
M.D. CHOUDHURY, R. SEN, B.I. SHARMA

Department of Physics, Assam University
(Silchar, Assam, India; e-mail: rupamsen@sscollegekd.ac.in)

VIBRATIONAL IR ACTIVE FREQUENCIES OF C₃₆: AN ALGEBRAIC APPROACH

UDC 539

The one-dimensional $U(2)$ Lie algebra is employed to calculate the structural and vibrational properties of C_{36} . The lowest energy configuration of the C_{36} cage is confirmed to have D_{6h} symmetry. The Lie algebraic method is based on the idea of dynamic symmetry, which can be expressed in terms of $U(2)$ Lie algebra. By applying the algebraic techniques, a local Hamiltonian, which conveniently describes the rovibrational degrees of freedom of the physical system, can be obtained. In this technique, the Hamiltonian is constructed, by considering the invariant Casimir and Majorana operators replacing every bond of the molecule by a corresponding Lie algebra. At the same time, the fundamental stretching vibrational energy levels of the molecule C_{36} are calculated. Finally, the calculated results are compared with other theoretical findings.

Keywords: Lie algebra, Hamiltonian, C_{36} , dynamic symmetry.

1. Introduction

As a matter of keen interest of the research community, to unfold the different properties of atoms and molecules, the spectroscopy is considered nowadays as an active dependable arena. The spectroscopy deals with the interaction between electromagnetic radiation and matter. This interaction results in the spectra characterized by wavelengths or frequencies. The spectroscopic data are considered as a measure of the radiation intensity as a function of the wavelength. Electromagnetic radiation propagates through the free space or through a material medium in the form of electromagnetic waves. The electric field varying in time can induce a magnetic field which induces, in turn, an electric field. They oscillate in mutually perpendicular directions and take the form of an electromagnetic wave.

For the calculations of the frequencies of the vibrational modes of polyatomic molecules, there are many theoretical approaches like the tight-binding molecular dynamics [1], first principles calculation [2], force

field model [3], modified neglect of diatomic overlap (MNDO) model [4], quantum-mechanical consistent force field method for pi-electron systems (QCFF/PI) [5], Austin model 1 (AM1) [6], density functional theory (DFT) [7], *etc.* has been reported so far. Besides these, the Lie algebraic approach has also been successfully analyze the vibrational spectra of many medium and large-sized molecules. A brief review work of Iachello *et al.* reflects the scenario of the field up to 2002 along with the perspectives for the algebraic method in the first decade of the 21st century [8].

In this study, we consider the vibrational spectra of a small carbon cluster, being a very interesting momentous element. Most of the results regarding the study of the vibrational modes of small- and medium-sized carbon clusters are based on experiments. In recent years, researchers have performed many experimental observations in this relevant field. Though the experimental observations are good enough and signify an important role in interpreting the results on the basis of the analysis of data, the theoretical approaches are also indispensable to unfold the endless

possibilities to study the characteristics of small- and medium-sized molecules and to predict hitherto unknown states [9].

Here, our purpose persists to report the vibrational infrared frequencies of fullerene molecules C_{36} . Our interest in C_{36} is driven by the persistent incomplete experimental evidence (mainly concerning the infrared spectrum), as well as by the speculations of Fowler *et al.* [10] about the potential role of C_{36} as a building block in fullerene compounds and many solids.

Various properties of C_{36} molecules have been investigated experimentally over the last several years [11–14]. However, the synthesis of solid form C_{36} was achieved only recently [15]. Solid-state NMR measurements indicate that the molecule has D_{6h} symmetry, and the electron diffraction patterns suggest the crystal has hexagonal symmetry. The IR absorption spectrum of the powdered crystal shows a number of broad features between 400 and 1800 cm^{-1} , and, to the best of our knowledge, no other measurements of vibrational frequencies of C_{36} have been reported.

The most distinctive calculations of the vibrational frequencies of C_{36} reported up to now are the tight binding molecular dynamics of Beu *et al.* [1] and first principles calculations of Jishi *et al.* [2], using a spin-polarized DFT approach within the local density approximation (LDA). For the IR spectrum, the overall agreement of the calculated frequencies with the experimental data is very good. It is also found from the approach of density functional tight-binding (DFTB) level that the molecule C_{36} forms stronger interstage bonds than other larger fullerenes, say, C_{70} and C_{80} .

In such case, we use a mathematical model of molecular spectra to describe and predict the vibrational modes with high precision and accuracy. The algebraic approach was first given by Wulfman, Levine, and co-workers enthused from the interacting boson model of Arima and Iachello. Later on, Iachello developed this model with the introduction of the vibron model, where the rotation-vibration spectra of molecules were described by $U(4)$ algebra. But this becomes very difficult to use $U(4)$ algebra, when the number of atoms increases. This difficulty compels them to apply another algebraic model to the polyatomic molecules, and, henceforth, the $U(2)$ algebraic model, in which rotations and vibrations are completely separated, has been introduced.

Using the simple algebraic technique, we can easily find the different fundamental energy levels of concerned molecules. The level of accuracy can be estimated by the one-dimensional $U(2)$ Lie algebraic method [16].

2. The Algebraic Approach

The algebraic method has been extensively used as a computational tool for the analysis and interpretation of the experimental rotational-vibrational spectra of large- and medium-sized molecules. This method is purely based on the idea of dynamic symmetry, which depends, in turn, on the Hamiltonian formalism with the help of Lie algebraic technique, which conveniently describes the rotational-vibrational degrees of freedom of the physical system. In the one-dimensional $U(2)$ model, the replacement of the interaction bond co-ordinates by a unitary algebra provides a specific formulation of the algebraic expressions of eigenvalues and eigenvectors of complex Hamiltonian operators, which also includes the intermode coupling term and the expectation values as well. Since the $U(4)$ algebra is very much complicated, when the number of molecules is more than four, we need to construct a simple version of the vibron model with $U(2)$ algebra that can be used for the vibrational analysis of polyatomic molecules [17].

The main advantages of the $U(2)$ algebraic approach over the conventional Dunham-like expansions are as follows:

1. The algebraic models lead to a local Hamiltonian formulation of the physical problem.
2. Its expansions are intrinsically anharmonic in the zero-order approximation.

These two elements significantly reduce the number of parameters in comparison to the harmonic series for medium- and small-sized molecules. Hence the local Hamiltonian formulation can be used in the analysis of highly excited overtones of the polyatomic molecules.

The algebraic framework is based on the isomorphism of the $U(2)$ Lie algebra with that of the one-dimensional Morse oscillator. The Hamiltonian of the one-dimensional Schrödinger equation with the Morse potential [18],

$$h(p,x) = \frac{p^2}{2\mu} + D[1 - e^{(-\alpha x)}]^2, \quad (1)$$

can be put into the one-to-one correspondence with the representations of $U(2) \supset O(2)$ characterized by quantum numbers $|N, m\rangle$ with the provision that one takes only the positive branch of m , i.e., $m = N, N - 2, K, 1$ or 0 for $N = \text{odd}$ or even ($N = \text{integer}$). The Morse Hamiltonian in Eq. (1) corresponds in the $U(2)$ basis to a simple Hamiltonian [19]

$$h = \epsilon_0 + AC,$$

where C is the invariant operator. The eigenvalues of h are

$$\epsilon = \epsilon_0 + A(m^2 - N^2), \quad (2)$$

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

Here, we introduce the vibrational quantum number, $\nu = (N - m)/2$.

Thus, Eq. (2) can be rewritten as

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

where $\nu = 0, 1, \dots, \frac{N}{2}$ or $\frac{N-1}{2}$ and ($N = \text{even}$ or odd).

The values of ϵ_0 , A , and N are given in terms of D , μ , and α , respectively, by using the relations

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

where D is the dissociation energy, and μ is the reduced mass.

In a good approximation, we can write the Hamiltonian of a polyatomic molecule in terms of the Morse anharmonic oscillator, by applying $U(2)$ algebra for each coordinate. This leads to the following algebraic Hamiltonian for the coupled oscillator [20]:

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

In the above Hamiltonian, the contributions of the three different classes are defined in the following manner: The first term, $\sum_{i=1}^n A_i C_i$, contributes to the description of n independent anharmonic sequences of vibrational levels (associated with N independent local oscillators) in terms of the operators C_i . The second one, $\sum_{i<j}^n A_{ij} C_{ij}$, leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij} . The third one, $\sum_{i<j}^n \lambda_{ij} M_{ij}$, depicts anharmonic nondiagonal interactions involving pairs of local oscillators in terms

of the operators M_{ij} . The C_i , C_{ij} and M_{ij} are the invariant algebraic operators. In the local basis, the operators C_i compose a diagonal matrix with eigenvalues [21]

$$\langle N_i, \nu_i | C_i | N_i, \nu_i \rangle = -4(N_i \nu_i - \nu_i^2). \quad (6)$$

The couplings between the bonds are introduced by the invariant operators C_{ij} and M_{ij} called Casimir and Majorana operators, respectively. The Casimir operator has only the diagonal matrix elements, whereas the Majorana operators have both diagonal and off-diagonal matrix elements, which are given by

$$\langle \nu | C_i | \nu \rangle = -4\nu_i(N_i - \nu_i), \quad (7)$$

$$\langle \nu | C_{ij} | \nu \rangle = -4(\nu_i + \nu_j)(N_i + N_j - \nu_i - \nu_j),$$

$$\langle \nu'_i | M_{ij} | \nu \rangle = (\nu_i N_i + \nu_j N_j - 2\nu_i \nu_j) \delta_{\nu'_i \nu_i} \delta_{\nu'_j \nu_j},$$

$$\langle \nu'_i | M_{ij} | \nu \rangle = -[(\nu_i + 1)(N_i - \nu_i) \times \nu_j (N_j - \nu_j + 1)]^{1/2} \delta_{\nu'_i - \nu_i} \delta_{\nu'_j + \nu_j}, \quad (8)$$

$$\langle \nu'_i | M_{ij} | \nu \rangle = -[(\nu_j + 1)(N_j - \nu_j) \times \nu_i (N_i - \nu_i + 1)]^{1/2} \delta_{\nu'_i + \nu_i} \delta_{\nu'_j - \nu_j}.$$

Thus, the eigenvalues of the Hamiltonian can be easily evaluated and provide a description of n coupled anharmonic vibrations.

3. Results and Discussion

In the algebraic theory, we introduce the vibron number N , which is directly related to the anharmonicity of the local C–C stretching bonds. At first, the value of vibron number N is determined by the relation [22]

$$N = \frac{w_e}{w_e x_e} - 1, \quad (9)$$

where w_e and $w_e x_e$ are the spectroscopic constants [22, 23] of diatomic molecules with the stretching interaction of the molecules considered. The value of N has to be taken as the initial guess depending on the specific molecular structure. One can expect a change of 20% of the value of N .

Table 1. Fitting algebraic parameters of C₃₆(A, λ, λ') (in cm⁻¹), whereas N is dimensionless)

| Vibron number | A | λ | λ' |
|---------------|--------|-------|-------|
| 140 | -0.776 | 0.275 | 0.058 |

Table 2. Calculated IR frequencies of C₃₆ (in cm⁻¹)

| Mode | Beu ^a (ν ₁) | Jishi ^b (ν ₂) | This work(ν) | Δ ₁ = ν - ν ₂ | Δ ₂ = ν - ν ₁ | $\frac{ \Delta_1 }{\nu}$ | $\frac{ \Delta_2 }{\nu}$ |
|---------------------|------------------------------------|--------------------------------------|--------------|-------------------------------------|-------------------------------------|--------------------------|--------------------------|
| E _{1u} (1) | 431 | 459 | 432 | -27 | 1 | 0.062 | 0.002 |
| E _{1u} (2) | 480 | 483 | 481 | -2 | 1 | 0.004 | 0.002 |
| A _{2u} (1) | 511 | 510 | 509 | -1 | -2 | 0.001 | 0.004 |
| E _{1u} (3) | 682 | 668 | 675 | 7 | -7 | 0.011 | 0.011 |
| E _{1u} (4) | 734 | 727 | 739 | 12 | 5 | 0.016 | 0.006 |
| A _{2u} (2) | 752 | 758 | 751 | -7 | -1 | 0.009 | 0.001 |
| A _{2u} (3) | 796 | 785 | 789 | 4 | -7 | 0.005 | 0.008 |
| E _{1u} (5) | 1027 | 1083 | 1035 | -48 | 8 | 0.046 | 0.007 |
| A _{2u} (4) | 1102 | 1103 | 1107 | 4 | 5 | 0.003 | 0.004 |
| E _{1u} (6) | 1259 | 1261 | 1263 | 2 | 4 | 0.001 | 0.003 |
| A _{2u} (5) | 1385 | 1340 | 1347 | 7 | -38 | 0.005 | 0.028 |
| E _{1u} (5) | 1375 | 1355 | 1359 | 4 | -16 | 0.002 | 0.012 |
| E _{1u} (9) | 1454 | 1465 | 1460 | -5 | 6 | 0.003 | 0.004 |

^aReference [1], ^bReference [2].

Second, the value of the parameter *A* can be obtained from the single-oscillator fundamental mode as

$$E_{\nu=1} = -4A(N - 1). \tag{10}$$

Lastly, on the third step, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators *M_{ij}*, the role of which is to degenerate the local modes. The value of these parameters can be calculated by considering the matrix structure of the molecules. By using a numerical fitting procedure (in a least-square sense) one can adjust the values of the parameters *N*, *A*, λ, λ', and *A'* (whose initial value can be taken as zero) to compare the results of the tight-binding molecular dynamics [1] and the first principles calculation [2].

Lastly, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the role of which is to degenerate the local modes. The values of the parameters can be calculated by considering the following matrix structure of the molecules:

$$\begin{pmatrix} -B & -\lambda N & -\lambda N & -\lambda N \\ -\lambda N & -B & -\lambda N & -\lambda N \\ -\lambda N & -\lambda N & -B & -\lambda N \\ -\lambda N & -\lambda N & -\lambda N & -BN \end{pmatrix}, \tag{11}$$

where $B = 4A(N - 1) - 4A'(2N - 1) + 3(\lambda + \lambda')$.

To obtain the initial guesses for the parameters λ and λ', we comprise the following relations from the

matrix equation (11):

$$\lambda = \frac{E_3 - E_1}{2N}, \tag{12}$$

and

$$\lambda' = \frac{E_2 - E_1}{6N}. \tag{13}$$

The fitting algebraic parameters used in the study of vibrational spectra of a small carbon cluster C₃₆ are given in Table 1, whereas Table 2 shows the fundamental IR frequencies in connection with C₃₆ from our study and the calculated frequencies from the tight-binding molecular dynamics [1].

4. Conclusion

The algebraic model presented here is a model of coupled one-dimensional Morse oscillators describing the C-C stretching vibrations of C₃₆. Using the one-dimensional algebraic model, one can avoid the complicated integrations in the solution of coupled differential Schrödinger equations. For the C-C stretching interbond interactions, this model can be used in a simple and straightforward way, and the reliable calculation of the stretching bonds can be explained in terms of the fitting algebraic parameters. In this work, we have presented the normal modes of vibrations of C₃₆, which are in agreement with the other theoretical results [1, 2]. We hope for that, with a further advancement of the *U*(2) model, the Raman active modes of vibrations of C₃₆ can be also explained with good accuracy.

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М.Д. Чоудхурі, Р. Сен, Б.І. Шарма

КОЛИВАЛЬНІ ІЧ-АКТИВНІ
ЧАСТОТИ C₃₆: АЛГЕБРАІЧНИЙ ПІДХІД

Резюме

Одновимірна U(2) алгебра Лі застосована для розрахунку структури і коливань C₃₆. Показано, що нижчий рівень енергії каркаса C₃₆ має D_{6h} симетрію. Алгебраїчний метод Лі заснований на ідеї динамічної симетрії, яка може бути описана U(2) алгеброю Лі. Із застосуванням алгебраїчної техніки отримано локальний гамільтоніан, що описує обертальні і коливальні ступені свободи даної фізичної системи. У цьому підході гамільтоніан побудований з використанням інваріантних операторів Казимира і Майорана із заміною кожного зв'язку молекули, що відповідає алгебрі Лі. Розраховані фундаментальні рівні енергії молекули C₃₆ для коливань з розтягуванням. Проведено порівняння з іншими теоретичними результатами.