A spectroscopic analysis of vibrational IR spectra of polymer phases of fullerene $C_{70}C_8H_8$ by Lie algebraic technique

ASHIM KALYAN*, RUPAM SEN, RAMENDU BHATTACHARJEE[a]
Department of physics, S. S. College, Hailakandi- 788151, India
[a]*Department of physics, Assam University, Silchar-788011, India*

Lie algebraic method is based on the idea of dynamic symmetry, which can be expressed in terms of U(2) Lie algebra. By applying algebraic techniques, an effective Hamiltonian operator can be obtained which conveniently describes the rovibrational degrees of freedom of the physical system. In this framework every C-C bond of the molecule is replaced by a corresponding Lie algebra and finally the Hamiltonian is constructed considering the interacting Casimir and Majorana operators. The fundamental stretching vibrational energy levels of Polymer Phases of $C_{70}C_8H_8$ are then calculated using this Hamiltonian to fit the experimental results.

(Received July 3, 2013; accepted November 7, 20013)

Keywords: Lie algebra, Vibrational spectra, $C_{70}C_8H_8$

---

1. Introduction

After the discovery of Fullerene, spectroscopic analysis of polyatomic molecules becomes one of the active areas of research in modern physics from many standpoints. Due to its numerous connections with other scientific areas, this branch is playing an essential role in both experimental and theoretical approaches to understand a huge number of important problems. Being fueled by the rapid development of sophisticated experimental approaches, at present, molecular spectroscopy is going through an essential change of renewed interest. Better initial-state preparation, improved light sources and specially designed pumping schemes, and more sensitive detection techniques are providing ever-improved resolution and a wider range of accessible final states.

In recent years the molecular spectroscopy is undergoing a change in different direction. One example of the changing attitudes is the increasing concern with time evolution. The time-energy uncertainty relation and the pursuit of higher resolution means that traditional spectroscopy is implicitly equivalent to the study of the stationary states determined by the long-time limit of the intramolecular dynamics. The recent increasing interest in the role of anharmonicities and resonance couplings made unavoidable by the study of higher-lying rovibrational states and the experimental reality of avoiding inhomogeneous broadening [1] makes the entire time domain of direct interest to spectroscopists [2].

The formalism in modern spectroscopy discusses both level structure beyond harmonic limit and corresponding dynamics. A Hamiltonian is thus unavoidable since it is the generator of time evolution. There needs a practical method for the determination of the eigen values of the Hamiltonian. In case of traditional Dunham-like expansion, the spectra are well approximated by a small number of constants for the simple molecule. But for larger molecules it is still not practicable to compute the required potential with sufficient accuracy. It is therefore often approximated using convenient functional forms. Not too far from deep equilibrium point, the potential is expanded in term of displacement coordinates relative to equilibrium configuration.

In the traditional approach, based on integrodifferential techniques, the molecular Hamiltonian is parameterized in terms of internal coordinates [3]. Here, the potential is modeled in terms of force field constants either through complex calculations involving the molecular electronic energy for several configuration [4] or experimentally, by fitting of spectroscopic data [5]. Although for diatomic molecules very accurate information on force fields is now available [6], this is not the case for polyatomic molecules where the knowledge of force fields are poor due to the large number of force constants. The potential may also be modeled by representing the anharmonicity of the bonds, as a first approximation, by a sum of anharmonic Hamiltonians; among these the Morse potential is the most commonly used [7].

In this approach**,** the molecular rotation-vibration spectrum is provided by the Dunham expansion [8, 9]. This is an expansion of energy levels in terms of vibration-rotation quantum numbers. For diatomic molecules, the expansion is

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

The coefficients y_{ij} are obtained by a fit to the experimental energy levels. But in this approach, there is no Hamiltonian operator is available, one needs a large number of parameters for polyatomic molecules (obtained by fitting large experimental data base) which is not always available and this expansion does not contain any information about the wave function of individual states. Thus the matrix elements of operators can not be calculated directly.

The second approach, called potential approach provides more sophisticated analysis. Here, energy levels are obtained by solving the Schrödinger equation with an interatomic potential. The potential V is expanded in terms of interatomic variables. For diatomic molecules, the possible expansion is [10]

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

The coefficients a_n are obtained by a fit to the experimental energy levels. The solution of the Schrödinger equation also provides wave function $\psi(r)$ from which matrix elements of various operators can be calculated. In this approach, all manipulations are either differentiations or integrations.

The third approach to analyze molecular rotation-vibration spectra is based on the algebraic techniques. The success of the Interacting Boson Model of Arima and Iachello [11, 12] has stimulated new interest in the study of many body systems governed by algebraic Hamiltonian. The algebraic Hamiltonian is written in terms of boson creation and annihilation operators characterizing the normal modes of the system. Contrary to potential approach, all manipulations are algebraic. The technical advantage of an algebraic approach is the comparative ease of algebraic operations. However, the result obtained by comparison with experiment is equally important. Another important advantage of this approach is that entire class of molecules can be described by general form of algebraic Hamiltonian where only the parameters are different for different molecules. The algebraic (or matrix) formulation of quantum mechanics is less familiar than differential (or wave) formulation. For diatomic molecules, the solution of Schrödinger equation with interatomic potential is very simple, thus, algebraic approach is not very much useful in application in diatomic molecules. But, in case of tri-atomic and polyatomic molecules, the algebraic approach gives very useful results in a simplified manner**.** The formalism necessary to analyze experimental data has been developed in two ways; (i) in the first case, the rotations and vibrations are treated together and the full three dimensional space of coordinates, r and momenta p, is quantized with boson operators, giving rise to Lie algebras of $U(4)$ [13–15] and products thereof [16,17] (ii) in the second case, rotations and vibrations are treated separately and each one dimensional space of coordinates x and momenta p_x, is quantized with boson operators, leading to one dimensional Lie algebras $U(2)$ and products thereof [18,19].

In the last few years, Lie algebraic method has been introduced as a computational tool for the analysis and interpretation of experimental rovibrational spectra of small and medium-size molecules [13, 14]. 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, one obtains an effective Hamiltonian operator that conveniently describes the rovibrational 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 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.

Iachello, Arima [20] and Wulfman [21,22] have played a significant role in the algebraic approach to molecules. Wulfman is the pioneer who reported on the algebraic approach to molecules (the approach to the Morse oscillator) in 1979. Later, in 1981 Iachello used Lie algebraic methods in a systematic study of the spectra of molecules (the vibron model). This introduction was based on the second quantization of the Schrödinger equation with a three-dimensional Morse potential and described the rotation-vibration spectra of diatomic molecules [13, 14] and polyatomic molecules [18]. Besides these, Lie algebraic approach has also been successfully analyse the vibrational spectra of many medium and large sized molecules. A brief review work of Iachello et. al. [23] 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. Recently, Using Lie algebraic method Sarkar et. al. [24-27] reported better results for the vibrational energy levels of HCN, HCCF, HCCD, $SnBr_4$, than those reported earlier. Moreover, The $U(2)$ algebraic model was also particularly successful in explaining stretching vibrations of polyatomic molecules such as octahedral, benzene and Pyrrole-like molecules [28,29]. Recently, we have reported [30-32] the vibrational spectra of polyatomic fullerenes C_{70} and C_{80} using Lie algebraic method. As such, the approach is particularly appropriate for many challenges of modern spectroscopy, hence in this paper we used the algebraic model to report a comparative study of vibrational infrared frequencies of fullerene $C_{70}C_8H_8$ with the experimental results [33].

2. The algebraic theory

We use the $U(2)$ algebraic model as an alternative approach to the traditional Dunham expansion and potential approach for polyatomic molecules. In these approaches, the interpretation of experimental data by solving Schrödinger equation with interatomic potentials becomes increasingly difficult as the number of atoms in the molecule increases. The motivation behind 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

$$h(p, x) = \frac{p2}{2\mu} + D[1-\exp(-\alpha x)]^2 \qquad (3)$$

It can be put into one-to-one correspondence with the representation of the algebra $U(2) \supset O(2)$ characterized by the quantum numbers $|N, m\rangle$ with the provision that one takes only the positive branch of m, i.e., $m = N, N - 1, N - 2, \ldots\ldots, 1$ or 0 for N = odd or even (N = integer). However, to have complete description of molecular vibrations we need both stretching and bending modes. This is achieved by considering the isomorphism of $U(2)$ Lie algebra with the solution of Schrödinger equation with another potential called Poschl-Teller potential. This potential is very much applicable for calculating bending vibrations where Morse potential is not appropriate. The eigen states of Schrödinger equation with Poschl-Teller potential is

$$h(p, x) = \frac{p2}{2\mu} - \frac{D}{\cosh^2 \alpha x} \qquad (4)$$

It can also be put into one-to-one correspondence with the representation 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., $m = N, N-1, N-2\ldots\ldots, 1$ or 0 for N = odd or even (N = integer).

In this study we considered only the stretching vibration of the polyatomic molecule $C_{70}C_8H_8$ using the Morse potential. Thus the Hamiltonian corresponding to the Morse potential on the basis of $U(2)$ algebra is given by

$$H = \varepsilon_o + AC \qquad (5)$$

Where C is the invariant operator of O(2), with eigen values (m^2-N^2). So, the eigen Values of H are

$$E = \varepsilon_0 + A\left(m^2 - N^2\right) \qquad (6)$$

Where $m = N, N-2, \ldots\ldots\ldots 1$ or 0 (N = Integer) and A is the normalization constant.

Introducing the vibrational quantum number $\nu = (N-m)/2$, one can write the eigen value as

$$E = \varepsilon_0 - 4A\left(N\nu - \nu^2\right) \qquad (7)$$

with $\nu = 0,1,\ldots\ldots\ldots N/2$ or $(N-1)/2$ (for N = even or odd)

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

$$\varepsilon_0 = -D, \qquad -4NA = h\alpha(2D/\mu)^{1/2}, \qquad 4A = -h^2\alpha^2/2\mu$$

One can verify that these are the eigen values of the Morse oscillator.

According to the algebraic theory [34-36], polyatomic molecules consists of the separate quantization of rotations and vibrations in terms of vector coordinates $r_1, r_2, r_3, \ldots$. quantized by the algebra

$$G \equiv U_1(2) \otimes U_2(2) \otimes U_3(2) \cdots\cdots.$$

We introduce $U(2)$ Lie algebra to describe n stretching bonds (C-C). The two possible chains of molecular dynamical groups in these molecules are

$$U^1(2) \otimes \ldots \otimes - U^n(2) \supset O^1(2) \otimes \ldots. \otimes O^n(2) \supset O(2) \qquad (8)$$

$$U^1(2) \otimes \ldots\ldots \otimes U^n(2) \supset U(2) \supset O(2) \qquad (9)$$

which correspond to local and normal coupling respectively. The coupling to final $O(2)$ group in the first chain is carried out 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 [37]. For these two situations the Hamiltonian operator can be diagonalized analytically. The common algebraic model Hamiltonian in the case of stretching for these molecules can be considered as [24]

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

where C_i, C_{ij} and M_{ij} are the algebraic operators. In the local basis the operators C_i's are diagonal matrix with eigen values

$$\langle N_i, v_i | C_i | N_i, v_i \rangle = -4\left(N_i v_i - {v_i}^2\right)$$

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

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

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

$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_j\left(v_i + 1\right)\left(N_i - v_i\right) + \left(N_j - v_j + 1\right)}$$

$$\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_i\left(v_j + 1\right)\left(N_j - v_j\right) + \left(N_i - v_i + 1\right)}$$

Thus the eigen values of the Hamiltonian can be easily evaluated which provide a description of n coupled anharmonic vibrators.

3. Result and discussion

In the algebraic theory, we introduce the vibron number *N* which is directly related to the anharmonicity of local stretching bonds. The quantum numbers v_i corresponds to the number of quanta in each oscillator, while *V* is the total vibrational quantum number given by

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

For a particular polyad, the total vibrational quantum number is always conserved.

The value of vibron number *N* can be determined by the relation [38]

$$N = \frac{\omega_e}{\omega_e x_e} - 1 \qquad (12)$$

Where, ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules of stretching interaction of the molecule 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.

The value of the parameter A can be obtained from the single-oscillator fundamental mode as

$$E\left(v = 1\right) = -4A\left(N - 1\right) \qquad (13)$$

Lastly, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the role of which is to split the degenerate local modes and the value of the parameters can be calculated by considering the matrix structure of the molecules. To obtain an initial guess for the parameter λ and λ', we consider the following Hamiltonian matrix structure of the molecule

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

One can easily find,

$$\lambda = \frac{E_3 - E_1}{2N} \qquad (14)$$

And

$$\lambda' = \frac{E_2 - E_1}{6N} \qquad (15)$$

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 fit the experimental result.

The fitting parameters used in the study of vibrational spectra of fullerene $C_{70}C_8H_8$ is given in Table 1.

Table 1. Fitting parameters[a] of Fullerene $C_{70}C_8H_8$.

Vibron number	Stretching parameters		
N	*A*	λ	λ'
140	- 0.9586	0.1143	0.0095

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

(11)

Table 2. Calculated and experimental energies (cm^{-1}) of fullerene $C_{70}C_8H_8$.

Normal level	*Experimental[Ref.25]*	*Calculated*	Δ *(Expt-Cal)*
ν_1	533	532.98	+0.02
ν_2	541	540.96	+0. 04
ν_3	565	564.99	+0.01
ν_4	569	568.98	+0.02
ν_5	578	578.28	-0.28
ν_6	582	582.32	-0.32
ν_7	641	640.96	+0.04
ν_8	647	646.32	+0.68
ν_9	671	670.24	+0.76
ν_{10}	676	676.99	-0.99
ν_{11}	763	763.66	-0.66
ν_{12}	776	775.67	+0.33
ν_{13}	794	794.33	-0.33
ν_{14}	1086	1085.63	+0.37
ν_{15}	1132	1131.30	+0.70
ν_{16}	1154	1153.95	+0.05
ν_{17}	1190	1189.99	+0.01
ν_{18}	1202	1201.96	+0.04
ν_{19}	1217	1217.96	-0.96
ν_{20}	1413	1412.69	+0.31
ν_{21}	1427	1427.36	-0.36
ν_{22}	2964	2963.63	+0.37

Calculated Δ *(r.m.s)* = 0.466 cm^{-1} (by Lie algebraic method)

4. Conclusion

In this article we have studied the stretching vibrational IR spectra of Polymer Phases of $C_{70}C_8H_8$ by the algebraic model considering coupled one dimensional Morse oscillators describing the C-C stretching vibrations of the molecules. This study shows that the model can provide, without much effort and in a readily available standardized form, a simultaneous description of stretching vibrations with good rms accuracies with the experimental result. At the same time, the hurdle of complicated integrations in the solution of coupled differential Schrödinger equations of polyatomic molecules can also be avoided by making use of this algebraic model. Moreover the number of parameters in this case is also much less as compared to the traditional Dunham expansion calculations. So with the further advancement of this U(2) algebraic model, the other modes of vibrations of the molecule also can be explained and predicted for the interest of further experimental study.

Acknowledgement

One of the authors (A. Kalyan) gratefully acknowledges the financial support from University Grants Commission (NERO) India, for the work.

References

[1] M. Quak, Ann. Rev. Phys. Chem. **41**, 839 (1990).
[2] H. Bitto, J. R. Huber, Acc. Chem. Res. **25**, 65(1992).
[3] E. B. Wilson, Jr. J. C. Decions, P. Cross. Molecular vibrations, Dover, New York, (1980).
[4] W. T. Raynes, P. Lazzeretti, R. Zanasi, A. J. Sadlej, P. W. Fowler, Mol. Phys. **60**, 509 (1987).
[5] D. l. Gray, A. G. Robiette, Mol. Phys. **37**, 1901 (1979).
[6] J. E. Ogilivie, J. Mol. Spect. **69**, 169 (1978).
[7] L. Halonen, M. S. Child, Mol. Phys. **46**, 239 (1982).
[8] J. L. Dunham, Phys.Rev. **41**, 721(1932).
[9] T. G. Waech, R. B. Bernstein, J. Chem. Phys. **46**, 4905 (1967).
[10] M. Petri, U. Simon, W. Zimmermann, W. Urban, J. P. Towle, M. Brown, Mol. Phys. **72**, 315 (1991).
[11] F. Iachello, A. Arima, Phys. Lett. **B53**, 309 (1974).
[12] A. Arima, F. Iachello, Phys. Rev. Lett. **35**, 1069 (1975).
[13] F. Iachello, Chem. Phys. Lett., **78**, 581 (1981).
[14] F. Iachello, R. D. Levine, J. Chem. Phys. **77**, 3046 (1982).
[15] F. Iachello, S. Oss, J. Chem. Phys., **104**, 6956 (1996).
[16] O. van Roosmalen, A. E. L. Dieperink, F. Iachello, Chem. Phys. Lett. **85**, 32 (1982).
[17] O. van Roosmalen, F. Iachello, R. D. Levine, A. E. L. Dieperink, J. Chem. Phys. **79**, 2515 (1983).
[18] O. van Roosmalen, I. Benjamin, R. D. Levine, J. Chem. Phys. **81**, 5986 (1984).
[19] F. Iachello, S. Oss, Phys. Rev. Lett. **66**, 2976 (1991).
[20] A. Arima, F. Iachello, Ann. Phys. (NY) **99**, 253 (1976).
[21] C. E. Wulfman, Chem. Phys. Lett. **23**, 370 (1973).
[22] R. D. Levine, Chem. Phys. Lett. **60**, 372 (1979).
[23] F. Iachello, S. Oss, Euro. Phys. J. D. **19**, 307 (2002).
[24] N. K. Sarkar, J. Choudhury, R. Bhattacharjee, Mol. Phys. **104(19)**, 3051 (2006).
[25] N. K. Sarkar, J. Choudhury, R. Bhattacharjee, Mol. Phys. **106**, 693 (2008).
[26] N. K. Sarkar, J. Choudhury, R. Bhattacharjee, Indian J. Phys. **82**, 767 (2008).
[27] N. K. Sarkar, J. Choudhury, S. R. Karumuri, R. Bhattacharjee, Eur. Phys. J. D. **53**, 163 (2009).
[28] L. Lubich, S. Oss, J. Chem. Phys. **106**, 5379 (1996).
[29] J. L. Ping, J. Q. Chen, Ann. Phys. (N.Y.) **255**, 75 (1997).
[30] R. Sen, A. Kalyan, R. S. Paul, N. K. Sarkar, R. Bhattacharjee, ACTA Physica Polonica A. **120**, 3 (2011).
[31] A. Kalyan, R. Sen, N. K. Sarkar, R.Bhattacharjee, Fullerenes, Nanotubes, and Carbon Nanostructures, **21**, 429 (2013).
[32] R. Sen, A. Kalyan, N. K. Sarkar, R.Bhattacharjee, Spect. Lett. **45**, 273 (2012).
[33] G. Klupp, F. Borondics, E. Kovats, A. Pekker, G. Benyei, I. Jalsovszky, R. Hackl, S. Pekker, K. Kamaras, J. Phys. Chem.B. **111**, 12375 (2007).
[34] F. Iachello, S. Oss, J. Mol. Spect. **146**, 56 (1991).
[35] F. Iachello, N. Manini, S. Oss, J. Mol. Spect. **156**, 190 (1992).
[36] F. Iachello, S. Oss, Chem. Phys. Lett. **205**, 285 (1993).
[37] R. Lemus, A. Frank, Phys. Rev. B. **49**, 12738 (1994).
[38] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry, John Wiley & Sons, Inc. (1997).

---

*Corresponding author: ashimkalyan@yahoo.com