



Research Paper

Vibrational energy levels computations of H₂S and its isotopologues (HDS, D₂S)

Accepted 3rd September, 2020

ABSTRACT

The vibrational energy levels of the ground state of H₂S and its isotopologues (HDS, D₂S) are determined by both the discrete variable representation for three-dimension (DVR3D) program and modified DVR3D program. The calculated results derived from the two programs were compared with available experimental results for the title systems. It is shown that the calculated results for H₂S and D₂S agree well with the experimental results and the DVR3D results for HDS were better than the results from the modified DVR3D program when compared with experimental results. It is indicated that both the DVR3D program and the modified DVR3D program have proven to be powerful tools to determine the vibrational energy levels of many triatomic systems.

Ang- yang Yu

East China Jiaotong University, Nanchang, Jiangxi province, 330013, China.

Email: wisdomyay@ustc.edu.

Key words: Vibrational energy levels, hydrogen sulfide, discrete variable representation.

INTRODUCTION

Some studies have shown hydrogen sulfide (H₂S) to have a significant signaling role in biomedicine and biology. In particular, H₂S, which is produced in the cardiovascular system of mammals, was found as what leads to dilation of blood vessels and the lowering of blood pressure. A previous study uses a unique microelectrode to measure H₂S concentration^[1]. H₂S can be measured down to less than 0.1 Micro Molar concentration (less than 100 nano Molar).

The hydrogen sulphide molecule (H₂S) has been the subject of numerous experimental spectroscopic studies due to its importance in the chemistry of the atmospheres of Venus and other planets (Ding et al, 2003; Liu et al, 2005; Liu et al, 2006; Lamouroux et al.,**2008**; Onopenko and Russ 2009; Ulenikov et al, 2009), the interstellar medium, and for terrestrial remote sensing applications. It is one of the best experimentally studied asymmetric top molecules that shows a pronounced local vibration mode character (Child, 2006; Jensen, 2012; Cruz, 2018)

The H₂S molecule plays an important role as a fertile testing ground for PES constructions (Csaszar et al, 2001; Polyansky et al, 1996) Potential energy surface for ground-state H₂S has been constructed and used in reaction dynamics calculations recently. (Song et al., 2009; Song et al., 2009) The discrete variable representation or DVR which was developed by Light and co-workers has been successfully applied to

molecular reaction dynamics and molecular spectra (Light et al, 1985; Light and Carrington, 2000).

Tennyson and co-workers published DVR3D programs for calculating triatomic molecule ro-vibrational spectra (Henderson and Sueur, 1993; Henderson et al., 1993). A modified DVR program was developed which could be used to calculate the bound vibrational states of the ground electronic state of some triatomic molecules (Yu, 2013). In the modified DVR program, the sine basis functions are chosen to define the DVR for the radial coordinates.

In this study, both the DVR3D and modified DVR3D programs are utilized to calculate the bound vibrational states of the fundamental electronic state of H₂S and its isotopologues (D₂S, HDS). The theoretical results are compared with the experimental findings.

METHODS

The discrete variable representation (DVR) has a number of advantages over more traditional basis set methods in both reducing the computational costs and the simplicity of obtaining the DVR potential energy matrix directly from the potential energy function (Schneider and Nygaard, 2002). The calculations are performed in Jacobi coordinates. The

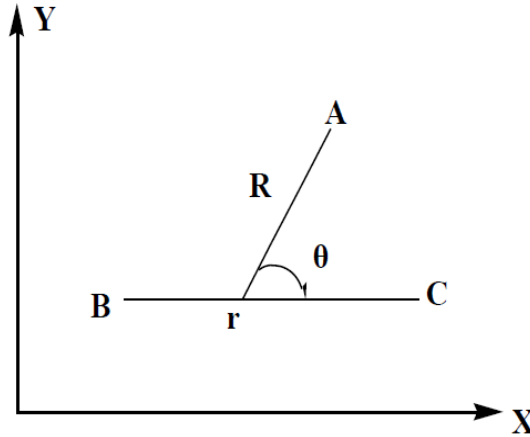


Figure 1: The Jacobi coordinates for a triatomic molecule ABC in the X-Y plane.

Jacobi coordinates for a triatomic molecule ABC have been presented in Figure 1, where R stands for the distance from A to the mass center of BC, r denotes the distance between B and C, and θ represents the angle between R and r. Using a finite basis representation (FBR), the Hamiltonian matrix for zero rotational angular momentum (J=0) can be written as (we used atomic units throughout) (Tennyson, 1986)

$$\begin{aligned} & \langle m, n, j | \hat{H} | m', n', j' \rangle \\ &= \langle m | -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} | m' \rangle \delta_{n,n'} \delta_{j,j'} + \langle n | -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} | n' \rangle \delta_{m,m'} \delta_{j,j'} \\ &+ \left(\langle m | \frac{1}{2\mu_R R^2} | m' \rangle \delta_{n,n'} + \langle n | \frac{1}{2\mu_r r^2} | n' \rangle \delta_{m,m'} \right) * j(j+1) \delta_{j,j'} \\ &+ \langle m, n, j | V(R, r, \theta) | m', n', j' \rangle, \end{aligned} \tag{1}$$

where it has been assumed that the angular basis functions

$|m\rangle, |n\rangle$ are Legendre polynomials, and $|m\rangle, |n\rangle$ are the appropriate radial basis functions. A three-dimensional DVR is obtained by applying the transformation:

$$H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} = \sum_{m,n,j} \sum_{m',n',j'} T_{m,n,j}^{\alpha,\beta,\gamma} \langle m, n, j | H | m', n', j' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \tag{2}$$

The 3D transformation is written as a product of 1D transformations:

$$T_{m,n,j}^{\alpha,\beta,\gamma} = T_m^\alpha T_n^\beta T_j^\gamma \tag{3}$$

The transformed Hamiltonian can be written at the DVR grid points as:

$$\begin{aligned} {}^{(3D)}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= \left(\sum_{m,m'} T_m^\alpha \langle m | -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} | m' \rangle T_{m'}^{\alpha'} \right) \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} \\ &+ \left(\sum_{n,n'} T_n^\beta \langle n | -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} | n' \rangle T_{n'}^{\beta'} \right) \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} \\ &+ \left(\sum_{m,m'} T_m^\alpha \langle m | \frac{1}{2\mu_R R^2} | m' \rangle T_{m'}^{\alpha'} \right) \left(\sum_j T_j^\gamma j(j+1) T_j^{\gamma'} \right) \delta_{\beta,\beta'} \\ &+ \left(\sum_{n,n'} T_n^\beta \langle n | \frac{1}{2\mu_r r^2} | n' \rangle T_{n'}^{\beta'} \right) \left(\sum_j T_j^\gamma j(j+1) T_j^{\gamma'} \right) \delta_{\alpha,\alpha'} \\ &+ \sum_{m,n,j} \sum_{m',n',j'} T_{m,n,j}^{\alpha,\beta,\gamma} \langle m, n, j | V(R, r, \theta) | m', n', j' \rangle T_{m',n',j'}^{\alpha',\beta',\gamma'} \\ &= K_{\alpha,\alpha'}^{(1)} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + K_{\beta,\beta'}^{(2)} \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} + L_{\alpha,\alpha',\gamma,\gamma'}^{(1)} \delta_{\beta,\beta'} + L_{\beta,\beta',\gamma,\gamma'}^{(2)} \delta_{\alpha,\alpha'} \\ &+ V(R_\alpha, r_\beta, \theta_\gamma) \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'}. \end{aligned} \tag{4}$$

In Eq.(4), the potential energy operator is diagonal because of the quadrature approximation (Dickinson et al.,1968),

where $(R_\alpha, r_\beta, \theta_\gamma)$ is the value (R, r, θ) at (α, β, γ) . In the modified DVR3D program, the sine basis functions was utilized to define a DVR for the radial coordinate as:

$$T_m^\alpha = \langle R_\alpha | m \rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi R'_\alpha}{L}\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{\alpha m \pi}{M+1}\right) \tag{5}$$

The corresponding DVR basis $|R_\alpha\rangle$ is defined as:

$$\langle \bar{R}_\alpha | m \rangle = \sqrt{\Delta R} \langle R_\alpha | m \rangle$$

(6)

The matrix elements of the kinetic energy operator in DVR have already been given by Colbert and Miller (Colbert et al., 1992):

$$K_{\alpha,\alpha'}^{(i)} = \langle \bar{R}_\alpha | -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} | \bar{R}_{\alpha'} \rangle$$

$$= \frac{1}{2\mu_R} \frac{(-1)^{\alpha-\alpha'}}{L^2} \frac{\pi^2}{2} \left(\frac{1}{\sin^2[\pi(\alpha-\alpha')/2(M+1)]} - \frac{1}{\sin^2[\pi(\alpha+\alpha')/2(M+1)]} \right) \quad (\alpha \neq \alpha')$$

(7a)

$$K_{\alpha,\alpha}^{(i)} = \frac{1}{2\mu_R} \frac{(-1)^{\alpha-\alpha'}}{L^2} \frac{\pi^2}{2} \left(\frac{2(M+1)^2 + 1}{3} - \frac{1}{\sin^2[\pi\alpha(M+1)]} \right)$$

($\alpha = \alpha'$) (7b)

The other kinetic energy term in Eq.(4) is represented by applying the quadrature approximation

$$L_{\alpha,\alpha',\gamma,\gamma'}^{(i)} = \left(\sum_{m,m'} T_m^\alpha \langle m | \frac{1}{2\mu_R R^2} | m' \rangle T_{m'}^{\alpha'} \right) \left(\sum_j T_j^\gamma j(j+1) T_j^{\gamma'} \right) \cong \frac{J_{\gamma\gamma'}}{2\mu_R R_\alpha^2} \delta_{\alpha\alpha'}$$

(8)

Where:

$$J_{\gamma\gamma'} = \sum_j T_j^\gamma j(j+1) T_j^{\gamma'}$$

(9)

The other radial coordinate r should be treated in the same way. If ξ_j and w_j are the points and weights of N -point Gauss-associated Legendre quadrature, then the transformation for the r coordinate can be written as (Senekowitsch et al., 1989).

The sequential diagonalization/truncation techniques were used to generate efficient intermediate bases which reduces the size of the final Hamiltonian matrix to be diagonalized.

$$T_j^\gamma = [(2j+1)/2]^{1/2} \omega_\gamma^{1/2} P_j(\chi_\gamma)$$

(10)

RESULTS AND DISCUSSION

The computation of vibrational spectra has received a lot of

attention and some innovations regarding this topic have been made in recent years, to demonstrate very few prominent instances (Manzhos et al., 2018; Shane et al., 2019). In this study, both the DVR3D program and the Modified DVR3D program was used to calculate the vibrational levels of H₂S and its isotopologues (HDS, D₂S).

The description of the modified DVR3D program is listed below, which takes the H₂S system as an example: the radial coordinate r is the length of the H-H internuclear vector, R is the length of the vector from the H-H mass center to the S atom.

The parameters employed are as follows: the radial coordinate R extends from $R_{\min}=0.5$ a.u. to $R_{\max}=3.0$ a.u. with 32 grids. The coordinate r extends from $r_{\min}=1.5$ a.u. to $r_{\max}=6.0$ a.u. with 32 grids. 41 DVR points are taken to represent the wave packet in the ξ coordinate.

The H₂S and its isotopologues used the same potential energy surface which is issued from Senekowitsch et al. (1989). Table 1 lists the vibrational band origins for H₂S; Table 2 lists the vibrational band origins for HDS; Table 3 lists the vibrational band origins for D₂S. Both the modified DVR3D results and the DVR3D results are compared with the experimentally observed values (Tyuterev et al., 2001).

Both the DVR3D and modified DVR3D programs are reliable for the vibrational state calculations. Both programs gave similar results, which are in good accordance with the experimental results for the H₂S and D₂S systems; the results computed by the DVR3D program were much better than what the modified DVR3D program has gained for the HDS system.

The quality of the ground electronic state potential energy surface (PES) of the hydrogen sulfide molecule could be tested through such calculations. These theoretical methods could be used to calculate vibrational spectra of other triatomic molecules and eventually serve as a guide for future experimental observations.

CONCLUSION

Both the DVR3D program and modified DVR3D program proved to be good tools in calculating the vibrational energy levels of triatomic systems. These programs were utilized to calculate the vibrational spectra of the H₂S system and its isotopologues (HDS, D₂S). The results derived from the modified DVR3D program were compared with the results from the DVR3D program. Furthermore, these two types of theoretical results are also compared with the experimental results in order to test the reliability of the two programs. This study not only forms the basis for dealing with the vibrational spectra of the title systems but also the testing ground for the quality of the potential energy surface (PES). It is of significance to use these programs to deal with the vibrational spectra of other isotopologues of the hydrogen sulphide molecule in the future.

Table 1: Comparison of calculated and observed band origins for H₂S.

$\nu_1 \nu_2 \nu_3$	Revised DVR3D (cm ⁻¹)	DVR3D (cm ⁻¹)	Obs. (cm ⁻¹)
0 1 0	1190.4	1190.4	1182.6
0 2 0	2372.0	2372.0	2354.0
1 0 0	2620.5	2620.4	2614.4
0 0 1	2631.0	2631.0	2628.4
0 3 0	3543.5	3543.5	3513.8
1 1 0	3794.7	3794.6	3779.2
0 1 1	3799.8	3799.8	3789.1
0 4 0	4703.7	4703.7	4661.7
0 2 1	4960.0	4960.0	4939.2
1 2 0	4960.4	4960.1	4932.7
2 0 0	5155.0	5154.4	5145.1
1 0 1	5155.9	5155.5	5147.4
0 0 2	5251.7	5251.3	5243.1
0 5 0	5851.8	5851.6	5797.2
0 3 1	6110.4	6110.2	6077.6
1 3 0	6116.2	6115.7	6074.6
2 1 0	6308.5	6307.9	6288.3
1 1 1	6308.6	6307.9	6289.3
0 1 2	6403.8	6403.1	
0 6 0	6986.7	6986.4	

a (Tyuterev et al., 2001)

Table 2: Comparison of calculated and observed band origins for HDS.

$\nu_1 \nu_2 \nu_3$	Revised DVR3D (cm ⁻¹)	DVR3D (cm ⁻¹)	Obs. ^a (cm ⁻¹)
0 1 0	1010.0	1039.2	1032.7
0 2 0	2238.2	2071.9	2057.0
1 0 0	2013.9	1905.9	1902.9
0 0 1	2240.9	2625.6	2621.5
0 3 0	3235.2	3097.3	3072.5
1 1 0	3010.7	2934.9	2925.0
0 1 1	3236.8	3645.7	3634.3
0 4 0	3999.9	4114.6	
0 2 1	4410.4	4659.5	
1 2 0	4229.3	3957.3	
2 0 0	4223.6	3762.4	3756.3
1 0 1	4410.1	4530.3	
0 0 2	5215.0	5155.4	
0 5 0	5205.1	5123.1	
0 3 1	5392.9	5539.8	
1 3 0	4980.8	4972.5	
2 1 0	4478.3	4781.2	
1 1 1	5393.5	5569.8	
3 0 0	5461.4	5666.2	
2 2 0	5952.8	5793.6	

^a (Tyuterev et al., 2001).**Table 3:** Comparison of calculated and observed band origins for D₂S.

$\nu_1 \nu_2 \nu_3$	Revised DVR3D (cm ⁻¹)	DVR3D (cm ⁻¹)	Obs. ^a (cm ⁻¹)
0 1 0	860.4	860.4	855.4
0 2 0	1716.6	1716.6	
1 0 0	1900.7	1900.7	1896.4
0 0 1	1912.1	1912.1	1910.2

Table 3:

0 3 0	2568.0	2568.0	
1 1 0	2752.6	2752.6	2742.7
0 1 1	2761.4	2761.4	2754.5
0 4 0	3414.2	3414.2	
0 2 1	3600.4	3600.4	
1 2 0	3606.5	3606.5	
2 0 0	3760.6	3760.7	
1 0 1	3763.4	3763.4	
0 0 2	3814.6	3814.6	
0 5 0	4254.9	4254.8	
0 3 1	4443.5	4443.6	
1 3 0	4446.9	4446.9	
2 1 0	4602.5	4602.6	
1 1 1	4604.1	4604.2	
0 1 2	4654.4	4654.5	
0 6 0	5089.8	5089.4	

^a (Tyuterev et al., 2001).

REFERENCES

- Bačić Z, Light JC (1986). Highly excited vibrational levels of “floppy” triatomic molecules: A discrete variable representation—Distributed Gaussian basis approach. *J. Chem. Phys.* 85: 4594.
- Child MS (2006). *An International Journal at the Interface Between Chemistry and Physics.* *Mol. Phys.* 104(1): 3-9.
- Colbert DT, Miller WH (1992). A novel discrete variable representation for quantum mechanical reactive scattering via the S-matrix Kohn method. *J. Chem. Phys.* 96: 1982.
- Cruz H, Bermudez-Montana M, Lemus R (2018). Time-dependent local-to-normal mode transition in triatomic molecules. *Mol. Phys.* 116(1): 77-92.
- Csaszar AG, Tarczay G, Leininger ML, Tennyson J, Allen WD (2001). In: Demaison J, Sarka K (eds) *Spectroscopy from Space, NATO ASI Series C.* Kluwer, Dordrecht. Pp 317-339.
- Dickinson AS, Certain PR (1968). Calculation of Matrix Elements for One-Dimensional Quantum-Mechanical Problems. *J. Chem. Phys.* 49(9): 4209.
- Ding Y, Naumenko O, Hu SM, Zhu Q, Bertseva E, Campargue A (2003). The absorption spectrum of H₂S between 9540 and 10 000 cm⁻¹ by intracavity laser absorption spectroscopy with a vertical external cavity surface emitting laser. *J. Mol. Spectrosc.* 217: 222-238.
- Flynn SW, Mandelshtam VA (2019). Sampling general distributions with quasi-regular grids: Application to the vibrational spectra calculations. *J. Chem. Phys.* 151: 241105.
- Henderson JR, Le Sueur CR, Pavett SG, Tennyson J (1993). Coordinate ordering in the discrete variable representation. *Comput. Phys. Commun.* 74(2): 193-198.
- Jensen P (2012). Local modes in vibration-rotation spectroscopy. *Wiley Interdisciplinary Reviews: Comput. Mol. Sci.* 2(3): 494-512.
- Lamouroux J, Regalia-Jarlot L, Tyuterev VG, Thomas X, Von Der Heyden P, Tashkun SA, Borkov Y (2008). Measurements of line intensities and determination of transition moment parameters from experimental data for the v₁ and v₃ bands of D₂S₂. *J. Mol. Spectrosc.* 250(2): 117-125.
- Light JC, Carrington Jr T (2000). Discrete-Variable Representations and their Utilization. *Adv. Chem. Phys.* 114: 263-310.
- Light JC, Hamilton IP, Lill JV (1985). Generalized discrete variable approximation in quantum mechanics. *J. Chem. Phys.* 82: 1400.
- Liu AW, Gao B, Cheng GS (2005). High-resolution rotational analysis of HDS: 2v₃, v₂ + 2v₃, 3v₃, and v₂ + 3v₃ bands. *J. Mol. Spectrosc.* 232: 279-290.
- Liu AW, Ulenikov ON, Onopenko GA, Gromova OV, BEkhtereva ES, Wan L, Hao LY, Hu SM, Flaud JM (2006). Global fit of the high-resolution infrared spectrum of D₂S. *J. Mol. Spectrosc.* 238(1): 11-28.
- Manzhos S, Wang X, Carrington Jr T (2018). A multimode-like scheme for selecting the centers of Gaussian basis functions when computing vibrational spectra. *Chem. Phys.* 509(15): 139-144.
- Onopenko GA (2009). High-resolution spectrum of the first triad of D₂ 32S interacting states. *Russ. Phys. J.* 52: 113-118.
- Schneider BI, Nygaard N (2002). Orthogonal Functions, Discrete Variable Representation, and Generalized Gauss Quadratures†. *J. Chem. Phys.* 106(45): 10773-10776.
- Schryber JH, Polyansky OL, Jensen P, Tennyson J (1996). On the Spectroscopically Determined Potential Energy Surfaces for the Electronic Ground States of NO₂ and H₂O. *J. Mol. Spectrosc.* 185(2): 234-243.
- Senekowitsch J, Carter C, Zilch A (1989). Theoretical rotational-vibrational spectrum of H₂S. *J. Chem. Phys.* 90(2): 783.
- Song YZ, Caridade PJSB, Varandas AJC (2009). Potential Energy Surface for Ground-State H₂S via Scaling of the External Correlation, Comparison with Extrapolation to Complete Basis Set Limit, and Use in Reaction Dynamics. *J. Phys. Chem. A.* 113(32): 9213-9219.
- Song YZ, Varandas AJC (2009). Accurate ab initio double many-body expansion potential energy surface for ground-state H₂S by extrapolation to the complete basis set limit. *J. Chem. Phys.* 130: 134317.
- Tennyson J (1986). The calculation of the vibration-rotation energies of triatomic molecules using scattering coordinates. *Comput. Phys. Rep.* 4(1): 1-36.
- Tennyson J, Henderson JR, Fulton NG (1995). DVR3D: for the fully

pointwise calculation of ro-vibrational spectra of triatomic molecules. *Comput. Phys. Commun.* 86(1-2): 175-198.

Ulenikov ON, Bekhtereva ES, Leroy C, Gromova OV, Fomchenko AL (2009). On the determination of the intramolecular potential energy surface of polyatomic molecules: Hydrogen sulfide and formaldehyde as an illustration. *J. Mol. Spectrosc.* 255(2): 88-100.

Yang G, Wu L, Jiang B, Yang W, Qi J, Cao K, Meng Q, Mustafa AK, Mu W, Zhang S, Snyder SH, and Wang R (2008). H₂S as a physiologic vasorelaxant: hypertension in mice with deletion of cystathionine gamma-lyase. *Sci.* 322:587-590.

Yu A (2013). Vibration spectrum calculations of isotopic species of hydrogen sulfide using the discrete variable representation (DVR) method. *Can. J. Phys.* 91(10): 815-821.

Tyuterev VG, Tashkun SA, Schwenke DW (2001). An accurate isotopically invariant potential function of the hydrogen sulphide molecule. *Chem. Phys. Lett.* 348(3-4): 223-234.

Cite this article as:

Yu Ay (2020). Vibrational energy levels computations of H₂S and its isotopologues (HDS, D₂S). *Acad. J. Sci. Res.* 8(9): 273-278.

Submit your manuscript at

<http://www.academiapublishing.org/ajsr>