Theoretical electronic structure with rovibrational and dipole moment calculation of the SiS Molecule

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Abstract. The quantitative distribution of the molecular abundances in the universe is a classical problem in astronomy, astrophysics and cosmo-chemistry. Astrophysicists are interested in determining the abundances of molecular species in order to: (1) Know the primordial composition of the solar system, and its relation to the past and present composition of the earth. (2) Have a complete understanding of physical and chemical processes taking place in the stellar atmospheres and the interstellar medium (3) Test the hypotheses that have been proposed for element formation. To investigate the presence of astronomical sources, experimental astrophysicists usually study the wavelength and intensity of light that they emit. Many diatomic molecular species are present in various astrophysical sources, however, the theoretical studies on such species are not enough and information is missing in that area. Knowledge of the electronic structure, Franck-Condon factors (FCFs), and other related quantities for a band system of a diatomic molecule is essential to arrive at its astrophysically significant parameters such as kinetics of the energy transfer, radiative lifetimes, band intensity, vibrational temperature, etc. In this view, the spectroscopic and ro-vibrational constants, FCFs of several electronic states of the diatomic molecule SiS electronic have been evaluated in this work. We performed theoretical calculation of the low-lying electronic state, of the molecule SiS by using the Complete Active Space Self Consistent Field (CASSCF) method followed by the Multi Reference Configuration Interaction with Davidson correction MRCI+Q. The potential energy along with the dipole moment curves of these states have been calculated along with the spectroscopic constants R_{0}, \omega_{0}, B_{0}, and T_{0}. Additionally, the Rotation-vibration lines for the considered electronic states were obtained by direct solution of the nuclear motion Schrödinger equation using the canonical approach with program Rovib-1

1. Introduction

The silicon sulphide molecule SiS, is of important astrophysical interest. It has been detected from celestial mater in the interstellar media through the radio line emission near the circumstellar envelope of a late-type carbon star [1-12]. From Stark measurements of laboratory spectra, the spectroscopic constants, the permanent dipole moment, and the bond length of the ground state have been measured [13-30]. A limited number of spectroscopic constants of the ground and few excited electronic states have been investigated theoretically by using different techniques [31-40]. In 1952, the rotational analysis near the ultraviolet D''II-XΣ', has been studied by band Lagerqvist et al. [11] A number of perturbations has been found in the upper state, however it was challenging to determine the absolute numbering of the vibrational levels of the perturbing state. In 1961, Barrow et al. [14] carried out the rotational analysis of the E-X band system of SiS while Lakshman et al. [40] investigated the potential energy curves of three electronic state of SiS molecule and found their spectroscopic constants. Later on, Robbe et al. [32] computed the wave functions, SCF-CI energies, and spectroscopic constants of low-lying electronic states of SiS using ab-initio methods. The infrared vibration-rotation spectra of SiS molecule is still missing.
Because of the astrophysical interest in SiS molecule and the lack of information about its highly excited electronic states, we calculate in the present work the spectroscopic constants, the potential energy curves (PECs) and dipole moment curves (DMCs) of 27 low lying electronic states for the molecules SiS by the \textit{ab initio} method (CASSCF/MRCI +Q). Moreover, a further investigation of the different vibrational levels of some lowest bound states of SiS molecule was carried out via canonical function approach in which some of the necessary rovibrational constants are determined.

2. Computational Approach

The Complete Active Space Self Consistent Field (CASSCF) followed by Multireference Configuration Interaction (MRCI) method with Davidson correction (+Q) was employed in the present work in order to investigate the low-lying electronic states of the SiS molecule. This method is considered to be effective since it accounts for total electron correlation. The calculations have been performed accurately using the computational chemistry program MOLPRO [41] taking the advantage of the graphical user interface GABEDIT [42]. The 14 electrons of silicon atom (Si) are considered using the segmented basis set cc-pV5Z [43] being augmented by the diffuse function (aug-cc-pV5Z) [44] for the 16 electrons of the sulphur atom (S). Thus, the 30 electrons have been explicitly considered in the CI calculations. The active space contains 4\(\pi\) (Si: 4s, 3p\(^0\); S: 4s, 3p\(^0\)) and 1\(\pi\) (Si: 3p\(^\pm\); S: 3p\(^\pm\)) molecular orbitals in the C\(2v\) symmetry. This corresponds to 12 active orbitals distributed to irreducible representation a\(_1\), b\(_1\), b\(_2\) and a\(_2\) [4, 1, 1, 0].

3. Results and Discussion

3.1. Potential energy curves, dipole moment curves and the spectroscopic parameters

The investigated potential energy curves of 27 singlet and triplet states of SiS molecule have been investigated and plotted as a function of the internuclear distance in Figures (1-3).

Figure 1: Potential energy curves of the lowest \(^1\Pi\) electronic states of the SiS molecule.
Figure 2: Potential energy curves of the lowest $^1\Sigma^+$, $^1\Sigma^-$ and $^1\Delta$ electronic states of the SiS molecule.

Figure 3: Potential energy curves of the lowest $^3\Sigma^+$, $^3\Sigma^-$, $^3\Pi$ and $^3\Delta$ electronic states of the SiS molecule.
The repulsive section at small internuclear distance indicates the large coulomb force which originates from the overlap of electron clouds according to the Pauli Exclusion Principle. At large internuclear distance, the molecule reaches a constant asymptotic limit that expresses the dissociation of the molecule. The deep potential wells indicate the dominancy of attractive forces over the repulsive ones. While the dominancy of weak forces are justified by the shallow states of potential energy curves. The states (2)\(i\)\(\Sigma^+\), (2)\(i\)\(\Sigma^−\), (4)\(i\)\(\Sigma^+\), (2)\(i\)\(\Delta\), (1)\(i\)\(\Gamma\), (3)\(i\)\(\Sigma^+\), (2)\(i\)\(\Delta\) and (4)\(i\)\(\Delta\) are examples of shallow bound states while the states (2)\(i\)\(\Pi\), (5)\(i\)\(\Pi\), (6)\(i\)\(\Pi\), (1)\(i\)\(\Phi\), (2)\(i\)\(\Sigma^+\), (2)\(i\)\(\Delta\Pi\), (3)\(i\)\(\Delta\) and (4)\(i\)\(\Sigma^−\) are unbound states which indicate the highly repulsive forces between the two atoms.

The uneven distribution of charges in SiS molecule leads to the presence of permanent dipole moment values which can provide a useful information about the degree of ionic and covalent character in the bonding. The permanent dipole moment of the investigated states of SiS molecule curves are plotted in terms of internuclear distance R as shown in figures (4-6).

Figure 4: Permanent dipole moment curves of the lowest \(i\)\(\Sigma^+\), \(i\)\(\Sigma^−\) and \(i\)\(\Delta\) electronic states of the SiS molecule.
Figure 5: Permanent dipole moment curves of the lowest $^1\Pi$ electronic states of the SiS molecule

Figure 6: Permanent dipole moment curves of the lowest $^3\Sigma^+$, $^3\Sigma^-$, $^3\Pi$ and $^3\Delta$ electronic states of the SiS molecule
A positive value of the dipole moment occurs when the center of charge of the electrons is closer to atom taken at the origin than the center of positive charge. But if the center of electron charge is closer to the atom along the positive direction than the center of positive charge, this leads to a negative value of dipole moment. In addition, the behavior of dipole moment curves indicate the covalent character of SiS molecule since most of the dipole moment curves tend to zero at large internuclear distance which is the correct behavior of a molecule that dissociates into neutral fragments. The X-Σ° state has a covalent character at the dissociation limit and a mixed character at smaller internuclear separations. The dipole moment curve (DMC) of this state presents a largest magnitude |μ|=2.38 a.u at R=1.24 Å. This covalent character of the ground state is confirmed by calculating the percentage ionic character using the formula $f_{ionic}=\frac{\mu_e}{eR_e}$ [45] where it is found to be $f_{ionicity}=0.186$ which correspond to 18.6%.

The spectroscopic constants of SiS molecule have been calculated for the bound states by fitting the calculated potential energy values of the investigated electronic states into a polynomial in terms of the internuclear distance at equilibrium Re. These calculated parameters are reported in Table 1.

Table 1: Spectroscopic constants of the low-lying singlet and triplet electronic states of the molecule SiS.

| States (2\Sigma+/\Pi) | $T_e$ (cm$^{-1}$) | $R_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $B_e$ (cm$^{-1}$) | $D_e$ (cm$^{-1}$) | $\mu_e$ (a.u) |
|----------------------|----------------|----------|---------------------|----------------|----------------|--------------|
| X-Σ°                 | 0a             | 2.068a   | 584.61a             | 0.263a         | 33067a         | 0.722a       |
|                      | 0b             | 1.928b   | 749.64b             | 0.304b         |                |              |
|                      | 0c             |          | 795.00c             | 0.300c         |                |              |
| (1)Γδ+               | 17861a         | 2.373a   | 403.67a             | 0.199a         | 14899a         | 0.369a       |
|                      | 24160c         |          | 580c                | 0.252c         |                |              |
| (1)Δ                 | 20970a         | 2.397a   | 379.48a             | 0.196a         | 12120a         | 0.657a       |
|                      | 27460e         |          | 525e                | 0.243e         |                |              |
| (1)Γδ‐               | 22819a         | 2.435a   | 352.64a             | 0.190a         | 10316a         | 0.813a       |
|                      | 29360c         |          | 480c                | 0.234c         |                |              |
| (1)Π                  | 27393a         | 2.214a   | 330.54a             | 0.330a         | 5847a          | 0.896a       |
| (2)Γδ+               | 32935a         | 4.620a   | 236.35a             | 0.0527a        | 258a           | 0.005a       |
| (1)Π                  | 33422a         | 2.510a   | 285.9a              | 0.178a         | -224a          | 0.970a       |
|                      | 35026b         | 2.058b   | 513.1b              | 0.2664b        |                |              |
|                      | 38070c         | 510c     | 0.251c              |                |                |              |
|                      | 35027d         | 2.0596c  | 512.00c             |                |                |              |
| (3)Γδ+               | 43693a         | 2.9011a  | 291.61a             | 0.134a         | 9019a          | 2.200a       |
|                      | 48000c         | 330c     | 0.198c              |                |                |              |
|                      | 41915.8d       | 405.6c   |                    |                |                |              |
| (2)Π                 | 45330a         | 2.958a   |                    |                | 7470a          | 1.643a       |
| (3)Π                 | 49014a         | 3.224a   | 221.29a             | 0.108a         | 3795a          | 2.041a       |
| (4)Γδ‐               | 49849a         | 3.304a   | 157.72a             | 0.103a         | 2936a          | 0.460a       |

*Present work, bRef[11], cRef[32], dRef[14], eRef[40].

However, the absence of these constants for some electronic states is due to the crossing or avoided crossing near the minima of these curves. Concerning the ground state, the values of the equilibrium length $R_e$ are compatible with those values reported previously with relative difference of 6.7 %. [11] In addition, the comparison of the values of harmonic frequency $\omega_e$ shows an average relative difference...
of 24% with the values reported by Lagerqvist et al. and Robbe et al. [11,32]. The rotational constant value in the present work is also compared with the values given in literature where the relative error is $12.3\% < \Delta B_v/B_v < 13.5\%$. A similar comparison is also obtained for the excited states and reported in Table 1.

3.2. The Ro-vibrational Calculations

In order to induce different vibrational transitions, the vibrational rotational study of SiS molecule seems very important. Thus, the vibrational energy $E_v$, the rotational constant $B_v$, and the centrifugal distortion constant $D_v$ for the ground and many excited electronic states of SiS have been calculated using the canonical functions approach [46-49] and the cubic spline interpolation between each two consecutive points of the potential energy curves. Then the abscissas of the turning point $R_{\text{min}}$ and $R_{\text{max}}$ for each vibrational level were determined by using the calculated vibrational eigenvalues of energy and the potential energy curves of the investigated states. The vibrational constants corresponding to the ground state $X^1\Sigma^+$, $3\Sigma^+$, $2\Pi$, and $1\Pi$ are reported in Tables (2-3). This approach fails in case of crossing, avoided crossing and for shallow states.

Table (2): Values of the eigenvalues $E_v$, the rotational constants $B_v$, the centrifugal constant $D_v$, and the abscissas of the turning points for the different vibrational levels of state $X^1\Sigma^+$ of SiS molecule.

| $\nu$ | $E_v$  | $B_v \times 10^1$ | $D_v \times 10^7$ | $R_{\text{min}}$ | $R_{\text{max}}$ |
|------|-------|------------------|------------------|------------------|------------------|
| 0    | 292.81| 2.641            | 2.1789           | 2.008            | 2.133            |
| 1    | 872.21| 2.626            | 2.1745           | 1.968            | 2.185            |
| 2    | 1447.56| 2.612          | 2.1740           | 1.941            | 2.222            |
| 3    | 2018.69| 2.598          | 2.1870           | 1.921            | 2.254            |
| 4    | 2585.27| 2.584          | 2.1883           | 1.903            | 2.283            |
| 5    | 3147.49| 2.570          | 2.1764           | 1.889            | 2.309            |
| 6    | 3705.63| 2.556          | 2.1511           | 1.876            | 2.334            |
| 7    | 4259.73| 2.540          | 2.0820           | 1.864            | 2.358            |
| 8    | 4810.55| 2.524          | 2.0620           | 1.853            | 2.380            |
| 9    | 5358.22| 2.510          | 2.1177           | 1.843            | 2.402            |
| 10   | 5902.02| 2.495          | 2.1972           | 1.834            | 2.423            |
| 11   | 6441.05| 2.481          | 2.1997           | 1.826            | 2.444            |
| 12   | 6975.20| 2.466          | 2.1319           | 1.818            | 2.465            |
| 13   | 7504.89| 2.450          | 2.0672           | 1.810            | 2.485            |
| 14   | 8030.75| 2.435          | 2.1227           | 1.803            | 2.505            |
| 15   | 8552.44| 2.420          | 2.1966           | 1.796            | 2.524            |
| 16   | 9069.39| 2.406          | 2.1541           | 1.790            | 2.543            |
| 17   | 9582.00| 2.391          | 2.1214           | 1.783            | 2.562            |
| 18   | 10090.41| 2.376        | 2.0848           | 1.778            | 2.581            |
| 19   | 10594.73| 2.361        | 2.1308           | 1.772            | 2.600            |
| 20   | 11094.72| 2.346        | 2.1812           | 1.767            | 2.619            |
| 21   | 11590.16| 2.331        | 2.1545           | 1.762            | 2.637            |
| 22   | 12081.29| 2.317        | 2.0637           | 1.757            | 2.656            |
| 23   | 12568.83| 2.304        | 2.0262           | 1.752            | 2.673            |
Table (3): Values of the eigenvalues $E_v$, the rotational constants $B_v$, the centrifugal constant $D_v$, and the abscissas of the turning points for the different vibrational levels of state $(1)^3\Pi$ of SiS molecule

|  $\nu$ | $E_v$  | $B_v \times 10^4$ | $D_v \times 10^7$ | $R_{\text{min}}$ | $R_{\text{max}}$ |
|-------|--------|-------------------|-------------------|-----------------|-----------------|
|  0    |  164.42|  2.305            |  4.5839           |  2.132          |  2.300          |
|  1    |  490.26|  2.292            |  4.4491           |  2.077          |  2.368          |
|  2    |  815.52|  2.275            |  4.0077           |  2.045          |  2.419          |
|  3    | 1143.30|  2.254            |  3.5783           |  2.022          |  2.460          |
|  4    | 1473.68|  2.227            |  3.6902           |  2.00           |  2.501          |
|  5    | 1801.73|  2.198            |  3.7893           |  1.990          |  2.539          |
|  6    | 2126.16|  2.176            |  3.5557           |  1.973          |  2.575          |
|  7    | 2448.71|  2.154            |  3.8486           |  1.961          |  2.610          |
|  8    | 2766.31|  2.126            |  3.2366           |  1.950          |  2.643          |
|  9    | 3081.70|  2.102            |  3.7513           |  1.941          |  2.677          |
| 10    | 3392.06|  2.076            |  3.7644           |  1.932          |  2.710          |
| 11    | 3697.55|  2.053            |  4.0518           |  1.924          |  2.743          |
| 12    | 3996.81|  2.025            |  3.6894           |  1.916          |  2.776          |
| 13    | 4290.57|  1.996            |  4.3649           |  1.909          |  2.810          |
| 14    | 4576.44|  1.965            |  4.2924           |  1.903          |  2.845          |
| 15    | 4854.77|  1.934            |  4.9663           |  1.897          |  2.880          |
| 16    | 5124.06|  1.902            |  5.2563           |  1.891          |  2.917          |
| 17    | 5383.22|  1.862            |  5.7437           |  1.886          |  2.957          |
| 18    | 5630.41|  1.816            |  7.2863           |  1.881          |  3.000          |
| 19    | 5862.01|  1.760            |  9.0669           |  1.877          |  3.050          |
The accuracy of our vibration-rotation calculations are checked by referring to the following spectroscopic formulas:

\[ E_v = E(v) = \omega_v \left( v + \frac{1}{2} \right)^2 - \omega_v x_v \left( v + \frac{1}{2} \right)^3 + C_1 \]
\[ B_v = B(v) = B_v - \alpha_v \left( v + \frac{1}{2} \right) + C_2 \]

where \( C_1 \) and \( C_2 \) are high order correction terms.

For \( v=0 \) of the ground state \( X^1\Sigma^+ \), where \( \omega_v \) and \( \omega_v \) are very small.

\[ E_v = 0 = \frac{\omega_v}{2} \]

4. Conclusion
In the present work, the ab initio calculations of the lowest singlet and triplet electronic states for SiS molecule were carried out where the PECs and DMCs of this molecule have been studied via MCSCF/MRCI technique. The dipole moments of the electronic states tend to zero at the dissociation limit which indicates that the SiS molecule dissociates into neutral fragments. The spectroscopic constants \( (T_e, \omega_e, B_e, R_e, D_e) \) and the dipole moment have been calculated for most of the bound states. Also, the iconicity calculation shows that the ground state has a covalent character around its equilibrium bond length where \( f_{\text{ionicity}} = 0.186 \) which correspond to 18.6%. A good agreement is achieved with our previously published work, using the same calculation method \[47, 48\]. The ro-vibrational constants \( (E_v, B_v, D_v) \) with the abscissas of turning points \( R_{\text{min}} \) and \( R_{\text{max}} \) have been obtained for different vibrational levels of the ground state and some low-lying electronic states by the mean of canonical function approach and cubic spline interpolation.

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