The $S^+(^4S)+SiH_2(^1A_1)$ Reaction: Toward the Synthesis of Interstellar SiS

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Abstract. We have performed a theoretical investigation of the $S^+(^4S)$ + $SiH_2(^1A_1)$ reaction, a possible formation route of the $HSiS^+$ and $SiSH^+$ cations that are alleged to be precursors of interstellar silicon sulfide, SiS. Electronic structure calculations allowed us to characterize the relevant features of the potential energy surface of the system and identify the reaction pathways. The reaction has two exothermic channels leading to the isomeric species $^3HSiS^+$ and $^3SiSH^+$ formed in conjunction with H atoms. The reaction is not characterized by an entrance barrier and, therefore, it is expected to be fast also under the very low temperature conditions of insterstellar clouds. The two ions are formed in their first electronically excited state because of the spin multiplicity of the overall potential energy surface. In addition, following the suggestion that neutral species are formed by proton transfer of protonated cations to ammonia, we have derived the potential energy surface for the reactions $^3HSiS^+/^3SiSH^+ + NH_3(^1A_1)$.

Keywords: Ab initio calculations · Astrochemistry · Silicon sulfide

1 Introduction

Silicon, the seventh most abundant element in the universe, is mostly trapped in the dust grains present in the interstellar medium (ISM) in the form of silicates. Nevertheless, an increasing number of silicon-bearing molecules, have been detected in different regions of the ISM, with a molecular size going up to 8 atoms [1]. The presence of silicon in the gas phase is mainly related to violent events, such as shocks, in which the high energetic material ejected from young stars impact a quiescent zone and allows the sputtering of the refractory core

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of interstellar dust grains [2]. As soon as silicon is released in the gas phase, it can immediately react and it is mostly converted into SiO [3,4]. Therefore, the diatomic molecule SiO is the most abundant silicon-bearing species and it is considered a useful target to probe shock regions [2]. Formation routes of the SiO molecule are well characterized [5–7], while chemical processes leading to the formation of other Si-bearing molecules are still uncertain and poorly known.

Another interesting Si-bearing diatomic molecule is silicon sulfide, SiS, detected for the first time in 1975 by Morris et al. [8] towards the molecular envelope of the carbon-rich AGB star IRC+ 10216. From that first observation, silicon sulfide (SiS) has been detected sporadically, mostly in circumstellar envelopes around evolved stars [9,10] and towards high mass star-forming regions with shocks (such as Sgr B2 and Orion KL [4,11–14]). Recently, a census of silicon molecules has been performed by Podio et al. for L1157-B1, that is, a shocked region driven by a jet originated from a Sun-like protostar [2]. Together with the detection of SiO (and its isotopologues ^{29}SiO and ^{30}SiO), the authors reported the first detection of the SiS molecule in a low-mass star forming region. Interestingly, a surprisingly high abundance of SiS has been inferred in a well-localized region around the protostar, with a SiO/SiS abundance ratios decreasing from typical values of 200 to values as low as 25. Since the abundance of other sulfur-bearing species (e.g. SO) remains constant across the region, the reason for such diversity cannot be ascribed to a local overabundance of sulphur. The analysis of the spatial distribution shows a strong gradient across the shock (being SiS abundant at the head of the cavity and not detected at the shock impact region), suggesting a different chemical origin for SiO and SiS. The reason for such a peculiar diversity is unknown and represents a challenge to our comprehension of interstellar silicon chemistry.

Given the difficulties associated to the experimental investigation of the postulated reactions, theoretical quantum chemistry calculation appears to be pivotal to elucidate the chemistry of silicon-bearing species. Recently, some interesting analysis on the potential role of neutral gas-phase chemistry in the formation and destruction routes of SiS has been proposed. For instance, some of the present authors performed a theoretical characterization of the potential energy surface (PES) of the reactions SiH+S, SiH+S_2 and Si+HS [15,16], together with a kinetic analysis based on the capture theory and Rice-Ramsperger-Kassel-Marcus calculations [17]. In addition, Zanchet et al. [18] examined the reaction of atomic silicon with SO and SO_2 and used the derived rate coefficients to simulate SiS formation in the outflows of star-forming regions like Sgr B2, Orion KL, and L1157-B1. In particular, the PES of the SiOS system has been analyzed through ab initio calculations. Kinetics calculations on the derived PES lead to the conclusion that the two reactions can play a key role for the formation of SiS, while the reaction of silicon sulfide with atomic oxygen represents an important destruction pathway of SiS. Very recently, after the work by Rosi et al. [16], the reaction of the silicon atom with the SH radical has been re-investigated by Mota et al. [19]. Accurate multi-reference calculations were employed to derive the potential energy surface for the system and quasiclassical trajectory calculations were performed to derive the reaction rate coefficient. The inclusion of the

data in a gas-grain astrochemical model of the L1157-B1 shock region, suggested a very important role for the SiS formation.

One last example revealing the pivotal role of neutral gas phase chemistry for the formation of interstellar silicon sulfide is represented by the work of R. Kaiser and coworkers, reporting a synergistic theoretical and experimental analysis of different reaction involving silicon species [20,21]. The combined crossed molecular beam and electronic structure calculations analysis provided new data on the formation of silicon sulfide. The synergy with astrochemical modeling allowed a better understanding of the role of neutral gas-phase chemistry toward star forming regions.

In spite of the recent advances summarized above, the two main databases for astrochemical models (KIDA and UMIST) [22,23] still report the electron-ion recombination of the $HSiS^+$ ion as the only significant process leading to the formation of SiS:

$$HSiS^+ + e^- \rightarrow H + SiS \tag{1}$$

However, in those databases most of the ion-molecule reactions considered as possible formation routes of the $HSiS^+$ cation are inefficient according to laboratory experiments [24,25].

As a part of our systematic investigation on interstellar SiS formation, we have now focused on possible ion-molecules reactions. In particular, here we report on the theoretical characterization of the PES for the reaction between the S^+ cation (in its ground state, ^4S) and the $SiH_2(^1A_1)$ radical. Sulphur cations are easily formed because the sulphur ioniziation energy (10.36 eV) is lower than that of atomic or molecular hydrogen. The SiH_2 radicals can be formed by photodissociation or other high-energy processes involving SiH_4. This last species can be synthesized by successive hydrogenation processes of Si atoms on the surface of the interstellar dust grains [4,26] and subsequently released in the gas phase during shocks.

In addition to electron-ion recombination, other processes can be invoked for the formation of neutral molecules starting from a protonated charged species, that is, proton transfer to neutral molecules with a large proton affinity like ammonia. As proposed by Taquet et al. [27] proton transfer to ammonia can be considered a good alternative to electron-ion recombination. Therefore, we have also derived the PES for

$$HSiS^+/SiSH^+ + NH_3 \rightarrow SiS + NH_4^+ \tag{2}$$

With the present contribution we aim to add other new pieces to the complex puzzle of the chemistry of interstellar silicon.

2 Computational Details

The $SiH_2(^1A_1)$+$S^+(^4S)$ and $HSiS^+/SiSH^+$+$NH_3(^1A_1)$ reactions were analyzed adopting a computational strategy previously used with success in several cases [15,28–30]. A first investigation of the potential energy surface was performed

through Density Functional Theory (DFT) calculations, using the Becke3-parameter exchange and Lee-Yang-Parr correlation (B3LYP) [31,32] hybrid functional, in conjunction with the correlation consistent valence polarized set aug-cc-pV(T+d)Z [33–35]. Harmonic vibrational frequencies were calculated at the same B3LYP/aug-cc-pV(T+d)Z level of theory, using the Hessian matrix (second derivatives) of the energy, in order to determine the nature of each stationary point, i.e. minimum if all the frequencies are real and saddle point if there is one, and only one, imaginary frequency. Intrinsic Reaction Coordinates (IRC) calculations [36,37] were performed to assign each identified stationary point to the corresponding reactants and products. Subsequently, the energy of each stationary point was computed with the more accurate coupled cluster theory including single and double excitations as well as a perturbative estimate of connected triples CCSD(T) [38–40], with the same basis set aug-cc-pV(T+d)Z. The zero-point energy, computed using the scaled harmonic vibrational frequencies obtained at the B3LYP/aug-ccpV(T+d)Z level of theory, was added to correct both energies [B3LYP and CCSD(T)] to 0 K. All calculations were carried out using GAUSSIAN 09 [41] and the vibrational analysis was performed using MOLDEN [42,43].

3 Results

3.1 The $SiH_2(^1A_1) + S^+(^4S)$ Reaction

The quartet potential energy surface (PES) for the system $SiH_2(^1A_1)+S^+(^4S)$ shows three different minima (MIN1, MIN2, MIN3), linked by two transition states (TS1, linking MIN1 and MIN2; TS2 connecting MIN2 and MIN3). The reaction starts with the barrierless interaction of the S^+ cation with the SiH_2 radical, leading to the formation of the intermediate MIN1, located 280.6 kJ mol^{-1} below the reactant energy asymptote. MIN1 features a new Si-S bond with a bond distance of 2.351 Å. The so formed intermediate can directly dissociate, through a barrierless H-elimination process, leading to the formation of the $^3HSiS^+$ cation and an H atom. The global exothermicity of the process is −122.3 kJ mol^{-1}. Alternatively, MIN1 can isomerize to the MIN2 intermediate by overcoming a barrier of 93.1 kJ mol^{-1}. The related transition state, TS1, clearly shows the migration of a hydrogen atom from Si to S. Two possible combinations of products can be formed starting from the aforementioned MIN2. A barrier of 133.6 kJ mol^{-1} must be overcome in order to form the previously described $H+^3HSiS^+$ products. A transition state, TS3, was identified, showing an increase in the S-H bond distance up to 2.416Å. A different H elimination process can take place starting from MIN2, leading to the barrierless formation of the $^3SiSH^+$ cation and an H atom, located 90.1 kJ mol^{-1} below the reactant energy asymptote. The last isomerization process identified in the PES is related to the migration of a hydrogen atom from the Si atom to the S side of the intermediate MIN2, leading to the formation of MIN3, located 204.3 kJ mol^{-1} below the reactant energy asymptote, in which both H atoms are linked to the S atom of the adduct. A barrier of 99.3 kJ mol^{-1} must be overcome during the migration

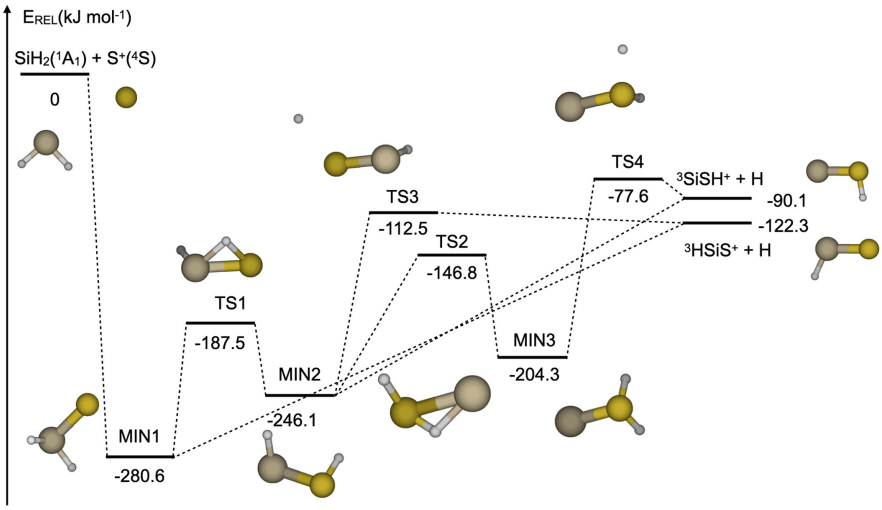

Fig. 1. Schematic representation of the Potential Energy Surface (PES) for the reaction $SiH_2(^1A_1)+S^+(^4S)$ with the energies evaluated at the CCSD(T)/aug-cc-pV(T+d)Z level of theory.

process. The so formed MIN3 can directly dissociate to $H+^3SiSH^+$, overcoming a barrier of 126.7 kJ mol^{-1}. The related transition state, TS4, clearly shows the breaking of a S-H bond, with a bond distance of 2.322Å. A schematic representation of the PES derived for the $SiH_2(^1A_1)$ + $S^+(^4S)$ reaction is reported in Fig. 1, while in Figs. 2, 3, 4 and 5 the geometry (bond distances in *Å* and angles in degree) of the stationary points are illustrated, together with those of reactants and products (at the B3LYP/aug-ccpV(T+d)Z level of theory). A list of enthalpy changes and barrier heights (in kJ mol^{-1}, corrected at 0 K) computed at the CCSD(T)/aug-cc-pV(T+d)Z and B3LYP/aug-cc-pV(T+d)Z levels of theory is reported in Table 1.

It is important to stress that, given the multiplicity of the investigated PES, the $^3HSiS^+/^3SiSH^+$ products are not formed in their ground singlet states, but in the first electronically excited triplet states.

3.2 The $^3HSiS^+/^3SiSH^+$+$NH_3(^1A_1)$ Reaction

The barrierless $^3HSiS^+$ + $NH_3(^1A_1)$ reaction shows a global exothermicity of −50.4 kJ mol^{-1} at the CCSD(T)/aug-cc-pV(T+d)Z level of theory. The interaction between the $HSiS^+$ cation and ammonia leads to the formation of the MIN4 intermediate, more stable than the reactants by 121.3 kJ mol^{-1}. Once formed, the intermediate can dissociate into silicon monosulfide (^3SiS) and ammonium ion. A similar mechanism was derived for the reaction $^3SiSH^+$ + $NH_3(^1A_1)$. In this case the global exothermicity is 82.3 kJ mol^{-1}, while the intermediate MIN5 shows a relative energy of −153.7 kJ mol^{-1} with respect to the reac-

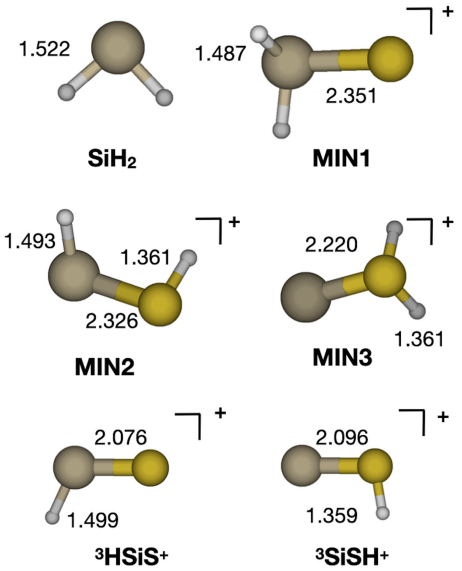

Fig. 2. Bond distances (reported in Angstroms) for the reactant, products and minima identified for the $SiH_2(^1A_1)$ + $S^+(^4S)$ reaction at the B3LYP/aug-cc-pV(T+d)Z level of theory.

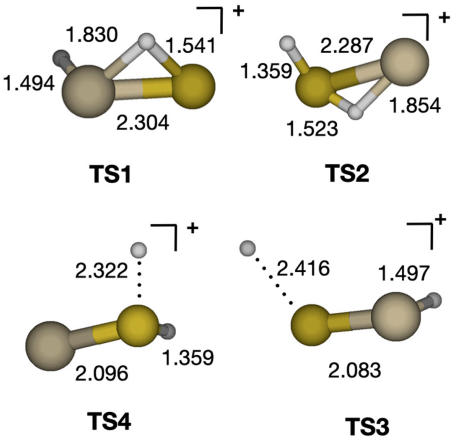

Fig. 3. Bond distances (reported in Angstroms) for the main transition states of the reaction $SiH_2(^1A_1)$ + $S^+(^4S)$, evaluated at the B3LYP/aug-cc-pV(T+d)Z level of theory.

tant energy asymptote. Both the reactions take place without the presence of entrance and/or exit barriers. The schematic PES of the two processes are reported in Fig. 6, while the optimized geometries of the most relevant stationary points are reported in Fig. 7. A list of enthalpy changes and barrier heights (in

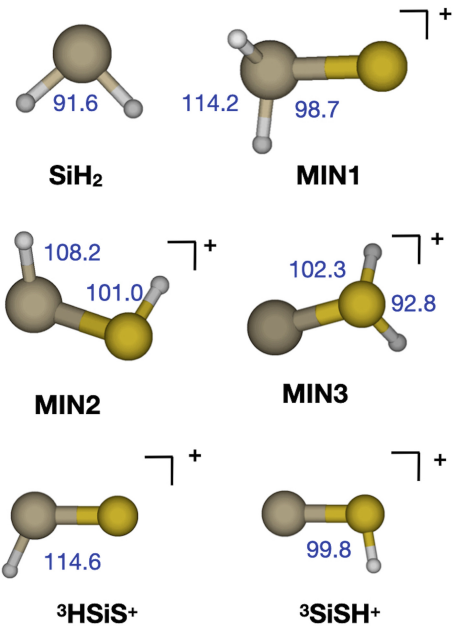

Fig. 4. Main angles (reported in degree) for the reactant, products and minima identified for the $SiH_2(^1A_1)$ + $S^+(^4S)$ reaction at the B3LYP/aug-cc-pV(T+d)Z level of theory.

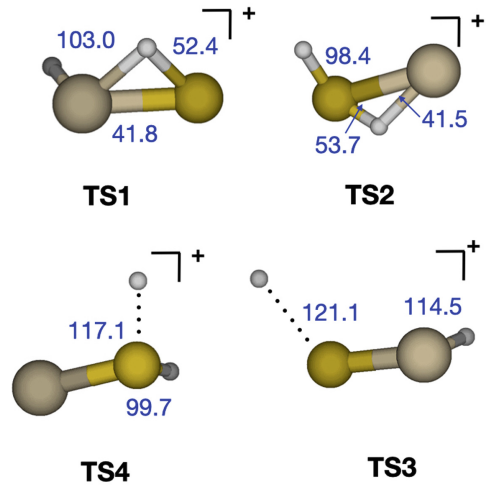

Fig. 5. Main angles (reported in degree) for the main transition states of the reaction $SiH_2(^1A_1)$ + $S^+(^4S)$, evaluated at the B3LYP/aug-cc-pV(T+d)Z level of theory.

kJ mol^{-1}, corrected at 0 K) computed at the CCSD(T)/aug-cc-pV(T+d)Z and B3LYP/aug-cc-pV(T+d)Z levels of theory is reported in Table 1.

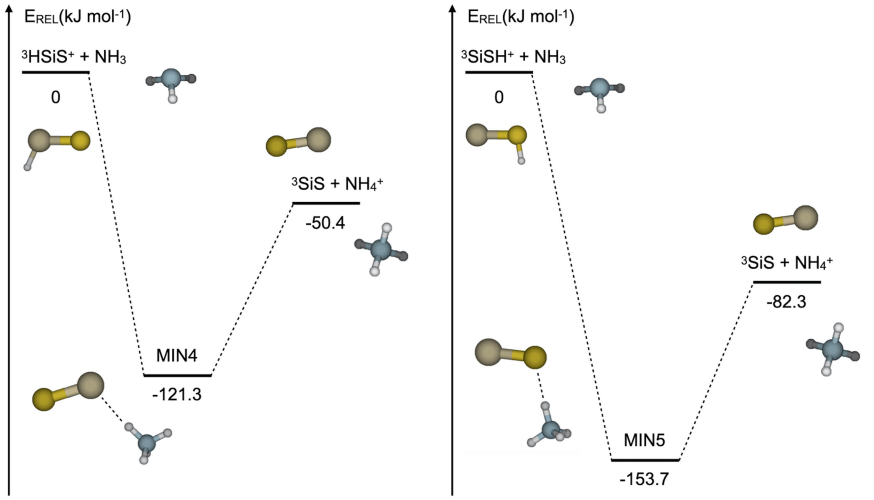

Fig. 6. Schematic representation of the Potential Energy Surface (PES) for the proton transfer processes $^3HSiS^+/^3SiSH^+ + NH_3(^1A_1)$ with the energies evaluated at the CCSD(T)/aug-cc-pV(T+d)Z level of theory.

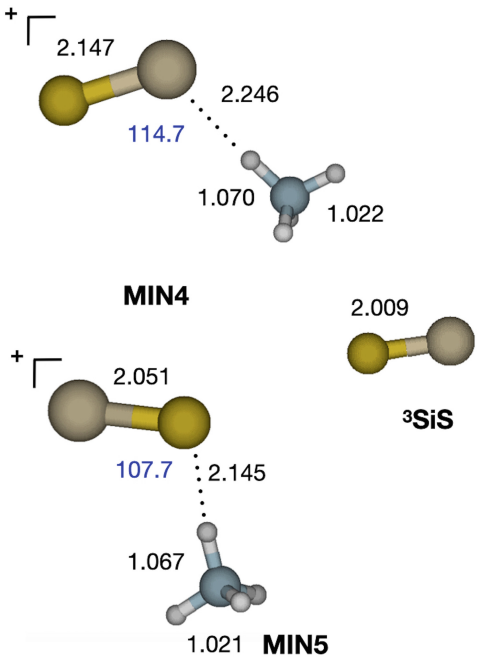

Fig. 7. Bond distances (in Angstroms) and angles (in degrees) for the main stationary points identified for the $^3HSiS^+/^3SiSH^+ + NH_3(^1A_1)$ reactions at the B3LYP/aug-cc-pV(T+d)Z level of theory.

Table 1. Enthalpy changes and barrier heights (kJ mol^{-1}, 0 K) computed at the CCSD(T)/aug-cc-pV(T+d)Z and B3LYP/aug-cc-pV(T+d)Z levels of theory for the system $SiH_2(^1A_1)$ + $S^+(^4S)$.

Reaction path	CCSD(T)		B3LYP	
	ΔH_0^0	Barrier heights	ΔH_0^0	Barrier heights
$SiH_2 + S^+ \rightarrow$ MIN1	−280.6	–	−320.4	–
MIN1 → MIN2	34.5	93.1	32.2	83.9
MIN2 → MIN3	41.8	99.3	62.9	109.1
MIN1 → H + $^3HSiS^+$	158.3	–	150.0	–
MIN2 → H + $^3HSiS^+$	123.8	133.6	117.8	120.7
MIN2 → H + $^3SiSH^+$	156.0	–	157.8	–
MIN3 → H + $^3SiSH^+$	114.2	126.7	94.9	101.2
$^3HSiS^+ + NH_3 \rightarrow$ MIN4	−121.3	–	−116.4	–
MIN4 → $^3SiS + NH_4^+$	70.9	–	80.9	–
$^3SiSH^+ + NH_3 \rightarrow$ MIN5	−153.7	–	−147.1	–
MIN5 → $^3SiS + NH_4^+$	71.0	–	71.7	–

4 Discussion and Conclusions

In this work, we have reported the results of a theoretical investigation of the reaction between the S^+ cation and the $SiH_2(^1A_1)$ radical. The reaction has two exothermic channels leading to the isomeric species $^3HSiS^+$ and $^3SiSH^+$ formed in conjunction with H atoms. The reaction is not characterized by an entrance barrier and, therefore, it is expected to be fast also under the very low temperature conditions of insterstellar clouds. The two ions are formed in their first electronically excited state because of the spin multiplicity of the overall PES. A subsequent proton transfer process with ammonia can well account for the formation of neutral triplet silicon sulfide, SiS, without invoking electron-ion recombination.

As already noted above, the PES derived for the reaction between the $SiH_2(^1A_1)$ radical and the S^+ cation (in its ground state ^4S) can only lead to the formation of the two aforementioned radicals in the triplet state, $^3HSiS^+/^3SiSH^+$. The successive proton transfer carried out by an ammonia molecule (whose ground electronic state is $^1A_1$) leads to a triplet potential energy surface. As a consequence, according to the 'correlation rules', the title reaction can only form silicon sulfide in a triplet spin state, ^3SiS. However, in systems of this kind, intersystem crossing from the triplet to the singlet PES is certainly possible, being also facilitated by the presence of atoms belonging to elements of the third period of the Periodic Table. In particular, once the first intermediate (MIN1) in the ^{3}PES for the S^++ SiH_2 reaction is formed, an intersystem crossing mechanism can allow reaching the singlet PES. Starting from this point both the $^1HSiS^+/^1SiSH^+$ cations can be formed and, consequently, the neutral

^{1}SiS molecule could be produced. To account for such an effect, it is necessary to derive the singlet PES (these calculations are currently under way) and to characterize the seam of crossing. Future work from our group will assess the role of intersystem crossing for this system, as already done for a series of reactions involving atomic oxygen [44–53].

As already mentioned in the 'Introduction' section, in the last years different theoretical investigation have been performed to access the viability of gas phase reactions for the formation of interstellar SiS, including a systematic study undertaken by some of the present authors to characterize the possible formation routes of SiS in low-mass star forming regions via neutral-neutral gas-phase processes [15–17]. With this contribution we plan to add useful information to the complex network of gas phase reactions involving Si-bearing molecules. The sputtering of dust grains in shocked regions leads to the release of silicon in the gas phase. Therefore, if we demonstrate that SiS is totally formed by neutral-neutral and/or ion-neutral gas-phase reactions, its presence and distribution in interstellar objects could become a kind of signpost for that type of chemistry being dominant in the above mentioned regions.

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