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SiS formation via gas phase reactions between atomic silicon and sulphur-bearing species

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ABSTRACT

The potential energy surface for the Si + SH and Si + SH2 reactions is explored using the highly accurate explicit correlation multireference configuration interaction method. For atomic silicon colliding with SH, SiS + H is predicted to be the main reaction channel with no activation energy. The reaction Si + SH2 → SiS + H2 is found to be largely thermodynamically favourable, but likely to be slow, due to its spin forbidden nature. Several details on possible mechanisms are evaluated, and implications for astrochemical models are discussed. Among other results, we show that SiS is stable towards collisions with H and H2, and that the HSiS molecule will quickly be converted to SiS in collisions with atomic hydrogen.

Key words: astrochemistry – molecular data – ISM: molecules.

1 INTRODUCTION

The SiS molecule was first detected in 1975 at CW Leonis (IRC+10216), a well-studied evolved carbon star, together with the SiO molecule (Morris et al. 1975). Dickinson & Kuiper (1981) also observed the two molecules together, and found SiS was less abundant than SiO (Dickinson & Kuiper 1981). Further studies detected the presence of SiS towards O-rich AGB stars, with abundances significantly lower than around C-rich AGB stars (Danilovich et al. 2018).

Apart from the envelopes of evolved stars, SiS was detected in a few star-forming regions associated with strong outflow activity, like Orion KL (Ziurys 1988, 1991; Tercero et al. 2011) and SgrB2 (Dickinson & Kuiper 1981).

Recently, a systematic search for SiS in low-mass star-forming regions was carried out in the framework of the IRAM Large Program ASAI (Lefloch et al. 2018). Emission from the SiS transitions Jup = 4–15 between 72 and 272 GHz was searched for in a sample of 10 regions at different stages of protostellar evolution, from pre-stellar to late Class I. SiS was detected towards the protostellar shock region, L1157-B1, only (Podio et al. 2017). The abundance was found very low (∼10−8), about 2 orders of magnitude less than SiO. The results of this survey led the authors to conclude that SiS cannot be a simple product of gas phase chemistry in molecular clouds. Its formation requires specific conditions, which are best found in shocks.

The lack of SiS detection in such environments is quite surprising in regard of the frequent observations of SiO, another silicon-bearing species, which has become a probe of protostellar shocks.

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Gusdorf et al. (2008) concluded that about 1 per cent of silicon abundance is present in the form of SiO on to the grain mantles in L1157-B1, based on their analysis of the SiO line emission. At the surface of dust grains, atomic Si gets easily hydrogenated into SiH₄. Hence, a small fraction of silicon, in the form of silicon hydrides, could be present on to the grain mantles and easily released in the gas phase either through thermal evaporation or non-thermal (sputtering) processes (Mackay 1995) and subsequently converted into SiH by photodissociation in the gas phase. These studies are in line with Podio et al. (2017) who speculated that in the interstellar medium SiS could form through slow gas-phase processes involving a fraction of the released silicon (either in the form of Si or SiH₄) with simple sulphur bearing species S/S₂/HS, instead of being released from grain cores (Podio et al. 2017).

In this article, we explore another possibility, based on revised chemical models of S-chemistry, which predict that depending on the evolutionary stage of pre-stellar cores, HS and H₂S could be highly abundant at the surface of dust grains and constitute the main reservoirs of sulphur (Vidal et al. 2017). In a shock violent enough to erode the core of dust grains and release atomic Si in the gas phase, the molecules HS and H₂S which constitute part of the grain mantles, would be also rejected into the gas phase. Here, we explore the viability of gas phase reactions between HS and H₂S with atomic silicon as sources of SiS in the interstellar medium.

2 AB INITIO METHODS

The energies reported in this work were obtained by explicitly correlated multireference configuration interaction (MRCI-F12) calculations (Shiozaki, Knizia & Werner 2011; Shiozaki & Werner 2011, 2013), using the cc-pVQZ-F12 (VQZ-F12) basis set (Petersson, Adler & Werner 2008). This method is state-of-the-art for accurately describing bond breaking/formation (Trabeski & Francisco 2018) and the results are close to the complete basis set limit. All energies were enhanced with the Davidson (+Q) correction, thus approximating up to quadruple excitations, (Werner & Knowles 1988a, b).

The reference wavefunction was obtained from complete-active-space-self-consistent-field (CASSCF) calculations (Knowles & Werner 1985; Werner & Knowles 1985), with 11 electrons in 9 orbitals for the Si + SH case, and 12 electrons in 10 orbitals for the Si + SH₂ one. For both reactions, several electronic states and different spin multiplicities were treated, in order to provide a complete description of both systems. Geometry optimizations, vibrational frequencies, and zero-point energy (ZPE) corrections are also at the CASSCF level.

The probabilities of singlet-triplet transitions are discussed in terms of the magnitude of the spin-orbit coupling (SOC). For this purpose, the full spin-orbit matrix was calculated with the Breit–Pauli operator (Berning et al. 2000) as implemented in MOLPRO (Werner et al. 2015). The spin-free electronic Hamiltonian eigenstates, labelled |S⟩, |T, 1⟩, |T, 0⟩ and |T, −1⟩, are used to build the total Hamiltonian matrix representation (H₀ + H₅). The singlet-triplet spin-orbit transition probabilities will depend on the magnitude of the V₅₀ term, which is defined as

\[ V_{50}^2 = \sum_{M_S=-1}^{1} |\langle T, M_S |H_{50}|S \rangle|^2. \]  

We have employed the MOLPRO (Werner et al. 2015) package in all calculations.

3 RESULTS AND DISCUSSION

3.1 Formation of SiS through Si + HS collisions

To study the reaction between the mercapto radical (HS) with atomic silicon we started at the dissociated limit and gradually approached the reactants by 0.05 Å while relaxing all other degrees of freedom (valence angle and HS bond distance). The results are shown in Fig. 1, where it can be seen that the formation of SiS via Si + HS collisions is largely favourable from the thermodynamic point of view, with an exothermicity of approximately 241 kJ mol⁻¹. A potential well corresponding to a bound SiSH molecule is achieved in the process. No activation energy is involved in the reaction, and therefore it is likely to happen very fast. It also occurs adiabatically in a single electronic state, without crossings with excited ones. The other electronic states lead to an excited form of the SiS radical, and the reaction is endothermic in this case, therefore not contributing significantly to the overall rate.

Although not visible in the energy scale of Fig. 1, the inverse reaction (H + SiS → SiSH) needs to overcome a small entrance barrier of 5.4 kJ mol⁻¹ (here named TS2) to achieve the potential well. In fact, this figure shows only one-dimensional cut over the minimum energy path for the Si + SH → SiS + H abstraction route, but another isomer of the triatomic system also exists, and an isomerization mechanism is also possible. These two reaction paths are described together in the schematic representation of Fig. 2. The energies (including ZPE corrections) and vibrational frequencies of the main structures are shown in Table 1.

When studying the SiH + S reaction, Rosi et al. (2018, 2019) also explored the ground doublet state of the SiSH triatomic system, and achieved results similar to those given in Fig. 2. This work explored further excited electronic states, contributing to a better understanding of the reactive system. Furthermore, our calculations are based on multireference methods, and are more suitable in bond breaking regions. Indeed, the barrier for the H + SiS reaction (TS2) calculated in this work is 44 per cent lower than formerly predicted.

Thus, we have two possible pathways for the formation of the SiS molecule: first, an attack of atomic silicon to the mercapto radical, followed by a direct HS bond break through a small exit barrier (TS2), and second, the formation of SISH followed by isomerization to HSiS (TS1), with no exit barrier involved. Finally, although a stable HSiS molecule has not been observed thus far, reactions between H and SiS in the surface of a grain could in principle yield this triatomic species. A more in depth discussion about this species will be given in Section 3.3.

3.2 Formation of SiS through Si + H₂S collisions

For the formation of SiS via hydrogen sulphide, the reaction paths are more complex and involve crossings between singlet and triplet electronic states of a bound SSiH₂ molecule. Since ground state silicon has a triplet electronic configuration, and H₂S is a singlet species, the collision process can only happen adiabatically on the triplet state of the tetratomic system, and for this reason we start the discussion considering triplet states only.

3.2.1 Triplet state

The reaction paths in the triplet electronic state are summarized in Fig. 3. It is shown that the reaction between the silicon atom in its ground (³P) state and H₂S molecule can generate three well-defined isomers of the tetratomic system. First, the interaction leads
SiS formation through HS + Si and H₂S + Si

Figure 1. Dissociation of the SiSH molecule at the MRCI(Q)-F12/VQZ-F12 level. Each step is separated by 0.05 Å. The black and grey lines correspond to doublet states of \( A' \) and \( A'' \) symmetry, respectively, while the red and pink ones correspond to triplet states.

Figure 2. Schematic view of the potential energy surface for the SiS formation reaction through Si + HS. Energies are at the MRCI(Q)-F12/VQZ-F12 level without ZPE corrections.

Table 1. Properties of the stationary points of HS + Si PES.a

<table>
<thead>
<tr>
<th>Point</th>
<th>( E ) (kJ mol(^{-1}))</th>
<th>( E(ZPE) ) (kJ mol(^{-1}))</th>
<th>( \omega_1 ) (cm(^{-1}))</th>
<th>( \omega_2 ) (cm(^{-1}))</th>
<th>( \omega_3 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiSH</td>
<td>18.2</td>
<td>18.4</td>
<td>496</td>
<td>614</td>
<td>2524</td>
</tr>
<tr>
<td>TS1</td>
<td>87.5</td>
<td>79.2</td>
<td>570</td>
<td>1206</td>
<td>1638</td>
</tr>
<tr>
<td>TS2</td>
<td>138.9</td>
<td>123.6</td>
<td>348</td>
<td>680</td>
<td>1228</td>
</tr>
<tr>
<td>SSH</td>
<td>0.0</td>
<td>0.0</td>
<td>690</td>
<td>702</td>
<td>2200</td>
</tr>
<tr>
<td>Si + HS</td>
<td>376.7</td>
<td>370.8</td>
<td>2600</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SiS + H</td>
<td>135.4</td>
<td>118.2</td>
<td>724</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

aEnergies are given in kJ mol\(^{-1}\) and frequencies (\( \omega \)) in cm\(^{-1}\).

barriercless to H₂SSi, which lies 53 kJ mol\(^{-1}\) below reactants and shows a SiS bond distance of 2.56 Å. After a H atom migration transition state (TS1) is overcome, the SHSiH isomer is obtained, with a shorter SiS bond distance of 2.13 Å and a dihedral angle of 90 deg. Note that the energy of the transition state lies below reactants, and thus this isomerization is open for collision at whatever temperature. The deepest minimum in the triplet electronic state is however the SSHiH structure, which can only be obtained from the initial reactants through two subsequent isomerization steps. It is easily seen that the bonding of the two hydrogen atoms to silicon is much more energetically favourable than to sulphur, the energetic difference between H₂SSi and SSHiH being 94 kJ mol\(^{-1}\).

3.2.2 Singlet state

Fig. 4 shows the main stationary structures of the singlet PES together with the triplet ones discussed above. Three isomers also exist in the singlet (closed shell) PES, with their energy lying much lower than the triplet ones. The overall global minimum corresponds to the SSHiH molecule, lying even lower (19.2 kJ mol\(^{-1}\)) than the lowest dissociation limit H₂ + SiS. This structure shows a double SiS bond with a bond length of 1.94 Å. There are also trans and cis planar SHSiH structures, which are metastable with respect to H₂ + SiS dissociation and have SiS bond lengths of 2.13 and 2.15 Å, respectively. The isomerization barrier between SSHiH and the trans structure (TS3) is seen to be very high, making this structure quite...
stable, if ever formed. The cis-trans isomerization barrier (TS6) lies 69 kJ mol$^{-1}$ above the trans minimum.

The $\text{H}_2 + \text{SiS}$ reaction does not have the possibility of reaching any low lying dissociation limit, and for this reason SiS is stable with respect to collisions with $\text{H}_2$ in the gas phase. Therefore, we predict here that SiS will not be destroyed by neither atomic nor molecular hydrogen, which is relevant for understanding its abundance in the ISM.

### 3.2.3 Intersystem crossings and the $\text{Si} + \text{H}_2\text{S} \rightarrow \text{SiS} + \text{H}_2$ reaction

As argued above, the title reaction can only happen via a triplet to singlet crossing, which makes the rate constant for such process likely to be much lower than the $\text{Si} + \text{HS} \rightarrow \text{SiS} + \text{H}$ case. Nevertheless, it occurs without a reaction barrier (and thus have zero activation energy in the Arrhenius equation). After surveying the whole singlet and triplet PES of the tetratomic complex, we are in a position to describe the overall mechanism.

Starting at the $\text{Si} + \text{H}_2\text{S}$ reactants on their ground state (triplet PES), the collisions will likely form the $\text{H}_2\text{SiS}$ species, which may easily isomerize to the $\text{SHSiH}$ (through TS1), all in the triplet PES. Within this reaction path, we have found a singlet-triplet crossing, at which point both states become degenerate and a transition among them is more likely to occur. This crossing is actually a seam on the potential energy hypersurface, and the minimum energy on the seam of crossing (MSX) has geometry and energies very close to that of TS1 (the structure is hereafter named MSX1). If a spin transition occurs at this point, the system will likely dissociate to form the SiS molecule, as there are no other singlet dissociation channel below $\text{Si} + \text{H}_2\text{S}$ reactants. These product molecules would carry the excess energy as translational or rovibrational excitation of the diatomics.

Another crossing point was found at the same path, but with lower energy (MSX2). The geometry and energy of this crossing is very close to the triplet $\text{SHSiH}$ minimum. The red arrows displayed in Fig. 4 show the path that a steepest descent on the singlet PES would leave, if the crossing occur exactly at MSX1 or MSX2. Although any given trajectory could dissociate directly right after the crossing process, two probable reaction mechanisms are:

\[
\begin{align*}
\text{H}_2\text{S} + \text{Si}(^3\text{P}) & \rightarrow ^3\text{H}_2\text{SiS} \xrightarrow{\text{MSX1}} ^1\text{Cis} \\
& \rightarrow \text{H}_2 + \text{SiS}(^1\Sigma) + 309\text{kJ mol}^{-1} \\
\text{H}_2\text{S} + \text{Si}(^3\text{P}) & \rightarrow ^3\text{H}_2\text{SSi} \rightarrow ^3\text{SHSiH} \xrightarrow{\text{MSX2}} ^1\text{Trans} \rightarrow ^1\text{Cis} \\
& \rightarrow \text{H}_2 + \text{SiS}(^1\Sigma) + 309\text{kJ mol}^{-1}
\end{align*}
\]

The likelihood of such intersystem crossings will depend on the magnitude of the SO coupling. This was calculated at the MRCI/aug-cc-pVQZ level for both MSX1 and MSX2, with the results of 71 and 46 cm$^{-1}$, respectively. Therefore, the path described above going through MSX1 is the most likely, since it is more direct and easily reached, and also shows a larger SO coupling.

The energies (also including ZPE corrections) and vibrational frequencies for all stationary structures described above are given numerically in Table 2, including crossings points and asymptotic limits.
yield H2 species forms in the ISM, it will quickly react with H atoms to work, is a two-step process: (i) collisions between Si and SO/SO2, as proposed by Zanchet et al. (2018). However, it can also be inferred from Fig. 4 that if the HSiS species forms in the ISM, it will quickly react with H atoms to yield H2 + SiS, which is largely energetically favoured and shows no activation energy. Hence, HSiS will disappear very quickly in shock regions, making its detection all the more difficult.

Combining the two informations given above, another possible reaction pathway for several mechanisms are predicted and explored the energies involved in two SiS forming reactions in order to shed light on its formation in the interstellar medium. It is shown that SiS is stable towards destruction of SiS with O atoms. In the expanding circumstellar envelope, molecules are no longer protected from the external UV radiation field and photodissociation becomes important, affecting species like CO or H2O. This results into an increase of O abundance in the gas phase, which then rapidly reacts with SiS to produce SiO (Zanchet et al. 2018).

3.3 HSiS in the ISM

The HSiS molecule has not been detected in the interstellar medium thus far, although its rotational transitions have been measured experimentally by Brown, Yamamoto & Saito (1997). As discussed in Section 3.1, reactions between H and SiS at the surface of a grain could in principle yield this chemical species, although not the reaction in gas phase.

However, it can also be inferred from Fig. 4 that if the HSiS species forms in the ISM, it will quickly react with H atoms to yield H2 + SiS, which is largely energetically favoured and shows no activation energy. Hence, HSiS will disappear very quickly in shock regions, making its detection all the more difficult.

Combining the two informations given above, another possible source of the SiS molecule in the ISM that can be proposed from this work, is a two-step process: (i) collisions between Si + SH on the surface of grain-forming HSiS, followed by (ii) collision between HSiS + H leading to H2 + SiS, which is predicted above to be fast. We note that the scenario considered here could also occur in diffuse molecular clouds, where atomic Si and SH are present in the gas phase (Sofia, Cardelli & Savage 1994; Neufeld et al. 2015).

In the envelopes of evolved stars, as recalled in the Introduction, SiS is observed to form close to the stellar photosphere and is then injected into the expanding envelope (Prieto et al. 2015). The SiS spatial distribution appears to be more compact than those of other Si-bearing species like SiO and SiC2 (Massalkhi et al. 2019). Zanchet et al. (2018) proposed that this fact could result from the destruction of SiS with O atoms. In the expanding circumstellar envelope, molecules are no longer protected from the external UV radiation field and photodissociation becomes important, affecting species like CO or H2O. This results into an increase of O abundance in the gas phase, which then rapidly reacts with SiS to produce SiO (Zanchet et al. 2018).

4 CONCLUSIONS

Using highly accurate multireference calculations, we have explored the energies involved in two SiS forming reactions in order to shed light on its formation in the interstellar medium. It is shown that the HS molecule is easily converted to SiS by collisions with atomic silicon in the gas phase. The reaction between Si and H2S is also predicted to be possible despite its spin forbidden nature. The reaction pathway for several mechanisms are predicted and discussed. Among other results, we show that SiS is stable towards collisions with H2 and H, and that the HSiS molecule will quickly be converted to SiS in collisions with atomic hydrogen.

ACKNOWLEDGEMENTS

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Table 2. Properties of the stationary points of singlet and triplet PESs.

<table>
<thead>
<tr>
<th>Type</th>
<th>E (ZPE)</th>
<th>E/ZPE</th>
<th>ω1</th>
<th>ω2</th>
<th>ω3</th>
<th>ω4</th>
<th>ω5</th>
<th>ω6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cis</td>
<td>59.8</td>
<td>56.0</td>
<td>496</td>
<td>501</td>
<td>687</td>
<td>851</td>
<td>2159</td>
<td>2555</td>
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<tr>
<td>Trans</td>
<td>48.2</td>
<td>46.1</td>
<td>520</td>
<td>596</td>
<td>675</td>
<td>941</td>
<td>2161</td>
<td>2633</td>
</tr>
<tr>
<td>H2SSi</td>
<td>321.9</td>
<td>317.0</td>
<td>234</td>
<td>441</td>
<td>584</td>
<td>1310</td>
<td>2140</td>
<td>2346</td>
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<tr>
<td>SiS/H2</td>
<td>0.0</td>
<td>0.0</td>
<td>667</td>
<td>707</td>
<td>732</td>
<td>1093</td>
<td>2337</td>
<td>2343</td>
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<tr>
<td>TS1</td>
<td>404.9</td>
<td>381.2</td>
<td>314</td>
<td>441</td>
<td>584</td>
<td>1310</td>
<td>2140</td>
<td>2346</td>
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<tr>
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<td>226.4</td>
<td>214.2</td>
<td>541</td>
<td>572</td>
<td>775</td>
<td>1640i</td>
<td>1760</td>
<td>2194</td>
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<tr>
<td>TS3</td>
<td>123.3</td>
<td>115.2</td>
<td>400</td>
<td>617</td>
<td>657i</td>
<td>683</td>
<td>2314</td>
<td>2505</td>
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<td>TS4</td>
<td>190.1</td>
<td>178.1</td>
<td>588</td>
<td>974</td>
<td>999</td>
<td>1571</td>
<td>1601i</td>
<td>1737</td>
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<td>Minima on the seam of singlet-triplet crossings</td>
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<td></td>
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<td>MSX1</td>
<td>316.3</td>
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<td>–</td>
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<td>–</td>
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<tr>
<td>Asymptotic limits</td>
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<tr>
<td>H2 + SiS(1Σg)</td>
<td>36.7</td>
<td>19.2</td>
<td>724</td>
<td>4226</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>H2 + SiS(1Π)</td>
<td>365.5</td>
<td>346.5</td>
<td>482</td>
<td>4226</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td>H2S + Si(1P)</td>
<td>345.7</td>
<td>337.1</td>
<td>1182</td>
<td>2613</td>
<td>2637</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>H2S + Si(1D)</td>
<td>416.8</td>
<td>408.2</td>
<td>1182</td>
<td>2613</td>
<td>2637</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HSiS + H</td>
<td>361.9</td>
<td>336.6</td>
<td>690</td>
<td>702</td>
<td>2200</td>
<td>–</td>
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<td>–</td>
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</tbody>
</table>

*Energies are given in kJ mol$^{-1}$ relative to the global singlet minimum, and frequencies ($\omega$) are in cm$^{-1}$.
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