Vibrational spectral analysis of some isotopic species of hydrogen sulphide, hydrogen selenide and water using the U(4) algebraic model

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A successful application of U(4) algebraic model has been reported in the vibrational spectral analysis of some isotopic species of hydrogen sulphide, hydrogen selenide and water. The isotopic species of hydrogen sulphide, hydrogen selenide and water approximated in this study are H_2S^{32} , D_2S^{32} , H_2Se^{80} , D_2Se^{80} , H_2O^{17} and T_2O^{16} . The inclusion of intermode couplings in algebraic model has been stated on need base to give a deep insight into detailed spectroscopy for the mentioned isotopic species. With a detailed spectral analysis in the present study, it has been shown that the mentioned isotopic species of hydrogen sulphide, hydrogen selenide and water can be approximated very well using only two or three parameters in the U(4) algebraic model.

Keywords: Vibrational spectra, Lie algebra, Bent XY₂ molecule

1 Introduction

In recent years, molecular spectroscopy is undergoing through an exciting change. In terms of quantitative change, 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. Regarding qualitative change, a closer view suggests that not only better results but also new ideas are forthcoming.

To have a proper description and understanding of modern spectroscopy, one needs a theoretical framework, which can discuss both level structure beyond the harmonic limit and the corresponding dynamics. Hence, a Hamiltonian is unavoidable here to reach the goal since it is the generator of time evolution. Yet, one needs a practical method for the determination of the eigen values of this Hamiltonian. In the traditional Dunham-like expansion¹, it will be useful if the spectra can be well approximated by a small number of constants. However, one needs to be able to relate the parameters in this expansion directly to a Hamiltonian. The traditional familiar way of doing this proceed in two steps is: first, the electronic problem is solved in the Born-Oppenheimer approximation, leading to the potential for the motion of the nuclei. Then, the Schrodinger equation for the eigen values of this potential is solved. Since for any, but diatomic molecules, the potential is a function of many coordinates, neither the first nor the second step is simple to implement. For a number of test cases, this procedure has been carried out; and for diatomic molecules of lower row atoms, it can challenge experiments in its precision. For larger molecules, it is still not practical to compute the required potential with sufficient accuracy. It is, therefore, often approximated using convenient functional forms. Not too far from a deep equilibrium point, the potential can be expanded in the displacement coordinates relative to the equilibrium configuration. Such a 'force field' representation is quite convenient but is of limited validity for higher lying states due to the slow convergence of such a power series expansion. More flexible functional forms that can describe the asymptotic dissociation plateaus² require many

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parameters. The purely numerical solution of the Schrodinger differential equation for the eigen values of such a potential makes a large-scale numerical problem complicated.

In this work, an alternative approach is presented. The study puts particular emphasis on the traditional concerns, namely, determining the levels of the corresponding transitions. The approach presented retains, at least in part, the simplicity of a Dunham like approach in that, at least approximately, it provides the energy as an analytic function of the quantum numbers.

The Hamiltonian used in this approach is an algebraic one and so are all the operations in the method, unlike the more familiar differential operators of wave mechanics. The technical advantage of an algebraic approach is the comparative ease of algebraic operations. Another important advantage of this approach is that there are generic forms of algebraic Hamiltonians and the entire class of specific molecules can be described by a common Hamiltonian where only the (typically, linear) parameters are different for the different molecules. One more advantage of the algebraic approach is that a fewer parameters are needed here to approximate a molecule with a good accuracy.

The matrix formulation of quantum mechanics was introduced as early as 1925³⁻⁶. But till today, the algebraic (or matrix) formulation of quantum mechanics is less familiar than the differential (or wave) formulation. As per the view point, this is a disadvantage, and one purpose of the present work is to show, by explicit examples, the benefits of the algebraic approach. The interested readers may judge whether the benefits are sufficient enough or not to overcome the barrier to the understanding of a new approach. Through this study, the authors intend to demonstrate that the algebraic formulation is indeed a viable and better alternative in describing various complex molecular systems.

The algebras used in the present study are Lie algebras. These algebras were introduced at the end of the nineteenth century by Marius Sophus Lie but it is only in the much more recent past that its systematic large scale application could be seen in physics. It was in the 1930s that Lie algebras were being used in physics⁷⁻¹². Most of the early applications dealt with the algebra of rotations (Wigner-Racah algebra). An approach that starts from the algebra as the key tool for the construction of spectra originated in

elementary particle physics in the 1960s^{13,14} and had major applications in nuclear physics¹⁵⁻¹⁷. Later, since 1979, the applications of Lie algebras have been extended to the study of molecular spectra and some other related fields in physics by Levine¹⁸, Iachello¹⁹ and other researchers²⁰⁻³⁵.

In the study of vibrational spectra of poly atomic molecules, the U(2) and U(4) algebraic models^{18,19} have attracted a wider scientific community of the globe in recent years. The models already have been applied in the study of vibrational spectra of linear triatomic, linear tetratomic and some other small, medium and large-sized molecules^{20,21,25-31}. However, in vibrational spectroscopy, for bent XY₂ and bent XYZ molecules, only a few successful applications³²⁻ ³⁴ of the U(4) algebraic model could be reported so far. For U(4) algebraic model, more or less the entire kingdom of polyatomic molecules has been remained unattended till today. In this study, a successful application of the U(4) algebraic model has been reported in the vibrational spectral analysis of some isotopic species of hydrogen sulphide, hydrogen selenide and water. The isotopic species of hydrogen sulphide, hydrogen selenide and water approximated in this study are H_2S^{32} , D_2S^{32} , H_2Se^{80} , D_2Se^{80} , H_2O^{17} and T_2O^{16} . The inclusion of intermode couplings in algebraic models also has been stated on need base to give a deep insight into detailed spectroscopy for the mentioned isotopic species. With a detail spectral analysis, in this study, it has been shown that the mentioned isotopic species of hydrogen sulphide, hydrogen selenide and water can be approximated very well using only two or three algebraic parameters in the U(4) algebraic model.

2 Review of the Theory

The isotopic species of hydrogen sulphide, hydrogen selenide and water belong to the category of bent XY_2 molecules. The U(4) algebraic model¹⁹ to be used in the local mode study of bent XY_2 molecules, needs the understanding of coupling of bonds and subsequent formation of local mode Hamiltonian for bent XY_2 molecules within the algebraic framework. For some bent XY_2 molecules, intermode couplings are more prominent. To accommodate these intermode couplings, one will have to go for the local to normal transition study of the specific molecule with the incorporation of the Majorana operator. The behaviour (local or normal) of a molecule can be judged by using a well defined algebraic parameter

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called the locality parameter (ξ). All these items including the determination of the algebraic parameters involved in the model have been discussed in detail.

2.1 Coupling of bonds in U(4) algebraic model for bent XY_2 molecules – the local mode Hamiltonian

In the vibrational spectral analysis of bent XY_2 molecules, bonds are coupled in two main ways within the framework of the U(4) algebraic model²¹ which are as follows:

$$U_1(4) \otimes U_2(4) \supset O_1(4) \otimes O_2(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \dots (I)$$

$$U_{1}(4) \otimes U_{2}(4) \supset U_{12}(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \qquad \dots (II)$$

In the above algebraic representations, chain (I) and chain (II) correspond to local and normal coupling, respectively. The Hamiltonian operator can be diagonalized analytically for the above mentioned two situations.

The local basis characterized by the representations of chain^{20,21} is as follows:

$$\begin{vmatrix} U_{1}(4) \otimes U_{2}(4) \supset O_{1}(4) \otimes O_{2}(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ [N_{1}] & [N_{2}] & (\omega_{1}, 0) & (\omega_{2}, 0) & (\tau_{1}, \tau_{2}) & J & M_{J} \end{vmatrix} ,$$

$$\dots (2)$$

In the above expression, the number N_i labels symmetric irreducible representations of $U_i(4)$, i = 1, 2. This number is related to the total number of bound states supported by the anharmonic oscillator i, for the Morse potential realization. The number $_i$ labels symmetric irreducible representations of $O_i(4)$, while ($_1$, $_2$) denote non symmetric irreducible representations of $O_{12}(4)$, which are obtained from the reduction of $O_1(4)\otimes O_2(4)$. Finally, J and M_J represent the usual angular momentum quantum numbers. It may be noted here that the final $O_{12}(2)$ algebras in Eq. (1) are of no direct interest for the present study, as they refer to the action of external fields breaking the overall spherical symmetry.

The values of algebraic quantum numbers $_1$ and $_2$ are given by the rule:

$$_{1} = N_{1}, N_{1}-2, ----1 \text{ or } 0, N_{1} = \text{ odd or even}$$

 $_{2} = N_{2}, N_{2}-2, -----1 \text{ or } 0, N_{2} = \text{ odd or even}$
... (3)

The values of (1, 2) are obtained from the direct product of representations^{20,21,25}. They are given by:

$$1 = 1 + 2 - - , 2 = - ,$$

$$= 0, 1, \dots, \min(1, 2), = 0, 1, \dots, \dots, (4)$$

Having the detail concepts regarding the coupling of bonds for bent XY_2 molecules, the local mode Hamiltonian^{20,21,32-34} in U(4) algebraic model can be constructed as:

$$H^{\text{local}} = E_0 + A_1 C(O(4_1)) + A_2 C(O(4_2)) + A_{12} C(O(4_{12})) + \bar{A}_{12} | \overline{C} (O(4_{12})) + BC(O(3_{12})) \dots (5)$$

In Eq. (5), C(O(4₁)), C(O(4₂)), C(O(4₁₂), \overline{C} (O(4₁₂), and C(O(3₁₂)) are the bilinear Casimir invariants corresponding to the groups in chain I [Eq. (1)], A_1 , A_2 , A_{12} , and \overline{A}_{12} are the algebraic parameters; and *B* is the rotational constant. E_0 in Eq. (5) represents the zero of the energy scale. Corresponding to the groups in chain I [Eq. (1)], the eigen values of the bilinear Casimir invariants are given by^{20,21}:

$$C(O(4_{1})) \to \omega_{1}(\omega_{1} + 2)$$

$$C(O(4_{2})) \to \omega_{2}(\omega_{2} + 2)$$

$$C(O(4_{12})) \to \tau_{1}(\tau_{1} + 2) + \frac{2}{2}$$

$$\overline{C} (O(4_{12}) \to \tau_{2}(\tau_{1} + 1))$$

$$C(O(3_{12})) \to J (J + 1) \qquad \dots (6)$$

From Eq. (6), it follows that the Hamiltonian (5) is diagonal in the local basis (2) with eigen values^{20,21}:

$$E(N_1, N_2, 1, 2, 1, 2, J, M_J) = E_0 + A_1 (1+2) + A_2 (2+2) + A_{12} [1(1+2) + 2] + \overline{A_{12}} [2(1+1)] + BJ(J+1) ... (7)$$

In Eq. (7), the last term on the right hand side is due to the rotational part of molecular motion. B is the rotational constant, which is related to the rigid rotational motion of the molecule.

In this study, the simple case is considered in which $\bar{A}_{12} = 2A_{12}$. In such a case, the energy eigen values (7) can be written as^{20,32-34}:

$$E(N_1, N_2, 1, 2, 1, 2, J, M_J) = E_0 + A_1 (1 + 2) + A_2 (2 + 2) + A_{12}[(1 + 2) (1 + 2 + 2)] + BJ(J + 1) ... (8)$$

The Eq. (8) can be converted to the usual spectroscopic notation using the local vibrational quantum numbers, _a, _b, _c (Fig. 1). The two sets of quantum numbers are related as follows^{20,21}:

Quantum number, $_2$, now has been converted to the quantum number *K* describing the projection of the rotational angular momentum on the molecular fixed axis. Here, local stretching vibrations are denoted by the quantum numbers $_a$ and $_c$, while the quantum number $_b$ denotes the bending vibration of the bent XY₂ molecule (Fig. 1).

Vibrational part of the spectrum can now be achieved simply by putting B = 0 in Eq. (8). The contribution to the spectrum from the quantum number K now must collapse on the corresponding vibrational level as the authors are not interested here in rotational levels. This has been achieved here simply by letting $\bar{A}_{12} = 2A_{12}$. It is clear that the resulting spectrum is now a purely vibrational one and represents a bent triatomic molecule in the strict local



Fig. 1—Local vibrational quantum number of bent triatomic (XY_2) molecules.

limit. In terms of the set of vibrational quantum numbers ($_{a}$, $_{b}$, $_{c}$), one can rewrite Eq. (8) to get the resulting spectrum as follows^{21,32-34}:

$$E(a, b, c) = E_{o} - 4A_{1}[(N_{1} + 1) a - V_{a}^{2}] - 4A_{2}[(N_{2} + 1) c - V_{c}^{2}] - 4A_{12}[(N_{1} + N_{2} + 1) (a + b + c) - (a + b + c)^{2}] \dots (10)$$

where,
$$E'_{o} = E_{o} + A_{1}(N_{1}^{2} + 2N_{1}) + A_{2}(N_{2}^{2} + 2N_{2}) + A_{12}[(N_{1} + N_{2})^{2} + 2(N_{1} + N_{2})].$$

In Eq. (10), the terms involving A_1 and A_2 are related to local stretching vibrational modes. The bending mode and interactions between modes are taken care of by the term in A_{12} and the zero of the energy scale is chosen as the lowest vibrational level (0, 0, 0).

2.2 Local to normal transition in bent XY_2 molecues: Locality parameter

It is the fact that even for a good local molecule especially at higher excitation, local vibrations start to mix among themselves to some extent. In the U(4) algebraic model, such couplings can be accommodated by an operator known as Majorana operator $(M_{12})^{20,21}$. In such a case, to have the proper approximation of a bent XY₂ molecule, one has to add non-diagonal interactions to the initial local model. It may be noted that for symmetric molecules, localmode splitting gives a direct measure of the action of M_{12} . For bent triatomic molecules, M_{12} is closely related (excluding constant terms) to the invariant operator of the coupled algebra $U_{12}(4)$ appearing in the 'normal' chain²⁰. Its physical role is to introduce intermode coupling terms in the local basis. By making explicit use of group theoretical techniques, it is possible to show that M_{12} , acting within a given irreducible representation (1, 2) of $O_{12}(4)$, couples states satisfying the selection rules $\Delta_1 = 0, \pm 2;$ $\Delta_2 = 0, \pm 2$. It may be noted here that in the threedimensional algebraic model, the preserved symmetry is $O_{12}(4)$ since it appears in both local and normal sub-algebra chains²¹. In the present case (this study), one therefore expects to have a block-diagonal structure of the Hamiltonian matrix. The conserved quantum numbers are now (1, 2) because they label the irreducible representations of $O_{12}(4)$. Consequently, the introduction of intermode coupling terms in the local picture will lead to a symmetry breaking, where only those states with the same $\begin{pmatrix} 1 & 2 \end{pmatrix}$ quantum numbers can interact among themselves. For the bent triatomic molecules, this is equivalent to say that M_{12} acts on polyads of states with the same total vibrational quantum number ($_{Total} = _{a} + _{b} + _{c}$).

For bent XY₂ molecules, the local to normal transition in U(4) algebraic model can be described by combining the operators of the local chain with those of the normal chain. To serve the purpose, it is convenient here to introduce M_{12} . To study the local to normal transition of bent XY₂ molecules, at the very outset, once again here one will have to consider the Eq. (5). Since all terms in Eq. (5) are diagonal, this Hamiltonian represents two Morse oscillators diagonal in the local mode basis. It is already told that although the local mode basis provides a good zeroth-order approximation, the actual situation departs from it. The transition from local to normal can be achieved in the algebraic approach by introducing the Majorana operator. This operator is non-diagonal in the local mode basis, but the matrix elements of this operator can be computed very easily^{20,35}. This operator has matrix elements that induce both local mode couplings (which replace the Darling-Dennison couplings of the traditional Dunham expansion) and Fermi couplings²⁰. The former are particularly important for the class of bent XY_2 molecules that are described in this study. For bent XY₂ molecules, in lowest order, addition of this operator results the Hamiltonian:

$$H = E_0 + A_1 C(O(4_1)) + A_2 C(O(4_2)) + A_{12} C(O(4_{12})) + {}_{12} M(U(4_{12})) \dots (11)$$

In Eq. (11), all the terms contributing to rotational energies are deleted.

Considering the Hamiltonian (11), the matrix elements of M_{12} from the references^{20,35}, and the algebraic parameters from the subsequent section, one can have the energies of the different vibrational bands of a bent XY₂ molecule in terms of N (independent parameter) and other algebraic parameters A_1 , A_2 , A_{12} and $_{12}$.

Having the concepts of local to normal transition, one can proceed to have the definition of locality parameter () in U(4) algebraic model for bent XY_2 molecules. For bent XY_2 molecules, corresponding to the two bonds, in general there are two locality parameters²¹ given by:

$$_{i} = \frac{2}{4} \tan^{-1} \left[\frac{8}{A_{i} + A_{12}} \right], i = 1, 2 \qquad \dots (12)$$

Here, A_1 , A_2 , A_{12} and $_{12}$ are algebraic parameters corresponding to the molecule under consideration.

A global locality parameter for bent XY_2 molecules can be defined as the geometric mean²⁰:

$$=\sqrt{\left(\begin{vmatrix} 1 & 2 \end{vmatrix}\right)} \qquad \dots (13)$$

It may be noted here that for bent XY₂ molecules $A_1 = A_2$, and hence, for these molecules $_1 = _2$ With the above mentioned definition^{20,21,36} of

With the above mentioned definition^{20,21,36} of locality parameter (), due to Child and Halonen³⁶, local mode molecules are near to the = 0 limit and normal mode molecules have $\rightarrow 1$. It may be noted here that for local mode molecules, intermode couplings are poor. Obviously, a molecule showing less local behaviour tends to proceed towards normal mode molecule and is associated with more prominent intermode couplings than that of the local mode molecule. Locality parameters of the bent XY₂ molecules under this study are given in Table 1.

2.3 Calculation of vibron numbers and otheralgebraic parameters

In the U(4) algebraic model, the number *N* represents the total number of bosons [label of the irreducible representation of U(4)] and is related to the total number of bound states supported by the potential well. Equivalently, one can put it in a one-to-one correspondence^{20,21} with the anharmonicity parameters x_e by means of:

$$\mathbf{x}_{\mathrm{e}} = \frac{1}{N+2} \qquad \dots (14)$$

Equation (14) can be rewritten as:

$$N = \left(\frac{e}{e^{x_e}}\right) - 2$$
, where, e, is spectroscopic constants ... (15)

Equations (14) and (15) show how the vibron number (N) of a particular diatomic bond is related to its anharmonicity ($_{e}$) and anharmonicity constants ($_{e}x_{e}$). The anharmonicity ($_{e}$) and anharmonicity constants ($_{e}x_{e}$) for the diatomic molecules of the type XY are obtained by analysis of rotational-vibrational fine structures of infrared or Raman spectra in the gaseous phase^{37,38}. Equations (14) and (15) indicate

Table 1 – Locality parameters () for different isotopic species of hydrogen sulphide, hydrogen selenide and water

Molecule	Locality parameter()
H_2S^{32}	0.0697
D_2S^{32}	0.0092
H_2Se^{80}	0.0739
D_2Se^{80}	0.0817
H_2O^{17}	0.3031
T_2O^{16}	0.5327

that one can have the initial guess for the vibron number (*N*) of a particular diatomic bond directly from the values of $_{e}$ and $_{e}x_{e}$.

For a bent XY₂ molecule, one can have the values of $_{e}$ and $_{e}x_{e}$ for the XY bond from the reference^{37,38}. Using the values of $_{e}$ and $_{e}x_{e}$ for the bond XY, one can have the initial guess for the value of the vibron number *N* from Eq. (15). In the U(4) algebraic model, there is provision to change (not more than ±20%) the value of *N* to get better results. This is equivalent to change the single-bond anharmonicity according to the specific molecular environment, in which it can be slightly different.

In case of a bent XY₂ molecule, two bonds are identical (XY, XY). Hence, one shall get here, $N_1 = N_2 = N$ (say). Similarly, also one shall have here, $A_1 = A_2 = A$ (say) corresponding to the similar bonds XY and XY. When N is determined, using the necessary observed energy levels from the data base, one can have the initial guess for the parameters A ($A_1 = A_2 = A$), A_{12} and $_{12}$. Starting from this initial guess, to get better results, the values of A ($A_1 = A_2 = A$), A_{12} and $_{12}$ can be adjusted using the numerical fitting procedure (in a least square sense). It may be noted here that during the calculation of the vibrational energy levels of a bent XY₂ molecule, the values of N_1 and N_2 are kept fixed and not used as free parameters.

3 Results and Discussion

In this work, the vibrational spectral analysis of the isotopic species of hydrogen sulphide, hydrogen selenide and water using a minimum number of parameters in U(4) algebraic model are demonstrated. The isotopic species of hydrogen sulphide, hydrogen selenide and water approximated in this study are H_2S^{32} , D_2S^{32} , H_2Se^{80} , D_2Se^{80} , H_2O^{17} and T_2O^{16} . To serve the purpose, around nine calculated vibrational energy levels of the mentioned isotopic species of hydrogen sulphide, hydrogen selenide and water have been shown in Tables 2-7 along with the corresponding available observed vibrational energy levels. In this study, only two and three algebraic parameters are used for the local mode and local to normal transition study, respectively. Locality parameters () for the mentioned isotopic species of hydrogen sulphide, hydrogen selenide and water have been shown in Table 1. In accordance with the values of locality parameters, attempt has been made to study the isotopic species of hydrogen sulphide and hydrogen

Table 2 — Vibrational energy levels of H_2S^{32} (cm ⁻¹)						
a	b	с	Expt ^a	Calc ^b	$\Delta^{\rm c}$	$\Delta^{\!\!\!d}$
0	1	0	1182.6	1191.62	-9.02	0.76
1	0	0	2614.4	2626.79	-12.39	0.47
0	0	1	2628.5	2626.79	+1.71	0.07
0	2	0	2354.0	2354.18	-0.18	0.01
1	1	0	3779.2	3789.35	-10.15	0.27
0	1	1	3789.3	3789.35	-0.05	0.00
2	0	0	5145.1	5154.50	-9.40	0.18
0	2	1	4939.2	4922.84	+16.36	0.33
2	1	0	6288.2	6288.00	+0.20	0.00

 Δ (r.m.s.) = 8.80 cm⁻¹

[a- Source: Refs³⁹⁻⁴⁴;

 $b^-N_1 = N_2 = 41$, $A_1 = A_2 = -8.751$, $A_{12} = -3.633$; A_1 , A_2 , A_{12} all are in cm⁻¹ except N_1 and N_2 which are dimensionless;

c - (Expt – Calc);

d - Percentage of error= ((Expt~Calc)/Expt) \times 100]

Table 3 — Vibrational energy levels of D_2S^{32} (cm ⁻¹)							
a	b	с	Expt ^a	Calc ^b	$\Delta^{\rm c}$	$\Delta^{\!\!\!\!\!\!d}$	
0	1	0	855.40	855.41	-0.01	0.00	
1	0	0	1896.38	1897.70	-1.32	0.07	
0	0	1		1897.70			
0	2	0		1696.31			
1	1	0	2742.77	2738.61	+4.16	0.15	
0	1	1	2754.44	2738.61	+15.83	0.57	
1	0	1		3780.90			
0	0	2		3745.57			
1	1	1	4592.32	4607.31	-14.99	0.33	
,		~	o. 4 −1				

 $\Delta(r.m.s.) = 9.94 \text{ cm}^3$

[a- *Source*: Refs⁴⁵;

b - $N_1 = N_2 = 59$, $A_1 = A_2 = -4.4165$, $A_{12} = -1.8123$; A_1 , A_2 , A_{12} all are in cm⁻¹ except N_1 and N_2 which are dimensionless; c⁻(Expt – Calc);

d - Percentage of error= ((Expt~Calc)/Expt) \times 100]

	Та	able	4 — Vibrational er	nergy levels of	H_2Se^{80} (cm ⁻¹))
a	b	с	Expt ^a	Calc ^b	$\Delta^{\rm c}$	$\Delta^{\!\!\!\!\!d}$
0	1	0	1034.17	1053.99	-19.82	1.91
1	0	0	2344.36	2351.00	-6.64	0.28
0	0	1	2357.66	2351.00	+6.66	0.28
0	2	0	2059.97	2037.73	+22.24	1.07
1	1	0	3361.72	3334.74	+26.98	0.80
0	1	1	3371.81	3334.74	+37.07	1.09
1	0	1	4617.40	4631.76	-14.36	0.31

 Δ (r.m.s.) = 21.66 cm⁻¹

[a- Source: Refs⁴⁵;

b - $N_1 = N_2 = 15$, $A_1 = A_2 = -21.6169$, $A_{12} = -8.7833$; A_1 , A_2 , A_{12} all are in cm⁻¹ except N_1 and N_2 , which are dimensionless;

c - (Expt - Calc);

d - Percentage of error = $((Expt~Calc)/Expt) \times 100)$]

Table 5 — Vibrational energy levels of $D_2Se^{80}(cm^{-1})$						
а	b	с	Expt. ^a	Calc. ^b	$\Delta^{\rm c}$	$\Delta^{\!\!\!\!\!\!d}$
0	1	0	741.42	741.43	-0.01	0.00
1	0	0	1686.70	1692.04	-5.34	0.32
0	0	1	1697.36	1692.04	+5.32	0.31
0	2	0		1441.66		
1	1	0		2392.27		
0	1	1		2392.27		
1	0	1		3342.88		
0	0	2		3237.26		
2	0	0		3237.26		

 Δ (r.m.s.) = 4.35 cm⁻¹

[a- Source: Refs⁴⁵;

b - $N_1 = N_2 = 18$, $A_1 = A_2 = -13.2029$, $A_{12} = -5.1488$; A_1 , A_2 , A_{12} all are in cm⁻¹ except N_1 and N_2 which are dimensionless; c - (Expt – Calc);

d - Percentage of error= $((Expt~Calc)/Expt) \times 100$]

	Table 6 — Vibrational energy levels of H_2O^{17} (cm ⁻¹)							
a	b	с	Expt ^a	Calc ^b	Δ^{c}	$\Delta^{\!\!\!\!d}$		
0	1	0	1591.32	1591.33	-0.01	0.00		
1	0	0	3653.15	3653.14	+0.01	0.00		
0	0	1	3748.32	3748.31	+0.01	0.00		
0	2	0	3144.98	3147.63	-2.65	0.08		
1	1	0	5227.75	5209.44	+18.31	0.35		
0	1	1	5320.26	5304.61	+15.65	0.29		
1	0	1	7238.73	7240.69	-1.96	0.03		
0	0	2		7253.81				
2	0	0		7199.54				

 Δ (r.m.s.) = 9.19 cm⁻¹

[a - *Source*: Refs⁴⁵;

b - $N_1 = N_2 = 40$, $A_1 = A_2 = -14.0759$, $A_{12} = -4.3781$, $_{12} = +1.1896$; A_1 , A_2 , A_{12} , $_{12}$ all are in cm⁻¹ except N_1 and N_2 , which are dimensionless;

c - (Expt – Calc);

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d - Percentage of error= ((Expt~Calc)/Expt) × 100]
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	Table 7 — Vibrational energy levels of T_2O^{16} (cm ⁻¹)							
а	b	с	Expt ^a	Calc ^b	$\Delta^{\rm c}$	$\Delta^{\!\!\!\!d}$		
0	1	0	995.37	995.38	-0.01	0.00		
1	0	0	2237.15	2237.16	-0.01	0.00		
0	0	1	2366.61	2366.62	-0.01	0.00		
0	2	0		1978.27				
1	1	0		3220.06				
0	1	1		3349.51				
1	0	1		4697.80				
0	0	2		4540.43				
2	0	0		4433.93				

 Δ (r.m.s.) = 0.01 cm⁻¹

[a - *Source*: Refs⁴⁵;

b - $N_1 = N_2 = 59$, $A_1 = A_2 = -6.3589$, $A_{12} = -1.5603$, ${}_{12} = +1.0971$; A_1 , A_2 , A_{12} , ${}_{12}$ all are in cm⁻¹ except N_1 and N_2 , which are dimensionless;

c - (Expt – Calc);

d - Percentage of error= ((Expt~Calc)/Expt) × 100]

selenide using the local mode Hamiltonian of the U(4) algebraic model. The isotopic species of water have been studied using the local to normal transition technique of the U(4) algebraic model.

In Tables 2 and 3, the calculated vibrational energy levels of the isotopic species of hydrogen sulphide are shown for some nine vibrational bands within the framework of the U(4) algebraic model using only two algebraic parameters. For the nine vibrational bands, here the RMS deviation for H_2S^{32} is reported as 8.80 cm⁻¹ (Table 2). In Table 3, the calculated vibrational energy levels of D_2S^{32} are shown. From the database, one could not have the observed vibrational energy levels for the bands (001), (020), (101) and (002) of D_2S^{32} . Hence, the calculated energy levels corresponding to these bands have been kept here only as predicted vibrational energy levels. The RMS. deviation for D_2S^{32} also has been calculated here excluding the mentioned predicted bands and the same has been reported as 9.94 cm⁻¹. Calculated vibrational energy levels of the isotopic species of hydrogen selenide have been shown in Tables 4 and 5. Here, also only two parameters are used in the U(4) algebraic model. In Table 4, for some seven vibrational bands, the RMS deviation is reported as 21.66 cm⁻¹ for the H₂Se⁸⁰ molecule. For the D_2Se^{80} molecule, one could have only three observed levels from the database. Hence, six out of the nine calculated vibrational energy levels of D_2Se^{80} have been left as predicted energy levels in Table 5. Here, predicted vibrational energy levels are corresponding to the bands (020), (110), (011), (101), (002) and (200). Excluding the predicted energy levels, here the RMS deviation for D₂Se⁸⁰ is reported as 4.35 cm⁻¹ (Table 5). In Tables 2-5, besides the RMS deviation, the percentage of error corresponding to each of the relevant cases of the calculated vibrational energy levels is also shown. It may be seen from Tables 2-5 that in each case, the percentage of error is either negligible or very small. This tells that the local mode Hamiltonian of the U(4) algebraic model may be a right choice to be used for the approximation of the isotopic species of hydrogen sulphide and hydrogen selenide. From Tables 1-5, it is clear that in accordance with the definition and conception of locality parameter, both the isotopic species of hydrogen sulphide and one of the isotopic species (D_2Se^{80}) of hydrogen selenide could be approximated very well using the local mode Hamiltonian of the U(4) algebraic model. This confirms that intermode couplings for these molecules are poor. However, from Table 4, it can be seen that one of the isotopic species (H_2Se^{80}) of hydrogen selenide, declined to obey the track properly as predicted by section 2.2 and Table 1. This indicates that the intermode couplings in case of H_2Se^{80} may be prominent to some extent compared to the present prediction and Table 1.

From Table 1, it can be seen that the locality parameters of the isotopic species of water approximated in this study are with higher values compared to those of the isotopic species of hydrogen sulphide and hydrogen selenide. Hence, attempt has been made here to study the vibrational spectra of the isotopic species of water using the local to normal transition technique of the U(4) algebraic model. Results reported in Tables 6 and 7 for the isotopic species of water, confirm the validity of the choice of the model. These results also confirm the presence of prominent intermode couplings in the isotopic species of water approximated in this study.

The detailed results are reported in Tables 6 and 7 for the isotopic species of water. The calculated energy levels are shown in Table 6 for H_2O^{17} for some nine vibrational bands. From the database, one cannot have the observed energy levels for the vibrational bands (002) and (200). Under such circumstances, calculated energy levels for the mentioned bands are left here as predicted vibrational energy levels. Excluding these two bands, RMS deviation for H_2O^{17} has been reported as 9.19 cm⁻¹. It's a good approximation for a theoretical model when the model uses only three parameters $(A, A_{12} \text{ and } _{12})$ in order to perform the process. Database for observed vibrational energy levels of T_2O^{16} is found to be very poor. One can have only three fundamental vibrational energy levels of T_2O^{16} from the database. Under such circumstances, six out of nine calculated vibrational energy levels of T_2O^{16} are left as predicted energy levels in Table 7. Predicted energy levels are corresponding to the vibrational bands (020), (110), (011), (101), (002) and (200). With the observed vibrational energy levels, the RMS deviation for T_2O^{16} has been reported here as 0.01 cm⁻¹. Along with deviation, corresponding to each of the relevant cases of the calculated vibrational energy levels, the percentage of error is also shown here in Tables 6 and 7. One can see that percentage of error in each case is either negligible or very small. This tells that the local to normal transition technique of the U(4) algebraic model may be the best fit for the vibrational spectral

analysis of the isotopic species of water. This also gives us the firm footing to say that the intermode couplings in all the mentioned isotopic species of water are more prominent compared to those of the isotopic species of hydrogen sulphide and hydrogen selenide. Introducing the Majorana operator, when the more prominent intermode couplings are taken care of in the local to normal transition study of the U(4)algebraic model, obviously one should get better results for a molecule showing more prominent intermode couplings. In terms of locality parameter (), a straight forward comparison of intermode couplings of different molecules under this study also may be obtained from this work (Table 1). As per the information obtained from the locality parameters, intermode couplings in D_2S^{32} should be less prominent than those of H_2S^{32} . Similarly, intermode couplings in D₂Se⁸⁰ should be more prominent than those of H₂Se⁸⁰. For the isotopic species of water, as per this study, the descending order of intermode couplings should be found in the series T_2O^{16} , H_2O^{17} . The nature of the intermode couplings demands that the U(4) algebraic model, in its local to normal transition should approximate T_2O^{16} better compared to H_2O^{17} . From Tables 6 and 7, it can be seen that the expected results for T_2O^{16} and H_2O^{17} exactly have been reflected in the trend of this study. It may be noted here that only on the basis of this study one is not in a position to provide an accurate theoretical verification of the comparison of intermode couplings among the mentioned isotopic species of all the molecules reported. This is due to the fact that one cannot have all the observed energy levels corresponding to the calculated vibrational energy levels of the molecules reported in this study. However, the predicted vibrational energy levels reported in this study for the isotopic species of hydrogen sulphide, hydrogen selenide and water may provide help to the experimental researchers for their further research.

To have a comparison of the present study with that of other traditional approaches, one should note here that the algebraic approach is especially useful when the potential energy surface is unknown or when it is too difficult to calculate the spectrum by starting with the potential surface using the traditional approaches. For example, in a large molecule (larger than a diatomic), the potential surface is a very complex function, composed of a discouragingly large number of coordinates. Under such circumstances, the traditional approaches face a tremendous difficulty in approximating the molecule as soon as one considers the highly excited levels. Further, a large number of parameters are also required here to obtain meaningful results. On the other hand, the algebraic approach needs a much more economical set of parameters to provide the fits of the spectra. This is a very important practical advantage of the algebraic approach over the traditional approaches. In algebraic approach, there are general forms of algebraic Hamiltonian and by using a common Hamiltonian entire classes of molecules can be approximated by changing only the parameters (typically linear) for different molecules. This is another remarkable advantage of the algebraic approach over the traditional approaches. Reference to this advantage of the algebraic approach, one can see that with the general form of the algebraic Hamiltonian (5), all other bent XY₂ molecules similar to that of the isotopic species of hydrogen sulphide, hydrogen selenide and water, can also be approximated well. Finally, one should also note the comparative ease of the algebraic operations used in the algebraic approach. This is a technical advantage of the algebraic approach over the traditional approaches.

4. Conclusions

In this study, vibrational spectral analysis of some isotopic species of hydrogen sulphide, hydrogen selenide and water using the U(4) algebraic model is reported. Local mode Hamiltonian of the U(4) algebraic model has been applied for the vibrational spectral analysis of the isotopic species of hydrogen sulphide and hydrogen selenide. For the vibrational spectral analysis of the isotopic species of water, the local to normal transition technique of the U(4)algebraic model is applied here. This study makes it clear that in algebraic approach, there are generic forms of algebraic Hamiltonians and the vibrational spectra of entire class of specific molecules can be described by a common Hamiltonian, where only the (typically linear) parameters are different for the different molecules. Hence, the techniques of the U(4)algebraic model used in this study can be applied in the vibrational spectral analysis of all bent XY_2 molecules in general.

On the basis of the present study, it is clear that the vibrational spectral analysis of the isotopic species of hydrogen sulphide, hydrogen selenide and water is possible with a good accuracy using the U(4) algebraic model only with two or three algebraic

parameters. To provide the same accuracy in traditional approaches, one will have to use more number of parameters. From this study, further it can be concluded that in general, the U(4) algebraic model provides a good accuracy in the vibrational spectral analysis of bent XY₂ molecules using only a fewer parameters compared to that of other traditional approaches. It is also clear that H_2S^{32} , D_2S^{32} , and D₂Se⁸⁰ show more local behaviour as intermode couplings in these molecules are poor. Obviously, Majorana and other intermode interactions are negligibly small for these molecules. As per the prediction of the U(4) algebraic model, H_2Se^{80} also shows more local behaviour but the results reported in this study for H₂Se⁸⁰ witness some deviation from the expected track. In the light of Majorana and other intermode interactions, this deviation may lead to a topic of further research. From the overall study, it may be concluded that the intermode couplings in the isotopic species of water are more prominent compared to that of the isotopic species of hydrogen sulphide and hydrogen selenide. Hence, it is obvious that the isotopic species of water show less local behaviour compared to those of the isotopic species of hydrogen sulphide and hydrogen selenide. For the isotopic species of same molecule, intermode couplings in H_2S^{32} are more than that of D_2S^{32} and D_2Se^{80} show more intermode couplings than that of H_2Se^{80} . In case of isotopic species of water, the serial descending order of intermode couplings are found in the series T_2O^{16} , H_2O^{17} .

Finally, it may be noted here that the U(4) algebraic model can approximate a lower order polyatomic molecule in a better way than that of the U(2) algebraic model. But the problem till persists with the U(4) algebraic model is that the matrix formulation of the model becomes more and more complicated as one proceeds towards higher order polyatomic molecules. Due to this reason, the model can have its easy access till today only up to the limit of linear tetratomic molecules. It is hoped that this study will stimulate further research in near future in the sector of the U(4) algebraic model in order to approximate large (larger than tetratomic) polyatomic molecules in general and large (larger than triatomic) bent polyatomic molecules in particular.

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