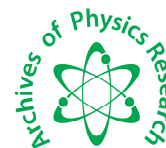




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### IR active spectroscopy of fullerene C<sub>78</sub> isomers

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#### ABSTRACT

*The vibrational energy levels of two C<sub>78</sub> fullerene isomers, having C<sub>2v</sub> symmetry are calculated considering the local Hamiltonian of Morse potential using the U(2) Lie 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 invariant operators. The normal IR active stretching modes of vibration of isomers of C<sub>78</sub> are then calculated using this Hamiltonian to fit the experimental results.*

**Keywords:** Lie algebra; Vibrational spectra; fullerene; C<sub>78</sub>.

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#### INTRODUCTION

Molecular spectroscopy is undergoing an essential change due to the rapid development of sophisticated experimental approaches, at present, molecular spectroscopy is going through an exciting time of renewed interest. Due to its numerous connections with other scientific areas, this branch of modern physics is playing an essential role in both experimental and theoretical approaches to understanding a huge number of important problems. In recent years the algebraic model attracted a wider scientific community for the analysis and interpretation of experimental rovibrational spectra of small and medium-sized molecules [1]. The proposed model is based on the idea of dynamic symmetry, which in turn, is expressed through the language of Lie algebras. By applying algebraic techniques, one obtains an effective Hamiltonian operator that conveniently describes the rovibrational degrees of freedom of the physical system. With this framework, any specific mechanism relevant for the correct characterization of the molecular dynamics and spectroscopy can be accounted. 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).

The new theoretical concept- Vibron model (based on Lie algebra) to study molecular spectra was 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) was 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 was applied successfully in describing the overtone frequencies of linear and bent molecules [5]. The main features and basic applications of these methods have been described by Iachello and Levine and Oss. The brief review of the research work done in this field up to 2000 and its perspectives in the first part of 21st century was presented by Iachello and Oss [6].

Both the isomers of  $C_{78}$  considered in this theoretical work have the same symmetry ( $C_{2v}$ ). 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 degeneracy in the energy spectrum and to introduce a meaningful labeling scheme for the corresponding eigenstates.

In this paper, U(2) Lie Algebraic theory is used, which is an excellent alternative mathematical treatment with less number of algebraic parameters to calculate more precisely the stretching vibrational IR active frequencies of two isomers of fullerene  $C_{78}$ , which shows a good agreement with respect to experimental values [ 7 ]. The algebraic approach may help us to determine the different energy bands other than the IR active range of isomers of fullerene  $C_{78}$ .

## 2. Review of U(2) Algebraic Theory:

One of the most interesting areas of current research in molecular physics is the study of the vibrational excited states of medium and large molecules. In view of the considerable amount of experimental activity in this area, one need the necessity of the theoretical models by which the interpretation of the experiential data can fit with desired degree of accuracy. For medium – size and large molecules , models based directly on the solution of the many body differential Schrödinger equation with interatomic potentials become rather awkward and difficult to apply. Similarly, straight forward Dunham like expansions contain a large number of parameters which can not be determined from the few available data.

Now, consider a model [8, 9] of  $n$  coupled anharmonic oscillators, which appear to describe IR active vibrational stretching energies with desired degree of accuracy in terms of less number of parameters. In constructing this model, we use the isomorphism of the Lie algebra of U(2) with that of one dimensional Morse oscillator. The eigenstates of the one dimensional Schrödinger equation,  $h\psi = \epsilon\psi$  with a Morse potential [10]

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

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,  $h = \epsilon_0 + AC$ , where  $C$  is the invariant operator of  $O(2)$ .

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.(2) can be rewritten as,

$$\epsilon = \epsilon_0 - 4A(N\nu - \nu^2), \text{ where, } \nu = 0, 1, \dots, N/2 \text{ or } \frac{N-1}{2} \text{ (where } N = \text{even or odd) } \tag{3}$$

The value of  $\epsilon_0$ ,  $A$  and  $N$  are given in terms of  $\mu, D$  and  $\alpha$  by using the following relations

$$\epsilon_0 = -D, \quad -4AN = h\alpha(2D/\mu)^{1/2}, \quad 4A = -h^2\alpha^2 / 2\mu$$

where  $D$  is the dissociation energy and  $\mu$  is the reduced mass. Now, one can easily 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  $h_i = \epsilon_{0i} + A_i C_i$  [11,12] 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 Casimir and Majorana operators respectively, where the Casimir operator has only the diagonal matrix element, where as 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 [12].

$$\begin{array}{ccc}
 & O_i(2) \otimes O_j(2) & \\
 & \swarrow \quad \searrow & \\
 U_i(2) \otimes U_j(2) & & O_{ij}(2) \\
 & \nwarrow \quad \nearrow & \\
 & U_{ij}(2) & 
 \end{array} \tag{4}$$

Their physical meaning can be seen from the matrix elements given by Eq. (6) and Eq. (7).

The algebraic model Hamiltonian we consider thus has the following form [12]

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij} \quad (5)$$

The matrix elements with the invariant Casimir and Majorana operators are as follows

$$\langle N_i, \nu_i; N_j, \nu_j | C_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = 4[(\nu_i + \nu_j)^2 - (\nu_i + \nu_j)(N_i + N_j)] \quad (6)$$

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

$$\langle N_i, \nu_i + 1; N_j, \nu_j - 1 | M_{ij} | N_i, \nu_i; N_j, \nu_j \rangle = -[\nu_j(\nu_i + 1)(N_i - \nu_i)(N_j - \nu_j + 1)]^{1/2} \quad (7)$$

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

Eq.(7) is a generalization to  $n$  bonds of the two-bond model. In Eq.(6), the operators  $C_{ij}$  describes anharmonic terms of the type  $\nu_i \nu_j$ , while in Eq.(7) the operators  $M_{ij}$  describes interbond couplings which in configuration space, are of the type  $r_i r_j$ , where  $r_i$  and  $r_j$  are the displacement vectors of bonds  $i$  and  $j$  from their equilibrium values.

In this study, we able to show that the model Hamiltonian (Eq. (5)) provides a complete description of stretching modes of polyatomic molecules whose precision is optimum satisfactory as that of any previously considered model. In addition, we derive an important result on the theory of discrete groups which opens the way for applications to molecules of any symmetry.

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

$$V = \sum_{i=1}^n \nu_i \quad (8)$$

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.

## RESULTS AND DISCUSSION

In this study, we use the algebraic parameters *i.e.*  $A, A', \lambda, \lambda'$  &  $N$ , to study the vibrational spectra of two  $C_{78}$  isomers where  $N$  is the vibron number. After considering the common coupled and uncoupled bond-bond interaction in the molecular configuration in case of two  $C_{78}$  isomers and also considering the Majorana couplings, on the basis of the symmetry of the molecules, the numbers 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 fewer 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 [12],

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1 \quad (i = 1, 2, \dots) \quad (9)$$

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

For two  $C_{78}$  isomers in normal mode, we can have the values of  $\omega_e$  and  $\omega_e x_e$  for the C-C bond from the study of Nakamoto [13] and that of Huber and Herzberg [14]. Using the values of  $\omega_e$  and  $\omega_e x_e$  for the bond C-C 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,

$$E(\nu = 1) = -4A(N - 1) \quad (10)$$

Using the Eq. (10),  $\bar{A}$  can be obtained as,

$$\bar{A} = \frac{\bar{E}}{4(1 - N)} \quad (11)$$

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

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.(11). Such an estimate is obtained by considering the following simple Hamiltonian matrix structure

$$\begin{pmatrix} -4A(N - 1) - 4A'(2N - 1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N - 1) - 4A'(2N - 1) + \lambda N \end{pmatrix} \quad (12)$$

We easily find that

$$\lambda = \frac{|E_1 - E_2|}{2N} \quad (13)$$

$$\text{and} \quad \lambda' = \frac{|E_1 - E_2|}{6N} \quad (14)$$

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 (Eq. 11), (Eq. 13) and (Eq. 14). Initial guess for  $A'$  may be taken as zero.

The fitting parameters along with the results based on experimental and calculated energies of distinct normal IR active modes of vibration of two C<sub>78</sub> isomers, numbered according to their observed frequencies.

Table: 1 shows the fitting algebraic parameters to study the normal IR active modes of vibration of C<sub>78</sub> isomers where as the data of the Table: 2 and Table 3 are taken from experimental observations [7], which show a good agreement with the algebraic calculations by Lie algebra.

**Table 1: Fitting algebraic parameters of Isomer 2 and 3 of C<sub>78</sub> ( $A, \lambda, \lambda'$  are in cm<sup>-1</sup> where as  $N$  is dimensionless)**

Molecules	Vibron number	Stretching algebraic parameters		
	$N$	$A$	$\lambda$	$\lambda'$
Isomer 2 of C <sub>78</sub>	140	-0.750	0.090	-0.020
Isomer 3 of C <sub>78</sub>	140	-0.785	0.075	-0.007

**Table 2: The values (in cm<sup>-1</sup>) for the 37 distinct normal IR active modes of frequencies of Isomer 2 of C<sub>78</sub> molecule**

Normal level	<i>Exp.</i> [7]	<i>Cal.</i>	Deviation $\Delta(\text{Exp.} - \text{Cal.})$	Percentage of error $\frac{\Delta \text{Exp.} - \text{Cal.} }{\text{Exp.}} \times 100\%$
$\nu_1$	419	417.0	2.0	0.48%
$\nu_2$	435	433.8	1.2	0.28%
$\nu_3$	444	442.2	1.8	0.41%
$\nu_4$	461	459.0	2.0	0.43%
$\nu_5$	467	467.4	-0.4	0.09%
$\nu_6$	482	483.4	-1.4	0.29%
$\nu_7$	488	484.2	3.8	0.78%
$\nu_8$	494	492.6	1.4	0.28%
$\nu_9$	505	501.0	4.0	0.79%
$\nu_{10}$	519	517.8	1.2	0.23%
$\nu_{11}$	524	526.2	-2.2	0.42%
$\nu_{12}$	532	534.6	-2.6	0.49%
$\nu_{13}$	538	543.0	-5.0	0.93%
$\nu_{14}$	545	551.4	-6.4	1.17%
$\nu_{15}$	554	553.3	0.7	0.13%
$\nu_{16}$	559	559.8	-0.8	0.14%
$\nu_{17}$	565	568.2	-3.2	0.57%
$\nu_{18}$	616	618.6	-2.6	0.42%

$V_{19}$	621	627.0	-6.0	0.97%
$V_{20}$	631	635.4	-4.4	0.69%
$V_{21}$	636	636.5	-0.5	0.08%
$V_{22}$	644	643.8	0.2	0.03%
$V_{23}$	652	652.2	-0.2	0.03%
$V_{24}$	659	660.6	-1.6	0.24%
$V_{25}$	679	677.4	1.6	0.24%
$V_{26}$	687	685.8	1.2	0.17%
$V_{27}$	692	694.2	-2.2	0.32%
$V_{28}$	698	702.6	-4.6	0.66%
$V_{29}$	705	711.0	-6.0	0.85%
$V_{30}$	717	719.4	-2.4	0.33%
$V_{31}$	725	727.8	-2.8	0.39%
$V_{32}$	741	744.6	-3.6	0.49%
$V_{33}$	768	769.8	-1.8	0.23%
$V_{34}$	781	778.2	2.8	0.36%
$V_{35}$	792	795.0	-3.0	0.38%
$V_{36}$	800	803.4	-3.4	0.43%
$V_{37}$	808	811.8	-3.8	0.47%

$\Delta(r.m.s.) = 3.036 \text{ cm}^{-1}$

Table 3 : The values (in  $\text{cm}^{-1}$ ) for the 34 distinct normal IR active modes of frequencies of Isomer 3 of  $\text{C}_{78}$  molecule

Normal level	<i>Exp.</i> [7]	<i>Cal.</i>	Deviation $\Delta(\text{Exp.} - \text{Cal.})$	Percentage of error $\frac{\Delta \text{Exp.} - \text{Cal.} }{\text{Exp.}} \times 100\%$
$V_1$	436	436.5	-0.5	0.11%
$V_2$	442	442.4	-0.4	0.09%
$V_3$	457	457.5	-0.5	0.11%
$V_4$	463	464.2	0.8	0.17%
$V_5$	473	472.6	0.4	0.08%
$V_6$	480	479.4	0.6	0.13%
$V_7$	486	485.2	0.8	0.16%
$V_8$	491	491.1	-0.1	0.02%
$V_9$	498	496.9	1.1	0.22%
$V_{10}$	503	502.8	0.2	0.04%

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$v_{11}$	507	506.2	0.8	0.16%
$v_{12}$	528	527.2	0.8	0.15%
$v_{13}$	544	544.8	-0.8	0.15%
$v_{14}$	552	550.7	1.3	0.24%
$v_{15}$	582	581.0	1.0	0.17%
$v_{16}$	621	623.0	-2.0	0.32%
$v_{17}$	629	628.9	0.1	0.02%
$v_{18}$	635	634.7	0.3	0.05%
$v_{19}$	640	641.5	-1.5	0.23%
$v_{20}$	646	647.3	-1.3	0.20%
$v_{21}$	652	653.2	-1.2	0.18%
$v_{22}$	658	659.1	-1.1	0.17%
$v_{23}$	678	676.7	1.3	0.19%
$v_{24}$	683	682.6	0.4	0.06%
$v_{25}$	690	689.3	0.7	0.10%
$v_{26}$	696	695.2	0.8	0.11%
$v_{27}$	708	707.0	1.0	0.14%
$v_{28}$	725	724.6	0.4	0.06%
$v_{29}$	767	766.6	0.4	0.05%
$v_{30}$	777	775.9	1.1	0.14%
$v_{31}$	781	781.7	-0.7	0.09%
$v_{32}$	787	787.6	-0.6	0.07%
$v_{33}$	793	791.0	2.0	0.25%
$v_{34}$	798	796.7	1.3	0.16%

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$$\Delta(r.m.s.) = 0.95 \text{ cm}^{-1}$$

### CONCLUSION

We have presented here an algebraic model of coupled one-dimensional Morse oscillators which can be used to describe C-C stretching IR active vibrations of any polyatomic molecule. This model is the algebraic analogue of the model of proposed by Child [5] By making use of algebraic methods we avoid complications due to the convergence of integration in the solution of coupled differential Schrödinger equations. The algebraic equation (Eq.5) can be solved easily even for large  $n$  and thus one can use it to study C-C stretches of small, intermediate and large molecules. The only limitation is the size of the matrices to diagonalize. However, we think that the most important (and novel) result is that, by making use of inter-bond interactions, one is able to impose the point symmetry of the molecule in a simple and straightforward way, thus bypassing the difficulty associated with the construction of symmetry adapted states. In view of



this result, we think that simple and yet reliable calculations of C-C stretches of molecules of any geometry can now be done in terms of few parameters representing the inter-bond interactions. Moreover by this method the hitherto unknown states can also be predicted which help enormously to detect the state experimentally.

In this paper we presented only IR active modes of vibrations of two isomers of C<sub>78</sub> which are in good agreement with other experimental result. Above all, the r.m.s. deviation values suggests the precision of the calculation. Since the approach is very much successful in explaining the IR active vibrational frequencies of isomers of fullerene C<sub>78</sub>, so it is hoped that with the further advancement of this U(2) model, the Raman active modes of vibrations of isomers of fullerene C<sub>78</sub> can also be explained.

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