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# Interaction of Molecular SiS with Silver Atoms in an Argon Matrix: IR Spectrum and Ab Initio Rationalization

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## ABSTRACT

*Co-condensation of silver atoms and SiS in an argon matrix leads to the formation of Ag(SiS). The IR spectrum can be interpreted in two different ways: Isotopic shifts ($^{28}Si/^{29}Si$, $^{28}Si/^{30}Si$, $^{32}S/^{34}S$) imply a side-on coordination of SiS to silver. On the other hand, the Si=S frequency and the isotopic shifts can be assigned to an isolated $SiS^-$ molecule. The SiS force constant is reduced from 5.0 mdyn/Å in free SiS to 3.9 mdyn/Å in AgSiS. Ab initio investigations confirm the formation of an ion pair $Ag^+(SiS)^-$, admitting some electron delocalization.*

## *INTRODUCTION*

The formation of a first transition metal complex with SiO as ligand [1] was immediately followed by theoretical [2, 3] and experimental [4] studies about the same molecule. Whereas the IR absorptions and isotopic shifts imply a strongly bent AgSiO structure (angle $\leq 90°$) or a side-on coordination [1], ab initio SCF and CI calculations by Schaefer *et al.* favor an energy minimum only for a linear molecule Ag—O—Si ($^2\Sigma^+$) [2]. Unfortunately these calculations could not reproduce the large red shift of the SiO stretching vibration with respect to the vibrational frequency of uncoordinated SiO. On the other hand, Tse [3] found a minimum for a bent Ag—Si—O species. Our theoretical results [5] performed both at the SCF and CI levels, evidenced only a minimum on the ground state potential energy surface, which corresponds to a weakly bound linear complex Ag—OSi ($^2\Sigma^+$) with Ag—O = 2.919 Å and O—Si = 1.508 Å. So far, no theoretical work that was carried out was able to confirm the experimental observations.

We found another minimum that represents the experimentally deduced bent structure. A CASSCF geometry optimization of a charge transfer complex $Ag^+(SiO)^-$ restricted to the $^2A'$ symmetry leads effectively to a bent structure (Ag—O = 2.133 Å; O—Si = 1.555 Å; < (AgOSi) = 125.5°). But this local minimum lies about 1 eV above the ground state of linear AgOSi.

To improve our knowledge of these kinds of complexes and to encourage theoretical investigations of small molecules with transition metal atoms, we co-condensed silver atoms with SiS in an argon matrix at 10 K.

## *RESULTS*

Silver atoms and SiS, produced by passing a stream of $H_2S$ over silicon and silver at 1550 K, were co-condensed with an excess of argon on a helium-

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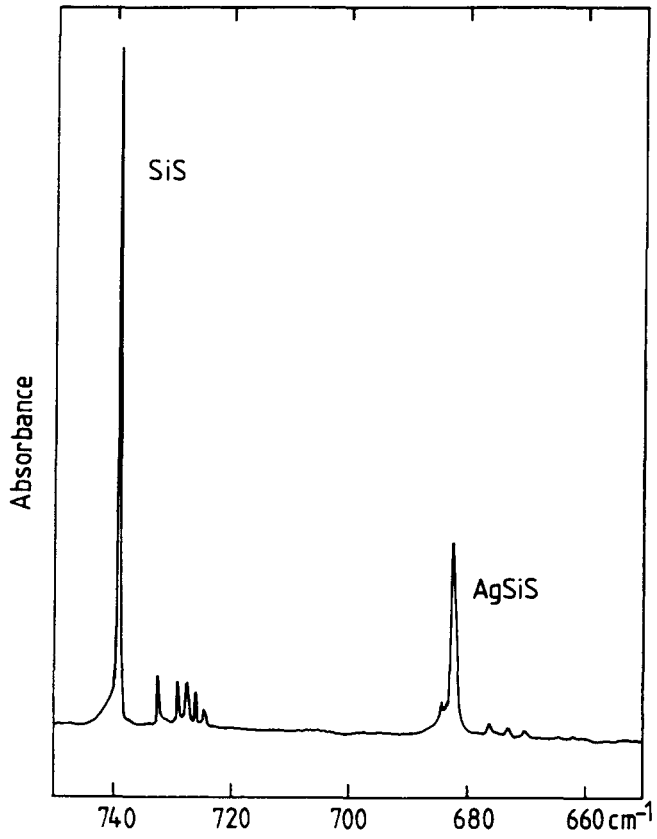


**FIGURE 1** Matrix IR spectrum of the high-temperature molecule SiS co-condensed with silver atoms.

cooled copper mirror (Ar:SiS:Ag = 1000:5:1). The matrix IR spectrum, recorded with a Bruker IFS 66v FTIR spectrometer, showed weak absorptions of $CO_2$, CO, COS, and stronger ones of SiS and $(SiS)_2$ (different amounts). Furthermore we observed a very intense band at 682.2 $cm^{-1}$ (Fig. 1) [6]. Annealing or photolysis of the matrix with a high pressure mercury lamp gave no changes in the IR spectrum.

## *DISCUSSION*

The intense band at 682.2 $cm^{-1}$ has to be assigned to an AgSiS species for the following reasons: (1) red shift with respect to 'free' SiS; and (2) in analogy to the observations of the AgSiO molecule, isotopic splittings ($^{32}S/^{34}S$, $^{28}Si/^{29}Si$) and intensity pattern are observed as expected.

The perturbation of $\nu$(SiS) of coordinated SiS with respect to uncoordinated SiS by 7.7% (739 $cm^{-1} \rightarrow$ 682 $cm^{-1}$) suggests strong interaction of the silver atom with the SiS molecule. As a consequence of the large red shift, the value of the SiS force constant is reduced (v.i.).

Although three normal modes are expected for a triatomic molecule AgSiS, we observed the SiS-stretching vibration only. The same was true for

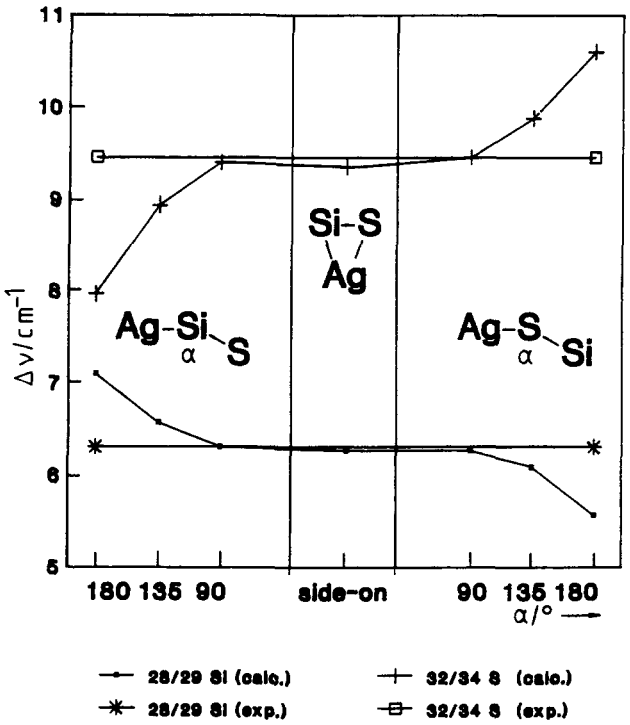


**FIGURE 2** Observed and calculated isotopic shifts of $\nu$(SiS) for the molecule Ag(SiS) (f(SiS) = 3.9 ± 0.1 mdyn/Å). Assumed frequencies and distances: (a) Ag—S: d(Ag—Si) = 2.5 Å, d(Si—S) = 1.92 Å, $\nu$(Ag—Si) = 200 $cm^{-1}$, $\delta$ = 60 $cm^{-1}$; (b) Ag—S—Si: d(Ag—S) = 2.4 Å, d(Si—S) = 1.92 Å, $\nu$(Ag—S) = 200 $cm^{-1}$, $\delta$ = 60 $cm^{-1}$; (c) Ag(SiS), side-on: d(Ag—S) = d(Ag—Si) = 2.5 Å, d(Si—S) = 1.92 Å, $\nu$(Ag—S), $\nu$(Ag—Si) = 200 $cm^{-1}$, 180 $cm^{-1}$. (Variation of the assumed parameters leads to qualitatively the same results.)

the experiments with AgSiO: The vibrations for $\nu$(AgSi) or $\nu$(AgO) could not be detected.

The IR spectrum can be interpreted in two different ways:

1. With the help of a normal coordinate analysis based on a simple valence force field, we calculated the isotropic splittings ($^{28}Si/^{29}Si$, $^{28}Si/^{30}Si$, and $^{32}S/^{34}S$) of $\nu$(SiS) for different bond angles on the grounds of assumed distances and frequencies. In Fig. 2, the bond angles of the isomers AgSiS and AgSSi are plotted versus the different calculated isotopic shifts. The experimental isotopic splittings can best be reproduced by the strongly bent molecules Ag—Si—S or Ag—S—Si (angles $\leq 90°$) or by a triangular, side-on coordinated, AgSiS molecule because of the opposite influence of Si and S substitution on the isotopical shifts.

   A linear Ag—Si—S cannot be reconciled with our measurements because of the too large $^{28}Si/^{29}Si$ and the too small $^{32}S/^{34}S$ shift. For the isotopic splittings of a linear

**TABLE 1** Comparison between Experimental and SCF Calculated SiS Frequency, Isotopic Shifts ($cm^{-1}$), and Related Force Constant (mdyn / Å).

| | $SiS\ (^1\Sigma^+)$ | | $SiS^-\ (^2\Pi)$ | $Ag(SiS)$ |
|---|---|---|---|---|
| | *Calc.* | *Exp.*[a] | *Calc.* | *Exp.*[a] |
| r(SiS) (Å) | 1.905 | 1.929[b] | 2.015 | — |
| $\nu$(SiS)($cm^{-1}$) | 821 | 739 | 654 | 682 |
| $\Delta\nu(^{28}Si-^{29}Si)$ | 7.7 | 6.8 | 6.1 | 6.3 |
| $\Delta\nu(^{28}Si-^{30}Si)$ | 14.9 | 13.1 | 11.9 | 12.1 |
| $\Delta\nu(^{32}S-^{34}S)$ | 11.2 | 10.1 | 8.9 | 9.5 |
| f(SiS) | 5.9 | 4.8 | 3.8 | 3.9 |

[a] This work.
[b] Ref. [7].

Ag—S—Si, the opposite behavior is expected.

The SiS force constant was determined to be 3.9 ± 0.1 mdyn/Å.

2. The second model is based on a charge transfer from Ag to SiS. The ionic bonding will cause nearly no vibrational coupling between Ag and SiS, which is in line with the isotopic splittings for the SiS vibration. The observed red shift of $\nu$(SiS) from SiS to AgSiS was qualitatively reproduced by ab initio SCF calculations for $SiS^-$ (Table 1). The formation of this anion is expected after a complete charge transfer.

**TABLE 2** Comparison between Experimental and SCF Calculated SiO Frequency, Isotopic Shifts ($cm^{-1}$) and Related Force Constant (mdyn / Å).

| | $SiO(^1\Sigma^+)$ | | $SiO^-\ (^2\Pi)$ | $Ag(SiO)$ |
|---|---|---|---|---|
| | *Calc.* | *Exp.*[a] | *Calc.* | *Exp.*[a] |
| r(SiO) (Å) | 1.472 | 1.510[b] | 1.519 | — |
| $\nu$(SiO)($cm^{-1}$) | 1411 | 1226 | 1214 | 1163 |
| $\Delta\nu(^{28}Si-^{29}Si)$ | 7.9 | 7.4 | 7.8 | 7.2 |
| $\Delta\nu(^{28}Si-^{30}Si)$ | 16.4 | 14.7 | 15.1 | 14.1 |
| $\Delta\nu(^{16}O-^{18}O)$ | 49.3 | 43.8 | 43.4 | 42.1 |
| f(SiO) | 11.9 | 9.0 | 8.8 | 8.0 |

[a] Ref. [1].
[b] Ref. [7].

We favor the second model for AgSiS as well as for AgSiO, as all experimental data, that is, the vibrational frequencies and related isotopic shifts, are in accordance with considerations concluded from SCF calculations for SiX and $SiX^-$ (X=O, S) (Tables 1 and 2).

A further confirmation for the interpretation presented in this article was obtained by cocondensation reactions of SiO with sodium and potassium [8].

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