , whose role is to split the initially degenerate local modes, placed here at the common value  $\bar{E}$  used in Eq. (10), we consider the following simple Hamiltonian matrix structure:

#### 4. Conclusion

The algebraic model presented here is a model of coupled one-dimensional Morse oscillators describing the C-C stretching vibrations of the molecules  $C_{80}$  &  $C_{80}$ -O. By using this algebraic model, one can avoid the complicated integrations by solving the coupled differential Schrodinger equations. For the C-C stretching inter-bond interactions, this model can be used in a simple straightforward way, and the 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  $C_{80}$  &  $C_{80}$ -O, which are in good agreement with the results of the computer-simulated semiempirical PM3 molecular modeling technique [13]. It is hoped that, with the further advancement of the  $U(2)$  model, the higher order modes of

**Table 3. Fitting parameters\* of fullerene  $C_{80}$**

Vibron number	Stretching parameters			
	$N$	$A$	$\lambda$	$\lambda'$
140		-2.181	0.3428	0.0708

\* $A, \lambda, \lambda'$  all are in  $\text{cm}^{-1}$ , whereas  $N$  is dimensionless

**Table 4. Simulated and calculated energies ( $\text{cm}^{-1}$ ) of fullerene  $C_{80}$**

Normal level	I	II	$\Delta(\text{I-II})$	Percentage of error $\frac{ \text{I-II} }{\text{I}} \times 100\%$
	Ref. [13]	Calculated		
$\nu_1$	1214.91	1213.10	+1.81	0.148%
$\nu_2$	1271.06	1272.57	-1.51	0.001%
$\nu_3$	1310.77	1309.08	+1.69	0.128%
$\nu_4$	1343.83	1345.31	-1.48	0.110%
$\nu_5$	1379.20	1382.11	-2.91	0.210%
$\nu_6$	1416.69	1418.61	-1.92	0.135%
$\nu_7$	1450.31	1455.12	-4.81	0.331%
$\nu_8$	1483.70	1491.63	-7.93	0.534%

$\Delta(\text{rms}) = 3.687 \text{ cm}^{-1}$

vibrations of  $C_{80}$  &  $C_{80}-O$  also can be explained with good accuracy considering the bending vibrations of the molecules along with stretching vibrations.

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ДОСЛІДЖЕННЯ КОЛИВАЛЬНИХ СПЕКТРІВ ФУЛЕРЕНУ  $C_{80}$  І ЙОГО ОКИСУ  $C_{80}-O$  НА ОСНОВІ  $U(2)$  АЛГЕБРИ ЛІ

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Резюме

На основі алгебраїчного методу Лі в рамках одновимірної алгебри  $U(2)$  розраховані енергії коливань зв'язків фулерену  $C_{80}$  і його окису  $C_{80}-O$ . З модельним гамільтоніаном, який включає інваріантні оператори Казимира і Майорана, знайдено рівні енергії локальних коливальних мод.