A study of the stretching vibrational spectra of $C_{120}O$ and $C_{120}O_2$ by $U(2)$ Lie algebra

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Abstract: The vibrational energy levels of the endohedral fullerene dimers $C_{120}O$ and $C_{120}O_2$ were calculated considering the local Hamiltonian of the Morse potential using algebra. Here, each bond of the molecules was replaced by a corresponding Lie algebra and finally the Hamiltonian was constructed considering the interacting Casimir and Majorana operators. The fundamental stretching modes of vibration of both dimers $C_{120}O$ and $C_{120}O_2$ were then calculated using this Hamiltonian to compare with the results of functional-based tight-binding (DF-TB) calculations.

Keywords: Lie algebra; vibrational spectra; $C_{120}O$; $C_{120}O_2$.

INTRODUCTION

In the last few years, theoretical studies of highly excited vibrational states of polyatomic molecules have been one of the most interesting topics for theoreticians and experimentalists because of the development of new laser spectroscopic techniques. Wulfman played a great role in the introduction of the algebraic approach to molecules. He was the pioneer who publish the first paper on the algebraic approach to molecules[1] (the algebraic approach to the Morse oscillator) in 1979. Later, in 1981, Iachello[2] used Lie algebraic method to study the spectra of molecules using $U(4)$ algebra. The $U(4)$ model takes rotation and vibration simultaneously into account but becomes intricate when the number of atoms in the molecules becomes more than four. After 1981, there was rapid progress in this field. Iachello *et al.*[3,4] proposed $U(4)$ algebra to calculate the stretching and bending vibrational excitations of linear triatomic and tetratomic molecules. The situation up to 1995 in this perspective was reviewed in a paper by Iachello and Levine.[5] In next year, Stefano Oss presented a contemporary and comprehensive up-to-date review of the mathematical concepts, physical aspects, practical applications and numerical implementation of algebraic models[6] in

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molecular spectroscopy. Later, Iachello and Oss jointly[7] presented a brief review of the work realized in this field and also provided a concrete outlook of the algebraic method in the first decade of the 21st century. Recently, using the Lie algebraic method, Sarkar *et al.* reported better results[8,9] for the vibrational energy levels of different polyatomic molecules than those reported earlier. The $U(2)$ algebraic model was particularly successful in explaining stretching vibrations of polyatomic molecules, such as tetrahedral, octahedral, endohedral and benzene-like molecules.[10] In the Lie algebraic method, there is provision for molecular vibrational energy to be studied by a normal and a local Hamiltonian. Using the powerful technique of the theoretical Lie algebraic group theory and by considering dynamical symmetry, the algebraic Hamiltonian was constructed. The application of the one-dimensional theoretical $U(2)$ algebraic model enabled the analysis and interpretation of experimental and theoretical rovibrational spectra of different polyatomic molecules, which might facilitate the exploration of a new dimension in the field of molecular chemistry and nano-technology.

Till date, no extensive experimental study of the vibrational spectra of endohedral fullerene dimers $C_{120}O$ and $C_{120}O_2$ have been reported, but only functional-based tight-binding (DF-TB) theoretical calculations in which a study of the vibrational spectra of fullerene dimers $C_{120}O$ and $C_{120}O_2$ with their different energy bands were analyzed.[11] By using the one-dimensional $U(2)$ algebraic model, which is an excellent alternative mathematical treatment for the determination of energy bands of fullerene dimers $C_{120}O$ and $C_{120}O_2$, the stretching vibrational energies of these dimers were determined and compared from a spectroscopic point of view.

THEORY: AN ALGEBRAIC APPROACH

Apart from Lie algebraic methods, two other well-defined methods already exist for the analysis of molecular vibrational spectra. These are:

1. The Dunham Expansion
2. The Potential Approach

Dunham Expansion approach was put forwarded by J. L. Dunham in 1932. Here, the molecular rotation-vibration spectrum is provided by the Dunham expansion. This is an expansion of energy levels in terms of vibration-rotation quantum numbers. For diatomic molecules, the expansion is:

$$E(v,J) = \sum_{i,j} y_{i,j} \left(v + \tfrac{1}{2}\right)^i \left[J(J+1)\right]^j \tag{1}$$

The Dunham Expansion approach has a few drawbacks. Here no Hamiltonian operator is available. Moreover, for large polyatomic molecules, one needs a large number of parameters are required to obtain by fitting a large experimental data base; these parameters are not always available. Furthermore, this expansion contains no information about the wave function of individual states. Thus, the matrix elements of the operators cannot be calculated directly. Lastly, the Dunham Expansion approach is unsuccessful for polyatomic molecules.

The second approach, called the Potential Approach provides more sophisticated analysis. Here, energy levels are obtained by solving the Schrödinger Equation with an interatomic potential. The potential is expanded in terms of interatomic variables. For diatomic molecules, a possible expansion is:

$$V(r) = \sum_n a_n \left(\frac{r - r_0}{b} \right)^n \qquad (2)$$

Here, the coefficients are obtained by a fit to the experimental energy levels. The solution of the Schrödinger Equation also provides a wave function from which matrix elements of various operators can be calculated. In the Potential approach, all the calculations are either differentiations or integrations Moreover; this approach is very tiresome when the numbers of atoms are larger.

The third approach is the algebraic model in which each bond is represented by either one dimensional $U(2)$ or three dimensional $U(4)$ Lie algebra,[3-5] which are popularly known as the one dimensional and three dimensional vibron model, respectively. Among these, the $U(4)$ model effectively explains simultaneously the stretching and bending vibrational energies of medium- and large-sized molecules. However, the one dimensional $U(2)$ algebraic model is very successful in explaining independently the stretching and bending vibrational energies of medium- and large-sized molecules. 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, the dynamical symmetries explored in this work constitute a big step forward over the 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 mechanism for describing transitions among different states. All these tasks can be realized within 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. The most important steps leading to the formulation of a dynamical symmetry are presented. This formulation should be thought of 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 Casimir operators of sub-algebras of the dynamical algebra. Such an "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.

In this study, the $U(2)$ algebraic model which was introduced as an alternative approach to the traditional Dunham expansion and Schrödinger equation for polyatomic molecules, was used. The motivation for the construction of this algebraic model is the isomorphism of the one dimensional Lie algebra, $U(2)$, with that of the one dimensional Morse oscillator, which is a good description of a stretching vibration of a molecule. The Hamiltonian of the one dimensional Schrödinger Equation with Morse Potential is:[7]

$$h(p,x) = \frac{p^2}{2\mu} + D\left[1 - \exp(-\alpha x) \right]^2 \qquad (3)$$

which can be put into one-to-one correspondence with the representation of the algebra $U(2) \supset O(2)$ characterized by the quantum numbers $\left|N_1,m\right\rangle$ with the provision that one takes only the positive branch of m, *i.e.*, $m = N_1$, N_1–1, N_1–2,…, 1 or 0 for N_1 odd or even (N_1 is an integer). However, to obtain a complete description of molecular vibrations, both stretching and bending modes are required. This is achieved by considering the isomorphism of the $U(2)$ Lie algebra with the solution of the Schrödinger Equation with another potential called the Poschl-Teller potential. This potential is very applicable for the calculation of bending vibrations, where the Morse potential is inappropriate. The eigenstates of the Schrödinger Equation with Hamiltonian Operator are:

$$h(p,x) = \frac{p^2}{2\mu} - \frac{D}{\cosh^2 \alpha x} \tag{4}$$

This can also be put into one-to-one correspondence with the representation of $U(2) \supset O(2)$ characterized by the quantum numbers $\left|N_2,m\right\rangle$ with the provision that one takes only the positive branch of m. In the above equation, the coordinate x is the product of the radius of the bender r multiplied the bending angle θ, *i.e.*, $x = r\theta$. For the fullerene dimers, n $U(2)$ Lie algebra are introduced to describe n stretching bonds (C–C and C–O). The two possible chains[8-10] of molecular dynamical groups in these molecules are:

$$U^1(2) \otimes \ldots \otimes U^n(2) \supset O^1(2) \otimes \ldots \otimes O^n(2) \supset O(2) \tag{5}$$

$$U^1(2) \otimes \ldots \otimes U^n(2) \supset U(2) \supset O(2) \tag{6}$$

which correspond to local and normal coupling, respectively. The coupling to the final $O(2)$ group in the first chain is realized though 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.[12] For these two situations, the Hamiltonian operator can be diagonalized analytically. Thus, the algebraic model Hamiltonian consider herein has the following form:[8,9]

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij} \tag{7}$$

If $\lambda_{ij} = 0$, the vibrations have a local behaviour. As the value of λ_{ij} increases, one goes more and more into normal vibrations. In Eq. (7), C_i is an invariant operator with eigenvalues $4(v_i^2 - N_i v_i)$ and the operator C_{ij}, known as the Casimir operator, contains diagonal matrix elements while the operators M_{ij}, known as the Majorana operators, have both diagonal and off-diagonal matrix elements.

Both the operators associated with coupling schemes involving algebras naturally arise from a systematic study of the algebraic formulation of the one-dimensional model for n interacting oscillators. Due to the restriction placed on the local uncoupled oscillators, the vibrational basis are represented as:

$$\left|V\right\rangle \equiv \left|v_1 v_2 v_3 \ldots v_n\right\rangle \tag{8}$$

in which the aforementioned operators have the following matrix elements:

$$\langle v | C_i | v \rangle = -4v_i(N_i - v_i)$$
$$\langle v | C_{ij} | v \rangle = -4(v_i + v_j)(N_i + N_j - v_i - v_j) \tag{9}$$
$$\langle v' | M_{ij} | v \rangle = (v_i N_i + v_j N_j - 2v_i v_j)\delta_{v'_i v_i}\delta_{v'_j v_j}$$
$$\langle v' | M_{ij} | v \rangle = -[(v_i+1)(N_i - v_i)v_j(N_j - v_j + 1)]^{1/2}\delta_{v'_i - v_i}\delta_{v'_j + v_j}$$
$$\langle v' | M_{ij} | v \rangle = -[(v_j+1)(N_j - v_j)v_i(N_i - v_i + 1)]^{1/2}\delta_{v'_i + v_i}\delta_{v'_j - v_j}$$

Here, in particular, the expressions above depend on the numbers N_i, popularly known as Vibron numbers (vibration rotation quantum number). Such numbers have to be seen as pre-determined parameters of well-defined physical meaning, as they relate to the intrinsic anharmonicity of a single, uncoupled oscillator through a simple relation.

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

$$C_{ij} = C_i - N_{ij}\left(\frac{C_i}{N_i} + \frac{C_j}{N_j}\right), \text{ where } N_{ij} = N_i + N_j \tag{10}$$

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:[13-15]

$$\langle v_i v_j | C_{ij} | v_i v_j \rangle = -4(v_i - v_j)^2 \tag{11}$$

i.e., the matrix elements do not depend on $N_i(N_j)$. As a result, C_{ij} would 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 $v_i v_j$.

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

$$V = \sum_{i=1}^{n} v_i \tag{12}$$

For particular polyatomic molecules, the total vibrational quantum number is always conserved. The inclusion of C_{ij} and M_{ij} in the local Hamiltonian operator cannot affect the above conservation rule.

RESULTS AND DISCUSSION

In this study, we use the different algebraic parameters, *i.e.*, A, A', λ, λ' and N, were used to study the vibrational spectra of the endohedral fullerene dimers C$_{120}$O and C$_{120}$O$_2$ molecules, where N is the vibron number.

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

$$N_i = \frac{\omega_e}{\omega_e x_e} - 2, \ \ i = 1, 2..., \ \ x_e = \frac{1}{N+2} \tag{13}$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants[16,17] of polyatomic molecules of the stretching interaction of the molecule considered. This numerical value
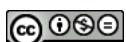
must be seen as an initial guess, *i.e.*, depending on the specific molecular structure, changes in such an estimate can be expected, which, however, should not be larger than ±20 % of the original value of Eq. (13). It may be noted that during the calculation of the vibrational frequencies of the fullerene dimers $C_{120}O$ and $C_{120}O_2$, the value of N is kept fixed and not used as a free parameter.

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

$$E(v = 1) = -4A(N - 1) \tag{14}$$

Using Eq.(14), A can be obtained as:

$$A = -\frac{E_1}{4(N - 1)} \tag{15}$$

To obtain an initial guess for the parameter λ, the role of which is to split the initially degenerate local modes, is obtained by considering the relation:

$$\lambda = \frac{E_3 - E_1}{2N} \tag{16}$$

and for the hyperfine splitting of the spectrum, the corresponding algebraic parameter is:

$$\lambda' = \frac{E_2 - E_1}{6N} \tag{17}$$

To obtain 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 Eqs. (15)–(17). The initial guess for A' may be taken as zero.

The fitting algebraic parameters used in the study of vibrational spectra of the fullerene dimers $C_{120}O$ and $C_{120}O_2$ are given in Table I, whereas in Tables II and III are listed the calculated energies and their deviations from the results of a theoretical functional-based tight-binding (DF-TB) calculation.

TABLE I. Fitting algebraic parameters of the fullerene dimmers $C_{120}O$ and $C_{120}O_2$ (all the parameters are given in cm^{-1}, accept N, which is dimensionless)

Fullerene dimer	Vibron number, N	Stretching algebraic parameters		
		A	λ	λ'
$C_{120}O$	140	–0.9473	0.0175	0.0034
$C_{120}O_2$	140	–0.9367	0.0230	0.0050

TABLE II. Calculated energies (cm^{-1}) of the fullerene dimer $C_{120}O$

Normal level	I[11]	II (this study)	Δ(I–II)	$100(I-II)/I$
v_1	526.60	526.70	–0.10	0.00019
v_2	529.50	529.55	–0.05	0.00009
v_3	531.50	531.60	–0.10	0.00018

TABLE II. Continued

Normal level	I[11]	II (this study)	I–II	$100(I–II)/I$
ν_4	563.50	564.27	–0.77	0.00136
ν_5	568.30	567.90	0.40	0.00070
ν_6	573.40	572.90	0.50	0.00087
ν_7	576.30	576.93	–0.63	0.00109

TABLE III. Calculated energies (cm^{-1}) of the fullerene dimer C$_{120}$O$_2$

Normal level	I[11]	II (this study)	$\Delta(I–II)$	$100(I–II)/I$
ν_1	520.80	520.85	–0.05	0.00009
ν_2	525.10	525.05	0.05	0.00009
ν_3	527.30	527.29	0.01	0.00001
ν_4	529.60	529.81	–0.21	0.00039
ν_5	563.70	564.25	–0.55	0.00097
ν_6	569.30	568.73	0.57	0.00100
ν_7	576.70	576.85	–0.15	0.00026

CONCLUSIONS

The algebraic model presented herein is a model of coupled one dimensional Morse oscillators describing the C–C, C–O stretching vibrations of the fullerene dimers C$_{120}$O and C$_{120}$O$_2$. By making use of this algebraic model, the complicated integrations in the solution of coupled differential Schrödinger equations can be avoided. For the C–C and C–O stretching inter-bond interactions, this model can be useful in a simple and straightforward way and very reliable in the calculation with a small number of algebraic parameters. In this study, we presented only a small number of the fundamental modes of vibrations of C$_{120}$O and C$_{120}$O$_2$ are presented, which are in good agreement with the results of functional-based tight-binding (DF-TB) calculations.[11] Hence, the method suggests that with the further advancement of this $U(2)$ algebraic model, other modes of vibrations of the molecules could also be explained and predicted for the interest of further experimental studies. This method has already successfully explained the vibrational spectra of many simple and polyatomic molecules. Thus, it can be concluded that the $U(2)$ algebraic method is a successful alternative theoretical approach to explore the hitherto unknown vibrational states of polyatomic molecules.

ИЗВОД

ИСПИТИВАЊЕ ВИБРАЦИОНЕ СПЕКТРОСКОПИЈЕ ИСТЕЗАЊА
C$_{120}$O И C$_{120}$O$_2$ УЗ ПОМОЋ $U(2)$ ЛИЕВЕ АЛГЕБРЕ

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Нивои вибрационих енергија димера ендохедралних фулерена C$_{120}$O и C$_{120}$O$_2$ су израчунавани коришћењем $U(2)$ алгебре, узимајући у обзир локалне Хамилтонијане

Морзеових потенцијала. Свака молекулска веза је замењена одговарајућом Лиевом алге-бром, а затим је, узимајући у обзир интеракције Казимир и Мајорана оператора, конс-труисан Хамилтонијан. Основни параметри вибрационог мода истезања оба димера су затим израчунати применом овог Хамилтонијана и упорђени са резултатима израчуна-вања методом функционалне густине и јаке везе (*functional-based tight-binding* - DFTB).

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