S.R. KARUMURI,[1] V.U.M. RAO,[2] J. VIJAYA SEKHAR,[3] M.S. SURENDRABABU,[4]
T.B. PATRUDU,[4] N. VAMSIKRISHNA,[4] K.S. BABU,[5] V.S.S. KUMAR,[6] G. SRINIVAS[7]

[1] Department of Electronics & Instrumentation,
  Lakireddy Bali Reddy College of Engineering Mylavaram, Krishna District
  (Andhra Pradesh, India; e-mail: srinivasakarumuri@gmail.com)
[2] Department of Applied Mathematics, College of Science & Technology, Andhra University
  (Andhra Pradesh, India)
[3] Department of Mathematics, Jawaharlal Nehru Technological University
  (Kakinada Andhra Pradesh, India)
[4] Department of Mathematics & Chemistry, GITAM University
  (Hyderabad, Andhra Pradesh, India)
[5] Department of Physics, Miracle Engineering College
  (Bhogapuram, Andhra Pradesh, India)
[6] Department of Electronics & Instrumentation, Rajeev Gandhi Memorial Engineering College
  (Nandyal, India)
[7] Department of Physics, KL University
  (Vadeswaram, Guntur, Andhra Pradesh, India)

STUDIES OF THE VIBRATIONAL ENERGY LEVEL OF H_2O BY ALGEBRAIC AND DFT APPROACHES

The molecular spectroscopy is a branch of physics that deals with the interaction of electromagnetic radiation with matter. Within new theoretical approaches, we have calculated the stretching and bending vibrational energy levels of a water molecule in fundamental and overtone modes. The present calculation not only predicts the higher overtones, but also shows good agreement with a few experimental data.

K e y w o r d s: Lie-algebraic method, vibrational spectra, density functional theory (DFT), H_2O.

1. Introduction

To maintain the resonance with a rapid development of sophisticated experimental approaches, theoretical physics has been constantly tested to provide a collection of satisfactory models that can account for the experimental observations. Characterizing these experimental data is also equally important for understanding the dynamics of chemical reactions and the structure of molecules. The presented model is based on the idea of dynamical symmetry, which is expressed in the language of Lie algebras. Using the algebraic technique, we obtain an effective Hamiltonian operator that conveniently describes the rotational vibrational degrees of freedom of the physical system [1–3]. We formulate algebraic models that contain the same physical information for *ab initio*

theories (based on the solution of the Schrödinger equation) and semiempirical approaches (that use the phenomenological expansions in powers of appropriate quantum numbers). Various approaches have been used so far in the study of molecular spectra. Among them, we separate two following important approaches: (i) Dunham expansion [4] and (ii) potential approach [5]. A simple analysis of molecular rotational-vibrational spectra is provided by the Dunham expansion. This is the expansion of energy levels in terms of vibration–rotation quantum numbers. However, this expansion does not contain any information about the wave functions of individual states. Thus, the matrix elements of operators cannot be directly calculated. In the Dunham expansion, one needs a large number of parameters to describe a large polyatomic molecule. Further, these parameters have to be adjusted by a fitting procedure over a conveniently large experimental database, which is not always available. This is another serious drawback for this approach. As compared with the Dun-

ham expansion, a better analysis of molecular spectra is provided by the potential approach. Energy levels are obtained by solving the Schrödinger equation with an interatomic potential. The potential is expanded in terms of interatomic variables. The solution of the Schrödinger equation provides wavefunctions, from which the matrix elements of various operators can be calculated. In this approach, all manipulations are either differentiations or integrations. Though the potential approach is better, as compared with the Dunham expansion, it should be noted that this approach also encounters difficulties as soon as we consider highly excited levels. Moreover, a large number of parameters are needed to achieve meaningful results for a large polyatomic molecule. It should be noted that the algebraic approaches to complex spectra have already been proved useful in other fields of physics. The algebraic models are successful models in the study of the vibrational spectra of small and medium-sized molecules. Some small or large molecules can be studied, by using the $U(4)$ and $U(2)$ algebraic models. But the $U(4)$ model becomes complicated, when the number of atoms in a molecule becomes more than four. On the other hand, the $U(2)$ model introduced by Wulfman and Levine is found to be successful in explaining the stretching vibrations of polyatomic molecules such as tetrahedral, octahedral, icosahedral, and benzene-like ones. The brief review of the research work done with the algebraic models up to the year 2000 and its outlook and perception in the first decade of the 21st century were presented by Iachello and Oss. Recently, it is found that the Lie algebraic method [6–10] is extremely successful and accurate in calculating the vibrational frequencies of polyatomic molecules as compare with the other methods such as the Dunham expansion and the potential approach method reported earlier [11]. As a specific complementary technique to the conventional approaches, the algebraic approach has already proved to be successful in the study of molecular spectra during the last 29 years. The highly accurate prediction of molecular vibrations has been a challenging task in theoretical physical chemistry [12, 13]. Quantum chemistry allows one to obtain the valuable estimations of vibrational energy levels. As one of the best recent advanced approaches, we mention the DFT method [14, 15].

In this paper, we use the algebraic and DFT (B3LYP) methods to study the vibrational energy levels of a water molecule in the fundamental mode and compare our results with experimental data.

2. Algebraic Framework

Before applications of the algebraic method, it is essential to begin with a brief review of the algebraic model. The algebraic method has been introduced as a useful computational tool for the analysis and the interpretation of experimental rotational vibrational spectra of large 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 in the language of Lie algebras. By applying Lie algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rotational-vibrational degrees of freedom of the physical system [4]. 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 semiempirical approaches (using the 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 [5]. In Lie algebraic approaches, $U(4)$ and $U(2)$ algebraic models 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 has been particularly successful in explaining the stretching vibrations of polyatomic molecules such as benzene-like, octahedral, and icosahedral ones.

The algebraic model is based on the isomorphism of the $U(2)$ Lie algebra and a one-dimensional Morse oscillator, whose eigenstates may be associated with $U(2) \supset 0(2)$ states. For a three-atom molecule like A_2B, we introduce two $U(2)$ Lie algebras to describe two stretching bonds (A–B), respectively. Two possible chains of molecular dynamical groups in three-atom molecules are described by

$$U_1(2) \otimes U_2(2) \supset 0_1(2) \otimes 0_2(2) \supset 0_{12}(2)$$

Quantum numbers: $\quad N_1 \qquad N_2 \qquad n \qquad m \qquad n+m, \; (1)$

$$U_1(2) \otimes U_2(2) \supset U_{12}(2)(2) \supset 0_{12}(2)$$

Quantum numbers: $\quad N_1 \qquad N_2 \qquad \qquad v_1+v_2, \quad (2)$

where Eqs. (1) and (2) correspond to local and normal couplings, respectively. The quantum numbers corresponding to various algebras are indicated by n, m in Eq. (1) and v_1, v_2 in Eq. (2). N_1 and N_2 are vibron numbers corresponding to the number of bound states of two oscillators and are constant for the system. It is to be noted that $n+m = v_1+v_2$ is a conserved quantity. The bending motion can now be assigned an algebra $U_3(2)$ to be combined with the algebra $U_1(2) \otimes U_2(2)$ associated with the interacting stretching motions.

The algebraic Hamiltonian in case of the stretching mode of pyramidal molecules can be constructed from two chains as

$$\widehat{H} = E_0 + \sum_{i=1}^{3} A_i \widehat{C}_i + \sum_{i\langle j=1}^{3} A_{ij} \widehat{C}_{ij} + \sum_{i\langle j=1}^{3} \lambda_{ij} \widehat{M}_{ij}. \quad (3)$$
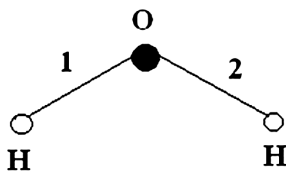
In Eq. (3), there are three types of contributions. The operators $\widehat{C}_i$ are the Casimir invariant operators of $O_i(2)$ algebras, $i=1, 2, 3$. Their diagonal matrix elements in the local basis $|v_1, v_2, v_3\rangle$ are of the form

$$\left\langle \widehat{C}_i \right\rangle = -4v_i(N_i - v_i), \quad i = 1, 2, 3, \quad (4)$$

with $N_1 = N_2 = N_3 = N$. Interbond couplings can be introduced in terms of operators associated with products of $U(2)$ and $O(2)$ algebras related to different interacting bonds. The term $\widehat{C}_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators. It is diagonal with matrix elements given by

$$\left\langle N_i, v_i; N_j, v_j | \widehat{C}_{ij} | N_i, v_i; N_j, v_j \right\rangle =$$

$$= 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)]. \quad (5)$$

The modes of three equivalent X-H bonds are now mixed, shifted, and split under the action of the operator $\widehat{M}_{ij}$. The Majorana operator is used to describe local mode interactions in pairs and has both

Optimized structure of an H$_2$O molecule

diagonal and non-diagonal matrix elements given by

$$\left. \begin{aligned} &\langle N_i, v_i; N_j, v_j | \widehat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = \\ &= v_i N_j + v_j N_i - 2v_i v_j, \\ &\langle N_i, v_i + 1; N_j, v_j - 1| \widehat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = \\ &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}, \\ &\langle N_i, v_i - 1; N_j, v_j + 1| \widehat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = \\ &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}. \end{aligned} \right\} \quad (6)$$

We now construct the local vibrational basis given by

$$\left| \begin{matrix} U_1(2) \otimes U_2(2) \otimes U_3(2) \supset O_1(2) \otimes O_2(2) \otimes O_3(2) \\ N_1 \quad\quad N_2 \quad\quad N_3 \quad\quad v_1 \quad\quad v_2 \quad\quad v_3 \end{matrix} \right\rangle. \quad (7)$$

The total vibrational quantum number is always conserved for a particular polyadic structure.

3. Results and Discussion

Using the $U(2)$ algebraic model, the vibrational modes of a water molecule are computed using the algebraic Hamiltonian up to the third overtone and are listed in Tables 1 and 2 with fewer algebraic parameters (i.e., A, A_{12}, λ_{12}, and N).

The vibron number N can be determined by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad i = 1, 2, 3, \quad (8)$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules [16]. The value of N must be such as initially guessed from Eq. (8); however, one can expect changes in an estimated N, being not larger than $\pm 20\%$ of the original value. The vibron numbers N between the diatomic molecules H–O and H–H are 44 and 28, respectively. From the Figure, it is noticed that some of the bonds are equivalent. It may be noted that, during the calculation of the vibrational modes of water molecules, the value of N is kept fixed and not used as a free parameter.

The next step is to obtain a guess for the second parameter A. The expression for the single-oscillator fundamental mode is

$$E(\nu = 1) = -4A(N - 1). \quad (9)$$

In the present case, we have three energies, corresponding to symmetric and antisymmetric combinations of the different local modes. A possible strategy

Table 1. **Comparison between experimental and calculated vibrational energy levels (in cm^{-1}) of H_2O**

$(v_1 v_2 v_3)$	Observed [a] (I)	Calculated		Population standard deviation	Standard deviation
		Algebraic method (II)	DFT (III)		
(1 0 0)	3657.05	3657.80	3737.96	37.9658	46.49842
(0 1 0)	594.74	1591.88	1603.23	4.81989	5.90314
(0 0 1)	3755.93	3747.56	3869.96	55.83175	68.37965
(2 0 0)	7201.54	7155.08	–	23.23	32.85218
(1 0 1)	7249.82	7244.48	–	2.67	3.77595
(0 0 2)	7445.05	7484.04	–	19.495	27.57009
(3 0 0)	10599.66	10580.76	–	9.45	13.36432
(2 0 1)	10613.41	10668.24	–	27.415	38.77066
(1 0 2)	10868.86	10794.43	–	37.215	52.62996
(0 0 3)	11032.40	11057.60	–	12.6	17.81909
(2 0 2)	13828.30	13665.93	–	81.185	114.81293
(3 0 1)	13830.92	13843.40	–	6.24	8.82469
(4 0 0)	14221.14	14211.45	–	4.845	6.85186
(1 0 3)	14318.80	14468.23	–	74.715	105.66297
(0 0 4)	14536.87	14536.44	–	0.215	0.30406

[a] Experimental data has taken from Ref. [17]

is to use the center of gravity of these modes, so the guess for

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

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. (10). Such an estimate is obtained by considering the simple matrix structure. We can find

$$\lambda_{12} \cong \frac{|E_1 - E_2|}{3N}. \tag{11}$$

With the help of a numerical fitting procedure (in a least-square sense), the parameters A and λ_{12} starting from values given by Eq. (10) and Eq. (11) and A_{12} (whose initial guess can be zero) were adjusted. Vibrational modes of a water molecule are computed using the algebraic Hamiltonian up to the third overtone and are listed in Table 1.

Thus, we can say that the algebraic model Hamiltonian is successful in predicting the energies in a complex molecular system. We believe that the more satisfactory results will be obtained if the higher order interactions are included in the algebraic Hamil-

Table 2. **Algebraic parameters* for H_2O**

Stretching parameters	Bending parameters
$N_1 = N_2 = N = 44$	$N_3 = 28$
$A_1 = A_2 = A = -18.98$	$A_3 = -14.76$
$A_{12} = -1.13$	$A_{13} = A_{23} = -3.66$
$\lambda_{12} = 1.02$	$\lambda_{13} = \lambda_{23} = 1.71$

*All parameters are in cm^{-1} except N, which is dimensionless

tonian. The fitting parameters for a water molecule are given in Table 2.

4. Conclusion

In Table 1, the theoretical values are compared with experimental vibrational energy levels of H_2O. Theoretical values obtained from algebraic calculations are in close agreement with the experimental values compared to DFT values. On the basis of a local model, the highly excited vibrational energy levels are predicted for an H_2O molecule with few numbers of parameters. We believe that the more satisfactory results will be obtained if quadratic terms of interactions will be taken into account. In last twenty five years, the Lie algebraic approach was found to be successful in explaining the vibrational energy levels of

small and medium molecules, polymers, biomolecules, and isopolymers. In view of many possible applications, it is hoped that the present calculation will open new windows in the field of spectroscopy.

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С.Р. Карумурі, В.У.М. Рао, Дж. Віджая Секхар,
М.С. Сурендрабабу, Т.В. Патруду, Н. Вамсікрішна,
К.С. Бабу, В.С.С. Кумар, Г. Срінівас

ДОСЛІДЖЕННЯ ВІБРАЦІЙНОГО РІВНЯ ЕНЕРГІЇ H_2O АЛГЕБРАЇЧНИМ МЕТОДОМ І МЕТОДОМ ТФГ

Р е з ю м е

Молекулярна спектроскопія – це область фізики, яка описує взаємодію електромагнітного випромінювання з речовиною. У рамках нових теоретичних схем розраховані рівні енергії молекули води для коливань з розтягуванням і вигином для основної моди і гармонік. Розрахунки не тільки передбачають вищі гармоніки, а і знаходяться в добрій згоді з експериментальними даними.