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A Comparative Spectroscopic Study of Ethylene & Benzene by using *U(2)* Lie Algebra

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ABSTRACT

In this paper the normal mode of vibrational energy levels of ethylene & benzene molecules are studied by U(2) Lie algebra. Its application to ethylene & benzene are presented with fewer algebraic fitting parameters. 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 operators. The normal modes of vibrational energy levels of these molecules are calculated and hence compared by considering the local Hamiltonian of Morse potential using the U(2) algebra.

Keywords: Vibrational spectra; Algebraic model; Energy levels; C_2H_4; C_6H_6.

INTRODUCTION

The study of fundamental and excited vibrational states of diatomic and polyatomic molecules have been one of the most interesting and advanced topics in the field of molecular spectra in the theoretical as well as experimental background in recent past due to the development and introduction of new laser techniques. Several experimental techniques [1] such as electronic luminescence spectroscopy including fine structure quasline spectra, X-ray, ESR, NMR, Mossbauer spectroscopy, magnetic susceptibility measurements, absorption, infrared and Raman spectroscopy has been applied to elucidate the physical and chemical properties of those molecules. At the same time many theoretical approaches including quantum chemical calculation as well as semi empirical programmees have been attempted by several researchers [2]. Although extensive studies by all these techniques on these molecules have clarified several aspects, many other aspects require further theoretical explanation. In this study we have used an alternative approach (Algebraic approach) to describe the vibrational spectra of molecules like ethylene & benzene.

In recent years, algebraic models, such as Lie algebraic methods [3] and boson-realization model [4] have been proposed for the descriptions of vibrations, rotations, and rotation-vibration interactions in polyatomic molecules. In Lie algebraic approaches, *U(4)* and *U(2)* algebraic models have been extensively used [5]. 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 was particularly successful in explaining stretching vibrations of diatomic & polyatomic molecules such as benzene-like molecules [6]. This model was extended to deal with stretching vibrations in diatomic and polyatomic molecules [7].

In this paper, we use the *U(2)* algebraic model to study the normal modes of vibrations of ethylene & benzene molecules [8].

2. Summary of the Algebraic Theory

In *U(4)* algebraic model (vibron model) [9], the rotations and vibrations of the molecules are taken into account simultaneously. But, it becomes impracticable when the number of atoms exceeds four. However separating the rotations and vibrations, it is possible to construct a simple version of the vibron model, which can be used for vibrational analysis of polyatomic molecules. In this study we apply the one dimensional algebraic model consisting of formal replacement of the interaction bond coordinate with unitary algebra *U(2)*. With this algebraic formulation, one can attain algebraic expressions of eigenvalues and eigenvectors even for a complex Hamiltonian operator, including inter-mode coupling terms as well as expectation values of any operator. The main advantages of this algebraic approach over the conventional Dunham [10] like expansions are

(i) The algebraic models lead to a local Hamiltonian formulation of the physical problem.
(ii) Its expansions are intrinsically anharmonic at their zero order approximation.

These two factors reduce drastically the no of arbitrary parameters in comparison to the harmonic series for medium and large size molecules. However in the local Hamiltonian formulations, the actual eigenvectors of the physical system cannot be directly accessed through diagonalisation of the Hamiltonian operators. Beside this disadvantage, which is not a serious one, the local Hamiltonian formulation can be used in the systematic study of fundamental and excited overtones of the diatomic & polyatomic molecules.

The motivation for the construction of this algebraic model is the isomorphism of *U(2)* one dimensional Lie algebra with that of the one dimensional Morse oscillator, which is a good description of a stretching vibration of a molecule. The eigenstates of the one dimensional Schrödinger equation with Morse potential [11] is

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

can be put into one to one correspondence with the dynamical symmetry $U(2) \supset O(2)$ 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,….., 1 or 0 for *N* = odd or even (*N* = integer). Thus the Hamiltonian corresponding to the Morse potential on the basis of *U(2)* algebra is given by

$$H = \varepsilon_0 + AC \tag{2}$$

where C is the invariant operator of *U(2)*, with eigenvalues $(m^2 - N^2)$. So, the eigenvalues of H are

$$\varepsilon = \varepsilon_0 + A\left(m^2 - N^2\right) \tag{3}$$

Introducing the vibrational quantum number $v = (N - m)/2$, one can write the eigenvalue as

$$\varepsilon = \varepsilon_0 - 4A\left(Nv - v^2\right) \text{,with } v = 0,1............N/2 \text{ or } (N-1)/2 \text{ (for } N = \text{even or odd)} \tag{4}$$

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

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

Since the potential in co-ordinate can be taken to a good approximation, as a Morse potential, we can write the Hamiltonian of a polyatomic molecule in terms of Morse anharmonic oscillators by introducing the *U(2)* algebra for each coordinate(C-H bonds). The algebraic Hamiltonian for the coupled oscillator is then can be written as

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i\langle j}^{n} A_{ij} C_{ij} + \sum_{i\langle j}^{n} \lambda_{ij} M_{ij} \tag{5}$$

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

$$\langle N_i, v_i | C_i | N_i, v_i \rangle = -4\left(N_i v_i - v_i^{\,2}\right) \tag{6}$$

The couplings between the bonds are introduced by the operators C_{ij} and M_{ij}, called Casimir and Majorana operators respectively. The role of the Majorana operators M_{ij} is to introduce off-diagonal couplings between pairs of local modes. In the simplest case of equivalent interacting bonds, the Majorana operator naturally leads to a solution for symmetrized coupled modes, in which the invariance of the Hamiltonian operator, under bond exchange, is explicitly taken into account. A rather appealing feature of this algebraic model is that such a ‘symmetrizing’ property of the Majorana operator, actually quite a trivial one for two equal bonds, can readily be extended to any molecular geometry, even a very complex one. The key point is that the basic information characterizing the specific molecular geometry can easily be incorporated by introducing proper linear combinations of Majorana operators.

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

$$C_{ij} = C_i - N_{ij}\left(\frac{C_i}{N_i} + \frac{C_j}{N_j}\right) \qquad \text{Where } N_{ij} = N_i + N_j \tag{7}$$

Furthermore, following the Eq.(7), it should be noted that one basically subtracts from C_i those terms arising from uncoupled single-oscillator contributions. 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

$$\langle v_i v_j | C_{ij} | v_i v_j \rangle = -4(v_i - v_j)^2 \tag{8}$$

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

The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain [5]

$$\begin{array}{ccccccccccccc} U^{(1)}(2) & \otimes & U^{(2)}(2) & \otimes & U^{(3)}(2) & \supset & SO^{(1)}(2) & \otimes & SO^{(2)}(2) & \otimes & SO^{(3)}(2) & \supset & SO(2) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ |\ [N_1], & & [N_2], & & [N_3]; & & v_1, & & v_2, & & v_3; & & V\rangle, \end{array} \tag{9}$$

where, below each group we have indicated the eigenvalues that label their irreducible representations. Explicitly this basis is given by,

$$|[N_1],[N_2],[N_3];v_1v_2v_3\rangle = |[N_1];v_1\rangle|[N_2];v_2\rangle|[N_3];v_3\rangle \tag{10}$$

Where, $|[N];v\rangle = \sqrt{\frac{(N-v)!}{N!v!}}(J_-)^{v_i}|[N],0\rangle$

Here , N is the total number of bosons fixed by the potential shape ,v corresponds to the number of quanta in the oscillator and J_- is the angular momentum operator (has both raising J_+ , lowering J_- connecting different energy states) in *U(2)* algebra. The quantum numbers v_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i \tag{11}$$

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 $4(v_i^2 - N_i v_i)$ and the operator C_{ij} for coupled bonds are diagonal with matrix elements, which are given by

$$\left.\begin{array}{l} \langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = -4\left[(v_i + v_j)(N_i + N_j) - (v_i + v_j)^2\right] \\ \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2 v_i v_j \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_j (v_i + 1)(N_i - v_i) + (N_j - v_j + 1)} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_i (v_j + 1)(N_j - v_j) + (N_i - v_i + 1)} \end{array}\right\} \quad (12)$$

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

3. The locality parameter (ξ)

The local-to-normal transition is governed by the dimensionless locality parameter (ξ). The transition from local to the normal mode limit is described by the parameter λ_{ij}/A. When this parameter is zero, the Hamiltonian (Eq. 5) is in the local limit, when the parameter is large the approaches the normal mode limit.

For ethylene (C_2H_4) and benzene (C_6H_6) molecules, the locality parameters are

$$\xi = (2/\pi)\tan^{-1}[8\lambda_{ij} / (A_i + A_{ij})], \qquad i, j = 1, 2, 3....... \quad (13)$$

corresponding to the number of bonds.
With this definition, due to Child and Halonen [12, 13, 14], local mode molecules are near to the $\xi = 0$ limit, normal mode molecules have $\xi \rightarrow 1$.

RESULTS AND DISCUSSION

In this work we use four algebraic parameters $i.e. A, A', \lambda, \lambda'$ & N, the vibron number, used to study the vibrational spectra of the ethylene (C_2H_4) and benzene (C_6H_6) molecules.
The value of N (vibron no.) can be determined by the relation

$$N = \frac{\omega_e}{\omega_e x_e} - 1 \quad (14)$$

Where ω_e and $\omega_e x_e$ are the spectroscopic constants [15] of stretching interaction of the molecules 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 $\pm 20\%$ of the original value (Eq. 14). It may be noted that during the calculation of the vibrational frequencies of ethylene (C_2H_4) and benzene (C_6H_6), the value of N is kept fixed and not used as free parameter.

Table 1: Fitting algebraic parameters of ethylene C_2H_4 (A, λ, λ' all are in cm^{-1} whereas N is dimensionless)

Vibron number	Stretching algebraic parameters		
N	A	λ	λ'
140	-1.4838	0.4428	-0.1369

Table 2: Vibrational frequencies (cm^{-1}) of ethylene C_2H_4

Mode[a]	Symmetry	Obs. freq.[b] (I)	Calc. freq.[c] (II)	Deviation $\Delta(I-II)$	Percentage of deviation $\frac{\Delta\lvert I-II\rvert}{I}\times 100\%$	Description
E1	A_g	3026.0	3030.3	-4.3	0.142%	CH_2 stretch
E2	A_g	1630.0	1631.4	-1.4	0.085%	$C=C$ stretch
E3	A_g	1342.0	1338.6	3.4	0.253%	CH_2 sciss
E4	B_{1g}	3086.0	3082.2	3.8	0.123%	CH_2 stretch
E5	B_{1g}	1220.0	1223.7	-3.7	0.303%	CH_2 rock
E9	B_{2u}	3105.0	3100.2	4.8	0.154%	CH_2 stretch
E10	B_{2u}	826.0	825.0	1.0	0.121%	CH_2 rock
E11	B_{3u}	3021.0	3021.3	-0.3	0.01%	CH_2 stretch
E12	B_{2g}	1444.0	1437.6	6.4	0.443%	CH_2 sciss
E6	B_{2g}	940.0	939.9	0.1	0.01%	CH_2 wagg
E7	A_u	1023.0	1020.9	2.1	0.205%	$C=C$ torsion
E8	B_{1u}	949.0	948.9	0.1	0.01%	CH_2 wagg

$\Delta(rms) = 3.287\ cm^{-1}$

[a] *Wilson No.;* [b] *reference [8];* [c] *U(2) Algebraic model*

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

$$E(v=1) = -4A(N-1) \tag{15}$$

Using the (Eq. 15), $\bar{A}$ can be obtained as,

$$\bar{A} = \frac{\bar{E}}{4(1-N)} \tag{16}$$

Table 3: Fitting algebraic parameters of benzene C_6H_6 (A , λ , λ' all are in cm^{-1} whereas N is dimensionless)

Vibron number	Stretching algebraic parameters		
N	A	λ	λ'
140	-0.7158	0.9857	-0.25

Table 4: Vibrational frequencies (cm^{-1}) of benzene C_6H_6

Mode[a]	Symmetry	Obs. Freq.[b] (I)	Calc. freq.[c] (II)	Deviation $\Delta(I-II)$	Percentage of deviation $\frac{\Delta\lvert I-II\rvert}{I}\times 100\%$	Description
E1	A_{1g}	993.1	1003.94	-10.84	1.09%	breathing
E2	A_{1g}	3073.9	3067.85	6.05	0.19%	CH stretch.in-phase
E3	A_{2g}	1350	1345.92	4.08	0.30%	CH bend. In-phase
E12	B_{1u}	1010	1015.98	-5.98	0.59%	CCC trigonal bend
E13	B_{1u}	3057	3055.82	1.18	0.04%	CH trigonal stretch
E14	B_{2u}	1309.4	1309.83	-0.43	0.03%	CC stretch
E15	B_{2u}	1149.7	1147.95	1.75	0.15%	CH trigonal bend
E6	E_{2g}	608.1	608	0.1	0.02%	CCC bend
E7	E_{2g}	3056.7	3055.82	0.88	0.03%	CH stretch
E8	E_{2g}	1601.0	1597.85	3.15	0.2%	CC stretch
E9	E_{2g}	1177.8	1177.85	-0.05	0.004%	CH bend
E18	E_{1u}	1038.3	1045.87	-7.57	0.72%	CH bend
E19	E_{1u}	1484.0	1489.93	-5.93	0.39%	CC stretch
E20	E_{1u}	3064.4	3063.85	0.55	0.017%	CH stretch
E11	A_{2u}	674.0	673.99	0.01	0.001%	CH wagg.in-phase
E4	B_{2g}	707	715.92	-8.92	1.26%	$CCCC$ puckering
E5	B_{2g}	990	991.1	-1.1	0.11%	CH trigonal wagg
E10	E_{1g}	847.1	859.93	-12.83	1.51%	CH wagg
E16	E_{2u}	398	398	0	0%	$CCCC$ torsion
E17	E_{2u}	967	967.5	-0.5	0.05%	CH wagg

$\Delta(rms) = 5.292$ cm^{-1}

[a] *Wilson No.;* [b] *reference [8];* [c] *U(2) Algebraic model*

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

$$\lambda = \frac{|E_1 - E_2|}{2N} \qquad (17)$$

and $$\lambda' = \frac{|E_1 - E_2|}{6N} \tag{18}$$

To have 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 (Eq. 16), (Eq. 17) and (Eq. 18). Initial guess for A' may be taken as zero.

The fitting algebraic parameters along with the simulated and calculated energies of ethylene (C_2H_4) and benzene (C_6H_6) are shown in Tables 1 - 4.

CONCLUSION

In this paper, we presented a systematic analysis of vibrational spectra of ethylene (C_2H_4) and benzene (C_6H_6) in the algebraic framework making use of the one-dimensional Vibron model i.e. *U(2)* Vibron model. Results of our study (Table 2, Table 4) show that the RMS deviation obtained for the vibrational spectra of ethylene (C_2H_4) and benzene (C_6H_6) using the algebraic mode Hamiltonian are 3.287 cm^{-1} and 5.292 cm^{-1} respectively, which are near to the accuracy of the results considering the other approaches [16, 17]. The present calculation demonstrates that *U(2)* model can also be applied successfully to the higher excited states of ethylene (C_2H_4) and benzene (C_6H_6).

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