

A Study of Vibrational Spectra of Fullerene C₇₀ and C₈₀: An Algebraic Approach

R. SEN^{a,*}, A. KALYAN^a, R. SUBHRA PAUL^b, N.K. SARKAR^b AND R. BHATTACHARJEE^c

^aDepartment of Physics, Srikishan Sarda College, Hailakandi-788151, India

^bDepartment of Physics, Karimganj College, Karimganj-788710, India

^cDepartment of Physics, Assam University, Silchar-788011, India

(Received February 10, 2011; in final form April 7, 2011)

Using the Lie algebraic method, the stretching vibrational energies of fullerenes C₇₀ and C₈₀ 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 frame work, we calculated the local mode vibrational energy levels of the fullerenes C₇₀ and C₈₀.

PACS: 03.65.Fd, 07.57.-c, 02.20.Sv, 78.30.Na

1. Introduction

The study of excited vibrational states of polyatomic molecules have been one of the most interesting and advanced topics in the field of molecular spectra in the theoretical as well as experimental background in recent past due to the development and introduction of new laser techniques. In 1979 the introduction of algebraic approach to the molecular spectra by Wulfman fetched a revolutionary change in the theoretical field (the algebraic approach to the Morse oscillator) to study the vibrational states of the molecules [1]. Two years later, in 1981, a new theoretical concept, known as 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 concrete and 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 by Wulfman and Levine [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 21st 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 compared to the other methods such as the Dunham expansion and potential approach method reported earlier [4].

After introduction of the Lie algebra at the end of the nineteenth century by Lie, only in recent past, it is much more familiar and popularized in the field of physics. This 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($n + 1$). In this work, we concentrate on the Lie algebraic techniques to C₇₀ and C₈₀. This Lie algebraic model does not take into account rotational motions. Nonetheless, it can be used to obtain a complete picture of the vibrational behavior of complex situations, falling even beyond the possibilities of a three-dimensional approach. We will see how this simple model can account for anharmonic couplings between local modes (both stretching and nondegenerate bending vibrations), anharmonic (Fermi) resonances, symmetry adaption of wave functions, and some other important aspects of molecular spectroscopy.

Both the molecules C₇₀ and C₈₀, considered in this theoretical work have the same symmetry (D_{5h}). The symmetry is an extremely important concept in the development of scientific knowledge. The beauty of symmetry rests in its connection to a possible invariance in a physical system. Such invariance leads directly to conserved quantities, which in a quantum mechanical framework allow one to observe specific degeneracies in the energy spectrum and to introduce a meaningful labeling scheme for the corresponding eigenstates.

* corresponding author; e-mail: rupamsen@ssccollege.net.in

Till date, no extensive experimental study of the vibrational spectra of C_{80} is reported, but is the only quantum mechanical approach of parametric method 3 (PM3) which comes forward to analyze the study of vibrational spectra of fullerene C_{80} with its different energy bands [7, 8], whereas there are sufficient experimental study of vibrational spectra of fullerene C_{70} [9]. By using the one-dimensional $U(2)$ algebraic model we calculate the stretching vibrational energies of fullerene C_{70} and C_{80} which is an excellent alternative mathematical treatment for determination of energy bands of fullerenes C_{70} and C_{80} in spectroscopic point of view.

The advantage of the algebraic models, as compared to that of the Dunham models is that typically the models need fewer parameters to obtain the same level of accuracy. The algebraic models also provide a simultaneous description of bending and stretching modes. Finally the models produce not only energies but also wave functions (similar to that of the potential approach) and hence they can be used to compute other observables. The algebraic models are particularly useful for large molecules where a few number of parameters plays a major role. Our purpose here is to show that the model can be brought to spectroscopy accuracy. Further, the species studied in this work is interesting due to its importance not only in human life but also in scientific research.

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 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 the 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 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 transitions among different states. All these tasks can be carried out in the extremely compact and convenient framework of the Lie groups and the 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. The most important steps leading to the formulation of a dynamical symmetry have been presented. This formulation should be thought as a very effective, specialized version of the usual second quantized realization of a quantum problem. In such a realization (1) the wave equation is replaced by an algebraic equation, (2) the wave functions are replaced with a Fock space, and (3) the most

general algebraic expansion, in terms of (boson) creation-annihilation operators, is restricted to invariant or the Casimir operators of sub-algebras of the dynamical algebra. Such "ultimate" algebraic structure turns out to be, for n -dimensional problems, the Lie algebra $U(n+1)$. These three steps constitute the basic components for the definition of the dynamical symmetry realization of the Hamiltonian operator.

Thus we obtain an effective Hamiltonian operator by applying Lie algebraic techniques that conveniently describes the ro-vibrational degrees of freedom of the physical system [10]. 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 [11]. In the 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 stretching vibrations of polyatomic molecules such as benzene-like and octahedral and icosahedral molecules. Thus, here we use the $U(2)$ algebraic model to study the higher excited vibrations of fullerene C_{70} and C_{80} .

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. The most appealing feature of the Morse potential is that one can solve the associated Schrödinger equation in an exact way for one-dimensional problems or in a quasi-exact way for two or three-dimensional problems, the error often being smaller than 1 part in 10^8 – 10^{10} (for zero angular momentum). Such an approximation comes from the fact that analytical solutions can be achieved only under the constraint that $V(r) \rightarrow \infty$ for $r \rightarrow 0$. Such a condition is only approximately fulfilled by the Morse potential [10].

The eigenstates of the one-dimensional Schrödinger equation, $h\psi = \varepsilon\psi$ with a Morse potential [12]:

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

which 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, $h = \varepsilon_0 + AC$, where C is the invariant operator of $O(2)$ with eigenvalues $m^2 - N^2$.

The eigenvalues of h are

$$\varepsilon = \varepsilon_0 + A(m^2 - N^2), \quad (2)$$

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. (2) can be rewritten as

$$\varepsilon = \varepsilon_0 - 4A(N\nu - \nu^2),$$

where

$$\nu = 0, 1, \dots, N/2$$

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

The value of ε_0 , A and N are given in terms of μ , D , and α by using the following relations:

$$\varepsilon_0 = -D, \quad -4AN = h\alpha(2D/\mu)^{1/2},$$

$$4A = -h^2\alpha^2/2\mu.$$

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

Now consider a molecule with n bonds. In the algebraic model, each bond i is replaced by an algebra with Hamiltonian $h_i = \varepsilon_{0i} + A_i C_i$ [13] where C_i is the invariant operator with eigenvalues $-4(N_i\nu_i - \nu_i^2)$. The bonds interact with a bond-bond interaction. Two types of interaction are usually considered in term of two operators C_{ij} and M_{ij} , called the Casimir and Majorana operators, respectively, where the Casimir operator has only the diagonal matrix element, whereas the Majorana operators have both diagonal and off-diagonal matrix elements. They are invariant operators of the combined algebras $O_{ij}(2)$ and $U_{ij}(2)$ in the group lattice. Their physical meaning can be seen from the matrix elements given by Eq. (5) and Eq. (6).

The algebraic model Hamiltonian we consider thus has the following form [5]:

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

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

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

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

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

Equation (6) is a generalization of the two-bond model to n bonds [11].

The role of the Majorana operators M_{ij} is to introduce off-diagonal couplings between pairs of local modes. In the simplest case of equivalent interacting bonds, the Majorana operator naturally leads to a solution for symmetrized coupled modes, in which the invariance of the Hamiltonian operator, under bond exchange, is explicitly taken into account. A rather appealing feature of this algebraic model is that such a ‘‘symmetrizing’’ property of the Majorana operator, actually quite a trivial one for two equal bonds, can readily be extended to any molecular geometry, even a very complex one. The key point is that the basic information characterizing the specific molecular geometry can easily be incorporated by introducing proper linear combinations of the Majorana operators.

In purely local limit of N oscillators, these oscillators are somehow correlated with each other through the C_{ij} operators, which account for (diagonal) cross-anharmonicities, represented by the following equation:

$$\begin{aligned} C_{ij} = C_i - N_{ij} \left(\frac{C_i}{N_i} + \frac{C_j}{N_j} \right) \\ \text{where } N_{ij} = N_i + N_j. \end{aligned} \quad (7)$$

Furthermore, following Eq. (7), it should be noted that one basically subtracts from C_i those terms arising from uncoupled single-oscillator contributions. In the special case of a pair of equivalent oscillators i and j ($N_i = N_j$), the above equation can be replaced by the following matrix elements:

$$\langle \nu_i\nu_j | C_{ij} | \nu_i\nu_j \rangle = -4(\nu_i - \nu_j)^2, \quad (8)$$

i.e., the matrix elements do not depend on N_i (N_j). As a result, C_{ij} will account for different contributions throughout different polyads and within the same polyad; the most important aspect of C_{ij} is the dependence of its matrix elements on the product $\nu_i\nu_j$.

The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain [13]:

$$\begin{aligned} U^{(1)}(2) \otimes U^{(2)}(2) \otimes U^{(3)}(2) \supset \\ \downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \\ | [N_1], \qquad [N_2], \qquad [N_3]; \\ \\ SO^{(1)}(2) \otimes SO^{(2)}(2) \otimes SO^{(3)}(2) \supset SO(2) \\ \downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \\ \nu_1, \qquad \nu_2, \qquad \nu_3; \qquad V \rangle, \end{aligned} \quad (9)$$

where, below each group we have indicated the eigenvalues that label their irreducible representations. Explicitly this basis is given by

$$\begin{aligned} |[N_1], [N_2], [N_3]; \nu_1\nu_2\nu_3 \rangle \\ = |[N_1]; \nu_1 \rangle |[N_2]; \nu_2 \rangle |[N_3]; \nu_3 \rangle, \end{aligned} \quad (10)$$

where

$$|[N]; \nu \rangle = \sqrt{\frac{(N-\nu)!}{N!\nu!}} (J_-)^\nu |[N], 0 \rangle.$$

Here, N is the total number of bosons fixed by the potential shape, ν corresponds to the number of quanta in the oscillator and J_- is the angular momentum operator (has both raising J_+ , lowering J_- connecting different energy states) in $U(2)$ algebra. The quantum numbers ν_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^n \nu_i. \quad (11)$$

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 uncoupled bond with eigenvalues $4(\nu_i^2 - N_i\nu_i)$ and the operator 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' , λ , λ' and N , the vibron number, to study the vibrational spectra of the C_{70} and C_{80} molecules. After considering the common coupled and uncoupled bond-bond interaction in the molecular configuration in case of C_{70} and C_{80} and also considering the Majorana couplings, on the basis of the symmetry of the molecules, the number of algebraic parameters are reduced to four. In this regard, one should note that this is the unique beauty of the algebraic model where one needs only a few parameters to describe the vibrational spectra of a molecule with a good accuracy.

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

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad i = 1, 2, \dots \quad (12)$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants.

For the C_{70} and C_{80} molecules in stretching mode, we can have the values of ω_e and $\omega_e x_e$ for the CC bond from the study of Nakamoto [14] and that of Huber and Herzberg [15]. Using the values of ω_e and $\omega_e x_e$ for the bond CC we can have the initial guess for the value of the vibron number N . It may be noted here that in the algebraic approach, there is provision to change (not more than $\pm 20\%$) the value of N to get better results. This is equivalent to change the single-bond anharmonicity according to the specific molecular environment, in which it can be slightly different.

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

$$E(\nu = 1) = -4A(N - 1). \quad (13)$$

Using Eq. (13), \bar{A} can be obtained as

$$\bar{A} = \frac{\bar{E}}{4(1 - N)}, \quad (14)$$

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

Now we can have the initial guess for λ using \bar{E} (Eq. (14)). The role of λ is to split the initially degenerate local modes. Such an estimate is obtained by considering the following simple Hamiltonian matrix structure:

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) + \lambda N \end{pmatrix}. \quad (15)$$

We easily find that

$$\lambda = \frac{E_1 - E_2}{2N} \quad (16)$$

and

$$\lambda' = \frac{|E_1 - E_2|}{6N}. \quad (17)$$

To have better results a numerical fitting procedure (in a least-square sense) is required to obtain the parameters A , A' , λ and λ' starting from the values as given by Eq. (14), Eq. (16) and Eq. (17). Initial guess for A' may be taken as zero.

The fitting parameters used in the study of vibrational spectra of fullerene C_{70} is given in Table I. Experimental and calculated energies [cm^{-1}] of fullerene C_{70} have been shown in Table II.

TABLE I
Fitting parameters* of fullerene C_{70} .

vibron number	Stretching parameters			
	N	A	λ	λ'
140		-0.962	0.382	-0.097

* A , λ , λ' all are in cm^{-1} whereas N is dimensionless.

TABLE II
Experimental and calculated energies (cm^{-1}) of fullerene C_{70} .

Normal level	I	II	$\Delta(I - II)$	Percentage of error
	Ref. [8]	Calculated		$\frac{\Delta(I - II)}{I} \times 100\%$
ν_1	458	453.39	+4.61	1.006%
ν_2	535	534.87	+0.13	0.024%
ν_3	642	641.83	+0.17	0.026%
ν_4	674	667.31	+6.69	0.992%
ν_5	795	799.75	-4.75	0.597%
ν_6	1086	1077.44	+8.56	0.788%
ν_7	1134	1131.76	+2.24	0.197%

$\Delta(\text{rms}) = 4.882 \text{ cm}^{-1}$.

The fitting parameters used in the study of vibrational spectra of fullerene C_{80} is given in Table III. Experimental and calculated energies [cm^{-1}] of fullerene C_{70} have been shown in Table IV.

TABLE III
Fitting parameters* of fullerene C₈₀.

vibron number	Stretching parameters			
	N	A	λ	λ'
140	-2.181	0.3428	-0.0708	

* A , λ , λ' all are in cm^{-1} whereas N is dimensionless.

TABLE IV
Simulated and calculated energies (cm^{-1}) of fullerene C₈₀.

Normal level	I	II	$\Delta(I - II)$	Percentage of error $\frac{\Delta(I - II)}{I} \times 100\%$
	Ref. [15]	Calculated		
ν_1	1214.91	1213.10	+1.81	0.148%
ν_2	1271.06	1272.57	-1.51	0.118%
ν_3	1310.77	1309.08	+1.69	0.128%
ν_4	1343.83	1345.31	-1.48	0.110%
ν_5	1379.20	1382.11	-2.91	0.210%
ν_6	1416.69	1418.61	-1.92	0.135%
ν_7	1450.31	1455.12	-4.81	0.331%

$\Delta(\text{rms}) = 2.560 \text{ cm}^{-1}$.

4. Conclusion

The algebraic model presented here is a model of coupled one-dimensional Morse oscillators describing the CC stretching vibrations of the molecules C₇₀ and C₈₀. By making use of this algebraic model one can avoid the complicated integrations in the solution of coupled differential Schrödinger equations. For the CC 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 C₇₀ and C₈₀ which are in good agreement with the results of experimental and computer simulated semi-empirical PM3 molecular modeling technique [8, 9]. It is hoped that with the further advancement of the U(2) model, the higher order modes of vibrations of C₇₀ and C₈₀ also can be explained

with good accuracy considering the bent vibrations of the molecules along with the stretch vibrations.

Acknowledgments

The author Rupam Sen is very much thankful to the anonymous referee of this paper for valuable suggestions and comments, which greatly helped to improve the quality of this paper.

References

- [1] R.D. Levine, C.E. Wulfman, *Chem. Phys. Lett.* **60**, 372 (1979).
- [2] F. Iachello, *Chem. Phys. Lett.* **78**, 581 (1981).
- [3] F. Iachello, R.D. Levine, *J. Chem. Phys.* **77**, 3046 (1982).
- [4] F. Iachello, S. Oss, *Eur. Phys. J. D* **19**, 307 (2002).
- [5] N.K. Sarkar, J. Choudhury, R. Bhattacharjee, *Mol. Phys.* **104**, 3051 (2006).
- [6] N.K. Sarkar, J. Choudhury, R. Bhattacharjee, *Indian J. Phys.* **82**, 767 (2008).
- [7] M. Ibrahim, *Acta Chim. Slov.* **52**, 153 (2005).
- [8] M. Ibrahim, Hanan El-Haes, *Chin. J. Phys.* **43**, 915 (2005).
- [9] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, G. Golden, *Chem. Phys. Lett.* **179**, 181 (1991).
- [10] S. Oss, *Adv. Chem. Phys.* **93**, 455 (1996).
- [11] F. Iachello, R.D. Levine, *Algebraic Theory of Molecules*, Oxford University Press, Oxford 1995.
- [12] F. Iachello, S. Oss, *Phys. Rev. Lett.* **66**, 23 (1991); S.R. Karumuri, N.K. Sarkar, J. Choudhury, R. Bhattacharjee, *J. Mol. Spectrosc.* **255**, 183 (2009).
- [13] F. Iachello, S. Oss, *J. Mol. Spectrosc.* **153**, 225 (1992).
- [14] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry*, Wiley, New York 1997.
- [15] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., New York 1979.