Spectroscopic studies on Nano-Molecules by using Lie algebraic model

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ABSTRACT

We have applied Lie algebraic model to nano sized molecules to determine the vibrational spectra of different stretching and bending vibrational modes. The Lie algebraic model of the Hamiltonian expression is

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

By using the Lie algebraic method, the stretching vibrational energies of fullerene (C_{80}) are calculated in the one-dimensional [U (2)] framework. Using the model Hamiltonian so constructed, we have calculated the local mode vibrational energy levels of the fullerene (C_{80}) accurately.

Key words: Vibrational Spectra; Lie Algebra; vibrational energy level, icosahedron.
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INTRODUCTION

Molecular spectroscopy is an area of active interest from many standpoints. Due to its numerous connections with other scientific areas, this branch of modern physics is playing an essential role

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in both experimental and theoretical approaches [1] to understanding a huge number of important problems. From the very outset, the interplay between quantum theory and experiments has revealed the importance of molecular spectroscopy. With the development of more powerful experimental techniques, such significance is getting broader-scale attention in the scientific community. In recent years, molecular spectroscopy [2] has been going through an exciting time of renewed interest, [3, 4, 5, 6, 7] which, once again, is being fueled by the rapid development of sophisticated experimental approaches. Recent developments include tunable, stable, and powerful lasers that are available to create complex excitation schemes, which allow for the investigation of highly excited levels with unprecedented resolution. Second, new detection techniques are constantly being developed with sensitivities far exceeding the limits of detectors used just a few years ago. Finally, a variety of molecules can be chosen among a very large number of extremely pure samples with careful initial state preparation. In such work, large amplitude distortions of a molecule from its equilibrium configuration are frequently encountered. This leads to both a decline in the usefulness of the conventional normal mode techniques, [8] which are based on the idea of small-amplitude motion, and a search for alternative methods.

In order to deal with these problems, a local mode method contrasted with the usual normal mode analysis has been developed. The theoretical description of the observed features has so far mostly focused on the study of the stretching modes but not the bending modes. Thus, the theoretical studies of excited vibrational states of molecules provide new challenges.

1. Approach to Algebraic method with Lie Algebra:

In the last few years, an algebraic method has been introduced as a computational tool for the analysis and interpretation of experimental ro-vibrational spectra of small- 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 algebraic techniques, [3, 4, 5] one obtains an effective Hamiltonian operator that conveniently describes the ro-vibrational degrees of freedom of the physical system. Within this framework, any specific mechanism relevant to the correct characterization of the molecular dynamics and spectroscopy can be accounted for. The algebraic methods [9] 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, [10] the results can be obtained in a more rapid and straightforward way. Now this approach and its hybrid is used to treat polyatomic vibrations and various other problems.

In recent years, algebraic models, such as Lie algebraic methods and boson-realization model have been proposed for the descriptions of vibrations, rotations, [11,12]and rotation-vibration interactions in polyatomic molecules. In Lie algebraic approaches, U (4) and U (2) algebraic models [13] 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 [8] was particularly successful in explaining stretching vibrations of polyatomic molecules such as benzene-like and Octahedral molecules.

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This model was extended to deal with stretching vibrations in tri-atomic molecules. In this paper, we use the U (2) algebraic model to study the higher excited vibrations of fullerenes such as C_{60}, C_{70}, C_{74}, C_{80} & other molecules. In this paper we concentrate only on the study of C_{80} molecule.

Fig. 1: C_{80} {D_{5d}}
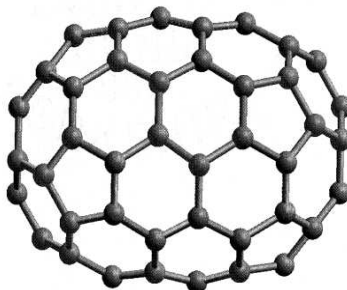
The C_{80} has been termed as one of the three 'missing fullerenes' due to its extremely low abundance in Huffman – Kratschmer soot. Recently, however, two C_{80} isomers were synthesized by dennis and shinohara, as a byproduct of the latter's work in generating endohedral metallofullerences [14]. One of these was first noted as a very – late – eluting fraction in HPLC separations using buckyprep columns, analysis with CNMR established its D_{5d} symmetry (Fig. 1)[15].

It was felt that this species would be an ideal subject for photo-physical analysis. Its strong retention on HPLC columns helps to keep it free from contamination by fullerenes of different mass, and by isomers of different structure . moreover, its structure is directly related to C_{60} and C_{70} via an extension of the famous ten-carbon-addition sequence: $C_{60}\{I_h\} \rightarrow C_{70}\{D_{5d}\} \rightarrow C_{80}\{D_{5d}\}$. Since the two lower species have high Φ_{ISC} values, strong transient absorptivities, and long triplet lifetimes , it was through that $C_{80}\{D_{5d}\}$ might display analogous properties [16].

The $C_{80}\{D_{5d}\}$ isomer lacks appreciable transient absorption, [17] this is apparently due to a combination of negligible quantum yield and small triplet-state epsilons. It does quench singlet oxygen emission, albeit at about $1/3^{rd}$ of the diffusion limit, this suggests that the T_1 state of $C_{80}\{D_{5d}\}$ is within I kT ($\approx$300 cm^{-1}) of 7880 cm^{-1}.

In constructing this U (2) algebraic model, we use the isomorphism of the Lie algebra of U (2) with that of the one-dimensional Morse oscillator. The Eigen states of the one-dimensional Schrodinger equation,   with a Morse potential

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

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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, ...,1 or 0 for N = odd or even (N = integer). The Morse Hamiltonian (1) corresponds in the U (2) basis to a simple Hamiltonian, $h = \bar{C}_0 + AC$, where C is the invariant operator of O (2), with Eigen values (m^2 - N^2).

The eigen values of h are $\bar{C} = \bar{C}_0 + A(m^2 - N^2)$,   (2)

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

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

$\bar{C} = \bar{C}_0 - 4A(Nv - v^2), v = 0, 1, ...N/2$ or $N - 1/2 (N = \text{even or odd})$.   (3)

The value of C_0 , A and N are given in terms of μ, D and α by

$C_0 = -D, -4AN = h\alpha(2D/\mu)^{1/2}, 4A = -h^2\alpha^2/2\mu$. One can immediately verify that these are the Eigen values of the Morse oscillator.

Now consider a molecule with n bonds. In the algebraic model, each bond i is replaced by an algebra (here $U_i(2)$), with Hamiltonian $h_i = \bar{C}_{0i} + A_i C_i$ where C_i is the invariant operator of $O_i(2)$ with Eigen values $-4(N_i v_i - v_i^2)$. The bonds interact with a bond–bond interaction. Two types of interaction are usually considered, which we denote by C_{ij} and M_{ij} and are called Casimir and Majorana [8] interactions, respectively.

The algebraic model Hamiltonian [18] we consider is thus,

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

In the equation (4) C_i is an invariant operator with Eigen values $4(v_i^2 - N_i v_i)$ and the operator C_{ij} is diagonal with matrix elements.

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \qquad (5)$$

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

$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = \langle N_i v_j + N_j v_i - 2v_i v_j \rangle$

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

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

(6)

Eq. (6) is a generalization of the two-bond model to n bonds.

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 eigen values of the corresponding invariant operator. *N* is the number of bosons related to stretching physical modes . The quantum numbers ν_i correspond to the number of quanta in each oscillator while *V* is the total vibrational quantum number given by [3, 4, 5],

$$V = \sum_{i=1}^{10} vi \tag{7}$$

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 eq. (5), 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 [3, 4].

RESULTS AND DISCUSSION

We have used U (2) algebraic model to study the vibrational spectra of the Fullerene (C_{80} & C_{80}-O) molecules with fewer algebraic parameters (*i.e.A, A', λ & N* (vibron number)).

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

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

Where ω_e and $\omega_e \chi_e$ are the spectroscopic constants of diatomic molecules of stretching interaction of the molecule considered. This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than ±20% of the original value [Eq. (8)]. The Vibron number N between the diatomic molecules C-C are 140. From the Fig. 1, it is noticed that some of the bonds are equivalent. It may be noted that during the calculation of the vibrational frequencies of fullerene C_{80} & C_{80}-O, the value of N is kept fixed and not used as free parameter. The second step is to obtain a starting guess for the parameter A. As such, the expression for the single-oscillator fundamental mode as

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

In the present case we have different energies, corresponding to symmetric and antisymmetric combinations of the different local modes. A possible strategy is to use the center of gravity of these modes, so the guess for

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

The third step is to obtain an initial guess for λ. Its role is to split the initially degenerate local modes, placed here at the common value E used in Eq. (9). Such an estimate is obtained by considering the simple matrix structure, we can find

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

A numerical fitting procedure to adjust (in a least-square sense, for example) the parameters A and λ starting from values Eq. (10) and Eq. (11), and A' (whose initial guess can be zero).

Table 1: Fitting parameters* used in the study of Fullerene (C_{80})

Vibron number	Stretching algebraic parameters		
N	A	λ	A'
140	-0.7463	0.1562	-0.0562

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

Table 2: Simulated and calculated energies (cm^{-1}) of fullerene (C_{80}) [19]

V	Normal level	Fullerene (C80) Molecule		Percentage of deviation
		I Ref [19]	**II** This study	Δ |I-II| /I*100%
1	υ_1	162.92	162.78	0.023%
	υ_2	227.54	228.38	0.197%
	υ_3	306.89	307.46	0.343%
	υ_4	376.13	375.23	0.238%
	υ_5	442.04	442.89	0.031%
	υ_6	470.79	472.29	0.456%
	υ_7	492.65	490.33	0.193%
	υ_8	515.37	514.39	0.147%
	υ_9	540.74	540.09	0.019%
	υ_{10}	607.34	606.78	0.145%
	υ_{11}	638.44	637.89	0.148%
	υ_{12}	655.08	654.09	0.146%
	υ_{13}	684.37	681.56	0.198%
	υ_{14}	704.19	704.87	0.018%
	υ_{15}	733.64	734.88	0.113%
	υ_{16}	768.40	767.77	0.145%
	υ_{17}	787.92	790.64	0.216%
	υ_{18}	833.73	836.56	0.254%
	υ_{19}	857.38	860.34	0.331%
	υ_{20}	868.71	869.33	0.116%
	υ_{21}	901.56	899.38	0.142%
	υ_{22}	912.58	910.99	0.196%
	υ_{23}	957.21	954.66	0.199%
	υ_{24}	1066.85	1063.52	0.198%
	υ_{25}	1183.11	1179.99	0.172%
	υ_{26}	1214.91	1215.62	0.001%

Δ(r.m.s) = 2.381 cm^{-1}

To get an estimation of the precession of both observed and calculated data, we use standard deviation (SD) denoted by σ at the bottom of two tables:

$$\sigma^2 = \frac{1}{o-p} \sum_{i=1}^{o} (E_{cal}^i - E_{obs}^i)^2 \tag{12}$$

Where o is the number of observed data and p is the number of parameters used in the fitting.

The fitting parameters used in the study of vibrational spectra of Buckminsterfullerene(C_{80}) is given in Table 1.

CONCLUSION

Using model Hamiltonian, we have presented an algebraic model of coupled one dimensional Morse oscillators which can be used to describe C-C stretching vibrations of polyatomic molecules with good accuracy. The model presented here describes the splitting of local C-C stretching modes due to residual inter-bond interactions. The splitting pattern determines the nature of interaction. Once we get the parameter, one then predict the splitting pattern of overtones. It is worth pointing out that most applications of the previous algebraic models are restricted to vibrations of gas molecules.

In this study, vibrational spectra of fullerene for 26 vibrational bands, we obtain the RMS deviation i.e Δ (r.m.s) = 2.381 cm^{-1}. The present calculations demonstrate that U (2) model can be applied successfully to the molecules having 80 number of atoms or even more than that. More accurate results can be obtained if the interaction between the stretch and bend is considered. It is believed that once we get the observed energy levels of higher overtones and combination bands, the comparison of calculated bands can be easily done with the help of model Hamiltonian using the parameters.

Hence, the results of our calculation on C_{80} considering both of its structural & vibrational properties by algebraic method and comparing the results obtained by semi empirical PM3 [20] calculations, establish the nearest precision.

We hope that this work will be stimulate further research in analysis of vibrational spectra of other Nano molecules like protein molecules where the algebraic approach has not been applied so far.

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