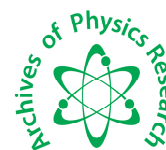




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Study of the vibrational spectra of H_2S and H_2O^{16} : An algebraic approach

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ABSTRACT

Using the algebraic model, in this work a study of the vibrational spectra of H_2S and H_2O^{16} has been reported. To give a deep insight into detailed spectroscopy for these bent XY_2 molecules, the inclusion of intermode couplings in algebraic models has been addressed. The aid of a new set of improved algebraic parameters to achieve improved RMS deviations also has been studied for these bent XY_2 molecules.

Keywords : Vibrational spectra; Lie algebra; H_2S ; H_2O^{16}

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INTRODUCTION

Since its inception, molecular spectroscopy has been an area of active interest from many stand points. This branch of Physics has been playing an essential role in both experimental and theoretical approaches to understand an enormous number of important problems of physical science as well as many other scientific areas. Importance of molecular spectroscopy has been revealed due to the interplay between quantum theory and experiments. This significance along with the continuous development of more powerful experimental techniques has been attracting a wider scientific community to the field of molecular spectroscopy. At present, molecular spectroscopy is going through an exciting time of renewed interest.

To maintain resonance with the rapid advancement of the experimental observations, theoretical physics is also constantly being tested to provide the satisfactory models that can account for the observations in its befitting manner. In this regard, it may be noted here that as a consequence of these new and quite often unexpected experimental results, an unprecedented effort towards constructing alternative theoretical models has been taken place in recent years. In the study of the molecular spectroscopy, these alternative theoretical models can act as concrete and complementary techniques to the traditional approaches. One such recently launched successful alternative theoretical model in the study of molecular spectroscopy is the algebraic model.

The algebraic approaches to complex spectra already have been proved useful in the fields of spectroscopy. Very detailed and yet simple description of complex rotation – vibration spectra[1] in nuclear physics has been well described using the algebraic approaches. We may thus expect that the similar techniques may also provide a relatively simple way to describe the rotation – vibration spectra in molecular physics.

It may be noted here that the algebraic approaches already have been used in molecular physics also. C. E. Wulfman and R. D. Levine studied[2] the ideal case of a one – dimensional Morse oscillator, whose energy levels can be written in the form

$$E(n) = - A(k - n)^2 \quad (1)$$

where k the total number of bound states, n the vibrational quantum number ($n = 0, 1, \dots, k$) and A is a constant. When an auxiliary label $m (= k - n)$ is introduced, the expression (1) can be written as

$$E(m) = - Am^2. \quad (2)$$

Wulfman and Levine described the spectrum generating algebra(SGA) for this problem as $SO(3) \approx SU(2)$. Using this ‘dynamical algebra’, Wulfman and Levine calculated several properties of the system.

In the light of the above study of Wulfman and Levine, later, it was proposed by Iachello[3] that it is possible to construct an SGA or ‘dynamical algebra’, to describe(within a certain approximation) the realistic rotation – vibration spectra in three dimensions. The algebra proposed by Iachello is $U(4)$, the algebra of the unitary group in four dimensions. From the group theoretical point of view, this algebra is on one hand, the simplest extension of the Wulfman – Levine algebra $U(2)$, and on the other hand, a simplification of the algebra, $U(6)$, of nuclear rotation – vibration spectra. It may be noted here that in general it is possible to construct[3] SGA of rotation – vibration spectra in r dimensions by making use of the groups $U(r + 1)$. In this regard, it may be seen that the Wulfman – Levine algebra corresponds to $r = 1$, the algebra we shall use in this study corresponds to $r = 3$ and the algebra reported in reference[1] corresponds to $r = 5$ [4].

As a concrete and complementary technique to conventional approaches, the algebraic models already have been proved successful in the study of the vibrational spectra of small and medium-sized molecules[5-6]. Some triatomic(linear), tetratomic(linear) and large molecules we studied[7- 18] earlier using the $U(4)$ and $U(2)$ algebraic models. In this work a study of the vibrational spectra of the bent XY_2 molecules H_2S and H_2O^{16} has been reported using the $U(4)$ algebraic model. To give a deep insight into detailed spectroscopy for these bent XY_2 molecules, the inclusion of intermode couplings in algebraic models has been addressed. In this study, the aid of a new set of improved algebraic parameters also has been reported to achieve improved RMS deviations for these bent XY_2 molecules.

2. Review of the theory

The theory of the $U(4)$ algebraic model[5-6,19] to be used in this study for the approximation of bent XY_2 molecules has been discussed below in detail.

2.1 Coupling of bonds in the algebraic theory[7, 15]

To study the vibrational spectra of triatomic molecules, in the algebraic models there are two main ways in which the bonds can be coupled [6]

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

$$U_1(4) \otimes U_2(4) \supset U_{12}(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \quad (II)$$

Which correspond to local and normal coupling respectively. For these two situations the Hamiltonian operator can be diagonalized analytically.

The local basis is characterized by the representations of chain I [5-6],

$$\left. \begin{array}{ccccccc} U_1(4) & \otimes & U_2(4) & \supset & O_1(4) & \otimes & O_2(4) & \supset & O_{12}(4) & \supset & O_{12}(3) & \supset & O_{12}(2) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ [N_1] & & [N_2] & & (\omega_1, 0) & & (\omega_2, 0) & & (\tau_1, \tau_2) & & J & & M_J \end{array} \right\} \quad (4)$$

The numbers N_1, N_2 are the vibron numbers of each bond. The numbers $\omega_1, \omega_2, \tau_1, \tau_2$ are related to the vibrational quantum numbers and J, M_j represent the usual angular momentum quantum numbers[15].

2.2 Local-mode Hamiltonian for bent triatomic molecules

For bent triatomic molecules we can construct the local mode Hamiltonian[2, 5-6, 19] as

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

In Equation (5) E_0 is the zero of the energy scale, A_1, A_2, A_{12} , and \bar{A}_{12} are the algebraic parameters, $C(O(4_1)), C(O(4_2)), C(O(4_{12}), \bar{C}(O(4_{12}))$, and $C(O(3_{12}))$ are the bilinear Casimir invariants corresponding to the groups in chain I(Equation 3), and B is the rotational constant.

The eigen values of the bilinear Casimir invariants corresponding to the groups in chain I(Equation 3) are given by

$$\begin{aligned} C(O(4_1)) &\rightarrow \omega_1(\omega_1 + 2) \\ C(O(4_2)) &\rightarrow \omega_2(\omega_2 + 2) \\ C(O(4_{12})) &\rightarrow \tau_1(\tau_1 + 2) + \tau_2^2 \\ \bar{C}(O(4_{12})) &\rightarrow \tau_2(\tau_1 + 1) \\ C(O(3_{12})) &\rightarrow J(J + 1) \end{aligned} \quad (6)$$

This allows us to say that the Hamiltonian(5) is diagonal in the local basis(4) with eigen values

$$\begin{aligned} E(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J, M_j) &= E_0 + A_1 \omega_1(\omega_1 + 2) + A_2 \omega_2(\omega_2 + 2) \\ &\quad + A_{12}[\tau_1(\tau_1 + 2) + \tau_2^2] + \bar{A}_{12}[\tau_2(\tau_1 + 1)] \\ &\quad + B J(J + 1) \end{aligned} \quad (7)$$

The last term in the right hand side of Equation(7) represents the rotational part.

The rotational constant B is related to the rigid rotational motion of the molecule.

For our study, we consider the simple case in which $\bar{A}_{12} = 2A_{12}$. The energy eigen values(7) then can be written as

$$\begin{aligned} E(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J, M_j) &= E_0 + A_1 \omega_1(\omega_1 + 2) + A_2 \omega_2(\omega_2 + 2) \\ &\quad + A_{12}[(\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2)] + B J(J + 1) \end{aligned} \quad (8)$$

Introducing the local vibrational quantum numbers, v_a, v_b, v_c (Fig.1), the expression(8) can be converted to the usual spectroscopic notation. The relation between the two sets of quantum numbers can be stated as follows :

$$\begin{aligned} \omega_1 &= N_1 - 2v_a \\ \omega_2 &= N_2 - 2v_c \\ \tau_1 &= N_1 + N_2 - 2v_a - 2v_b - 2v_c - K \\ \tau_2 &= K \end{aligned} \quad (9)$$

Here one of the quantum numbers, τ_2 , now has been converted to the quantum number K describing the projection of the rotational angular momentum on the molecular fixed axis. The quantum numbers v_a , v_c denote here local stretching vibrations, while the quantum numbers, v_b , denote the bending vibrations(Fig.1).

We are now in a position to focus our attention on the vibrational part of the spectrum given by the Equation (8). This is achieved simply by putting $B = 0$ in Equation(8). As we are not interested here in rotational levels, the contribution to the spectrum from the quantum number K must collapse on the corresponding vibrational level. It can be seen from above that this has been achieved here simply by letting $\bar{A}_{12} = 2A_{12}$. The resulting spectrum is a purely vibrational one and represents a bent triatomic molecule in the strict local limit. Using Equation (9), we can rewrite the Equation (8) in terms of the set of vibrational quantum numbers (v_a , v_b , v_c) to get the resulting spectrum, which now becomes

$$E(v_a, v_b, v_c) = E_0 - 4A_1[(N_1 + 1)v_a - \mathcal{V}_a^2] - 4A_2[(N_2 + 1)v_c - \mathcal{V}_c^2] - 4A_{12}[(N_1 + N_2 + 1)(v_a + v_b + v_c) - (v_a + v_b + v_c)^2] \quad (10)$$

In Equation (10), one should note that while the terms involving A_1 and A_2 may be related to local stretching vibrational modes, the term in A_{12} must take into account the bending mode and also interactions between modes. Also it may be noted here that in this study, in each case, E_0 , the zero of the energy scale is chosen as the lowest vibrational level, $(0, 0, 0)$ (the ground vibrational level).

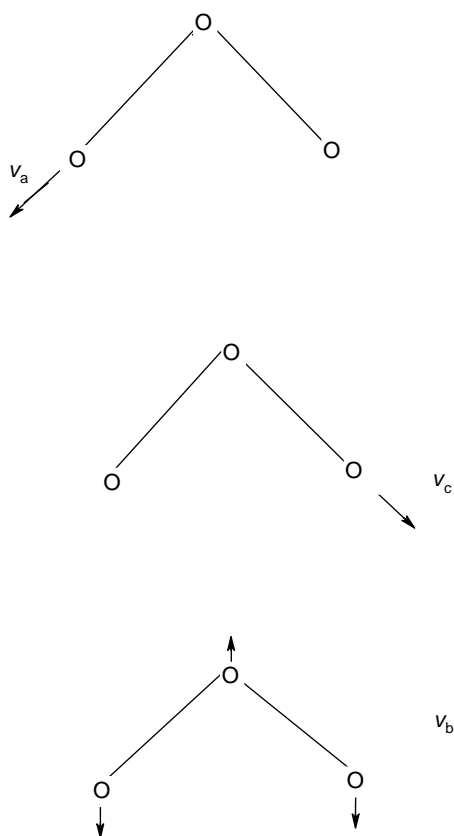


Fig.1 Local vibrational quantum numbers of bent triatomic(XY_2) molecules.

2.3 Intermode couplings in U(4) algebraic models : Majorana operator

It is observed that even for a good local molecule, especially at higher excitation energies, local vibrations start to mix among themselves to some extent. In algebraic U(4) models, such couplings can only be accommodated by an operator known as Majorana operator (M_{12}) [5-6]. In such a case, to have the proper approximation of the picture, we are to add non-diagonal interactions to our initial local model. It may be noted that for symmetric molecules, local-mode 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' chain [6]. 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 (τ_1, τ_2) of $O_{12}(4)$, couples states satisfying the selection rules $\Delta\omega_1 = 0, \pm 2$; $\Delta\omega_2 = 0, \pm 2$.

On the basis of the above cited preamble, now we can see the realistic case of a bent triatomic molecule in which local modes (either stretching or bending) are allowed to interact among themselves. Already it is told above that in the algebraic framework, this kind of interaction is properly accounted for by M_{12} . It should be noted here that in the three-dimensional algebraic model the preserved symmetry is $O_{12}(4)$ since it appears in both local and normal sub-algebra chains [6]. In the present case (this study), we therefore expect to have a block-diagonal structure of the Hamiltonian matrix. The conserved quantum numbers are now (τ_1, τ_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 (τ_1, τ_2) 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

$$\nu_{\text{Total}} = \nu_a + \nu_b + \nu_c \quad (11)$$

2.4 Local to normal transition

For bent triatomic molecules the local to normal transition can be described by combining the operators of the local chain with those of the normal chain. To serve the purpose in its befitting manner, it is convenient here to introduce M_{12} . To study the local to normal transition of bent triatomic (XY_2) molecules, at the very outset once again we consider the Equation (5). Since all terms in Equation (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. As stated earlier, the transition from local to normal can be achieved in the algebraic approach by introducing another class of operators, called Majorana operators. These operators are non-diagonal in the local mode basis, but the matrix elements of these operators we can compute very easily [5, 19]. These operators have matrix elements that induce both local mode couplings (which replace the Darling-Dennison couplings of the traditional Dunham expansion) and Fermi couplings [5]. The former are particularly important for the class of bent XY_2 molecules that we are describing in this study. It may be noted here that for bent triatomic molecules, in lowest order, there is only one such operator. Addition of this operator results the Hamiltonian

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

In Equation (12) we have deleted all the terms contributing to rotational energies.

In the light of the Section 2.3, we may now explicitly analyze the couplings induced by M_{12} . Since this operator is diagonal in the $O_{12}(4)$ basis, it couples only states with the same (τ_1, τ_2) quantum numbers. In bent triatomic molecules, where Equation (9) applies, this implies a coupling between all states with $\nu_a + \nu_b + \nu_c = \text{constant}$. It may be noted that to leading order in N , the couplings induced by the Majorana operator (M_{12}) are identical to the local mode couplings [20], while to next order, \sqrt{N} , they induce Fermi type couplings [5-6]. The situation is thus similar to that described in the study of Halonen and Carrington [21]. Also it may be noted that the local mode couplings, when converted to a normal mode picture, induce Darling-Dennison couplings [21]. Considering the Hamiltonian (12), the matrix elements of M_{12} from the references [5, 19], and the algebraic parameters from the subsequent section, we can have the energies of the different vibrational bands in terms of the algebraic parameters A, A_{12}, λ_{12} and N (independent parameter).

2.5 Determination of $N_1, N_2, A_1, A_2, A_{12}$ and λ_{12}

The number N [total number of bosons, label of the irreducible representation of $U(4)$] is related to the total number of bound states supported by the potential well. Equivalently it can be put in a one-to-one correspondence[5-6] with the anharmonicity parameters x_e by means of

$$x_e = \frac{1}{N + 2} \quad (13)$$

We have from Equation (13), $x_e = \frac{1}{N + 2}$; which we can rewrite as

$$N = \left(\frac{\omega_e}{\omega_e x_e} \right) - 2, \quad \omega_e \rightarrow \text{spectroscopic constant.} \quad (14)$$

Now, for a bent XY_2 molecule, we can have the values of ω_e and $\omega_e x_e$ for the XY bond from the study of K.P. Huber and G. Herzberg[22]. Using the values of ω_e and $\omega_e x_e$ for the bond XY we can have the initial guess for the value of the vibron number N from Equation (14). It may be noted here that in the algebraic approach, there is provision to change(not more than $\pm 20\%$) 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 triatomic molecule XY_2 , two bonds are identical(XY, XY). Hence here we shall get $N_1 = N_2 = N$ (say). Similarly, here also we shall have $A_1 = A_2 = A$ (say) corresponding to the similar bonds XY and XY .

When N is determined, parameters A ($A_1 = A_2 = A$), A_{12} and λ_{12} can be determined as follows :

Taking necessary observed energy levels from the data base, using the Hamiltonian(12), we can have the initial guess for the parameters A ($= A_1 = A_2$), A_{12} and λ_{12} . Starting from this initial guess, to get better results, the values of A ($= A_1 = A_2$), A_{12} and λ_{12} can be adjusted using the numerical fitting procedure(in a least square sense).

2.6 Locality parameter

Both for bent and linear triatomic molecules, corresponding to the two bonds, in general there are two locality parameters[5-6] given by

$$\xi_i = \frac{2}{\pi} \tan^{-1} \left[\frac{8\lambda_{12}}{(A_i + A_{12})} \right], \quad i = 1, 2. \quad (15)$$

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

A global locality parameter both for bent and linear triatomic molecules can be defined as the geometric mean [5]

$$\xi = \sqrt{(\xi_1 \xi_2)} \quad (16)$$

It should be noted here that both for bent and linear XY_2 molecules $A_1 = A_2$, and hence for these molecules $\xi_1 = \xi_2$.

With this definition[5-6,20] due to Child and Halonen[20], local-mode molecules are near to the $\xi = 0$ limit and normal mode molecules have $\xi \rightarrow 1$.

Locality parameters of the bent XY_2 molecules H_2S and H_2O^{16} are given in Table.1.

Table.1 Locality parameters of H_2S and H_2O^{16} .

Molecule	Locality parameter(ξ)
H_2S	0.07
H_2O^{16}	0.31

RESULTS AND DISCUSSION

Using the concepts of the study of Child and Halonen[20], from the value of the locality parameter [5-6] we can have a guess regarding the behaviour (local or normal) of a molecule. It may be noted here that the situation in case of bent XY_2 molecules will be different with respect to the linear triatomic & tetraatomic molecules we studied earlier[7, 8, 15]. In case of bent XY_2 molecules, the two stretching modes (1 0 0) and (0 0 1) have the same energy and therefore couple strongly, leading to normal behaviour in general.

A comparison of the observed vibrational energy levels of H_2S [23] and those calculated using the $U(4)$ algebraic model has been shown in Table 2. A comparison of the observed vibrational energy levels of H_2O^{16} [24] and those calculated using the $U(4)$ algebraic model has been shown in Table 3. In Table 2 and Table 3 we have shown the calculated vibrational energy levels of H_2S and H_2O^{16} for some 9 vibrational bands using the algebraic model. For 9 vibrational bands, here we have reported the RMS deviation(Δ (r.m.s.)) for H_2O^{16} as 7.4 cm^{-1} . We could not have the observed value of the vibrational band (0 0 2) of H_2S from the database available to us. Hence, RMS deviation we calculated here excluding this band. The RMS deviation for H_2S we have reported in this study is 4.6 cm^{-1} . Both for H_2S and H_2O^{16} , the intermode couplings have been accounted by introducing the Majorana operator as usual. Fermi interaction is important particularly for the molecules having accidental degeneracies. Obviously this is not the case for our study. Our desire in this study is to show the improved level of accuracy of the results using the less number of algebraic parameters. Hence, intentionally we drop here Fermi interaction and higher order correction terms[5] from the Hamiltonian. The improved RMS deviations both for H_2S and H_2O^{16} may be noted in this case as soon as the intermode couplings have been taken care of by introducing the improved set of algebraic parameters. From Table 1 and as per Section 2.6 one can see that in its behaviour, H_2S should approach a local molecule. This is to say that the intermode couplings in case of H_2S must not be so much prominent as compared to the case of a normal molecule. In this regard, however, one should keep in mind that even for a good local molecule, at higher excitation energies, local vibrations start to mix among themselves to some extent resulting considerable intermode couplings. In this light, it can be expected here that at higher excitation energies, H_2S also should have considerable intermode couplings. Value of the locality parameter(Table 1) and Section 2.6 tell us that H_2O^{16} must show more normal behaviour compared to that of H_2S . This is to say that the intermode couplings in H_2O^{16} are more prominent compared to that of H_2S . Obviously, this more prominent intermode couplings of H_2O^{16} could not be accounted as good as it could be done in case of H_2S . However, using only three algebraic parameters, the more prominent intermode couplings of H_2O^{16} along with the less prominent intermode couplings of H_2S have been accommodated in this study in a better way compared to other equivalent published works[19,25] used for the vibrational spectral analysis of bent XY_2 molecule. As a result, the RMS deviations both for H_2S and H_2O^{16} have come down here to the level of the experimental accuracy. Trends of the results(Table 2 & Table 3) show that the constancy of the RMS deviation will be well maintained even when the other higher overtones are also taken under consideration. In this context also one should note that in traditional approaches [21, 26-32], a large number of parameters would be needed to attain the RMS deviations we reported in this study for H_2S and H_2O^{16} using only three parameters.

In Table 2 & Table 3, for all the calculated vibrational energy levels of H_2S and H_2O^{16} , also we have shown the percentage of error(δ). It can be seen from Table 2 & Table 3 that for each of the calculated vibrational energy level of H_2S and H_2O^{16} , the percentage of error is either negligible or very small. This confirms the accuracy of the results we have reported in this study both for H_2S and H_2O^{16} .

Finally one should note that the isotope effects for the bent XY_2 molecules can be studied by analyzing the scaling properties of the A coefficients with masses m_x and m_y [6]. It is possible to construct simple scaling laws[5-6] for the algebraic parameters relating to isotopic substitution in a bent XY_2 molecule. One can apply these rules for the prediction of vibrational spectra of isotopic species of a bent XY_2 molecule with an expected good RMS accuracy.

Table 2. Vibrational energy levels of H₂S^a

v ₁	v ₂	v ₃	Expt. ^b	Calc. ^c	Δ ^d	δ ^e
0	1	0	1182.6	1186.9	-4.3	0.4
0	0	1	2628.5	2632.8	-4.3	0.2
1	0	0	2614.4	2618.7	-4.3	0.2
0	2	0	2354.0	2345.5	+8.5	0.4
1	1	0	3779.2	3777.3	+1.9	0.1
0	1	1	3789.3	3791.4	-2.1	0.1
1	0	1	5147.4	5152.0	-4.6	0.1
0	0	2	--	5217.5	--	--
2	0	0	5145.1	5149.3	-4.2	0.1

Δ(r.m.s.) = 4.7 cm⁻¹.

^aAll energies are in cm⁻¹.

^bReferences [23]

^cN = 41, A = -8.9025, A₁₂ = -3.5326, λ₁₂ = 0.1720.

A, A₁₂, λ₁₂ all are in cm⁻¹ except N which is dimensionless.

^d(Expt. - Calc.).

^ePercentage of error f = [(Expt. - Calc.)/Expt.] × 100. }

Table 3. Vibrational energy levels of H₂O^{16a}

v ₁	v ₂	v ₃	Expt. ^b	Calc. ^c	Δ ^d	δ ^e
0	1	0	1595.0	1601.6	-6.6	0.4
0	0	1	3755.9	3762.5	-6.6	0.2
1	0	0	3657.0	3663.6	-6.6	0.2
0	2	0	3151.4	3161.9	-10.5	0.3
1	1	0	5234.9	5223.9	+11.0	0.2
0	1	1	5331.2	5322.8	+8.4	0.2
1	0	1	7249.8	7251.9	-2.1	0.0
0	0	2	7445.0	7437.5	+7.5	0.1
2	0	0	7201.5	7199.2	+2.3	0.0

Δ(r.m.s.) = 7.4 cm⁻¹.

^aAll energies are in cm⁻¹.

^bReferences [24]

^cN = 34, A = -16.6161, A₁₂ = -5.1611, λ₁₂ = 1.4544.

A, A₁₂, λ₁₂ all are in cm⁻¹ except N which is dimensionless.

^d(Expt. - Calc.).

^ePercentage of error f = [(Expt. - Calc.)/Expt.] × 100. }

CONCLUSION

A study of the vibrational spectra of bent XY₂ molecules H₂S and H₂O¹⁶ has been presented in this work using the algebraic model. Inclusion of improved set of algebraic parameters and intermode couplings in algebraic models towards achieving the improved RMS deviations as well as to give a deep insight into the detailed spectroscopy has been addressed for the molecules H₂S and H₂O¹⁶.

On the basis of the results reported here, the conclusions of the study now may be drawn as follows :

- (i) Introducing the improved set of algebraic parameters, bent XY₂ molecules H₂S and H₂O¹⁶ can be approximated very well using the algebraic model in local to normal transition.
- (ii) Using the algebraic model in local to normal transition, H₂S can be approximated better compared to that of H₂O¹⁶.
- (iii) H₂S shows more local behaviour than that of H₂O¹⁶. Intermode couplings are much more prominent in case of H₂O¹⁶ compared to that of H₂S.
- (iv) Inclusion of intermode couplings in algebraic models provides improved RMS deviations as well as a deep insight into the detailed spectroscopy both for H₂S and H₂O¹⁶.
- (v) The RMS deviations reported in this study for the bent XY₂ molecules H₂S and H₂O¹⁶ are better compared to other equivalent published works. This implies that the algebraic parameters reported in this study provide the better three parameter fits to the spectra of H₂S and H₂O¹⁶ compared to other equivalent published works.

(vi) Percentage of error for each of the calculated vibrational energy levels of H₂S and H₂O¹⁶ is either negligible or very small. This confirms the better accuracy of the results reported in this study for H₂S and H₂O¹⁶ compared to other equivalent published works.

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