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# Raman Spectrum and Bonding of Matrix Isolated $GeS_2$ Molecules

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ABSTRACT: *A suitable method to synthesize molecules like S=Ge=S, which cannot be obtained by heating of the well known solids, is provided by the matrix-isolation technique. In solid noble or other inert gases, GeS molecules react with S-atoms, which are produced photochemically from cocondensed COS. The formation of the $CO_2$-like $GeS_2$ species was monitored by IR-spectroscopy some time ago. In order to get the complete force field, the Raman spectrum has now been obtained. On the basis of these experimental findings, bonding including ab initio calculations with the result that multiple bonding in the system GeS/$GeS_2$ is found to be different from that in the couple CS/$CS_2$.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:658–661, 1999

## INTRODUCTION

Molecular $GeS_2$ cannot be obtained by vaporization of solid $GeS_2$ (GeS is tetrahedrally coordinated in each of the different solid structures) because a decomposition reaction takes place under heating:

$$GeS_2 \text{ (solid)} \rightarrow GeS \text{ (gas)} + \frac{1}{2} \cdot S_2\text{(gas)} \quad [1]$$

Therefore, the matrix-isolation technique, which offers the possibility to generate new molecules such as, $SiO_2$ [2] in the solid inert matrix material at low temperatures, is the proper tool to investigate multiple bonded species such as molecular $GeS_2$. Some years ago, we were able to investigate this simple molecule by IR spectroscopy after its generation in solid argon via the following reaction: GeS + S-atom → $GeS_2$ [3]. The S-atoms are photochemically generated from COS, which is condensed simultaneously with the high-temperature molecule GeS and an excess of argon. The observed antisymmetric stretching vibration at about 650 $cm^{-1}$, together with a series of isotopic shifts (Ge and S), was a strong confirmation for the expected linear $CO_2$-like structure [4].

## EXPERIMENTAL DETAILS

The cryostat for matrix isolation experiments, the Raman spectrometer, and the laser equipment are described elsewhere [5]. Germanium is heated resistively in an $Al_2O_3$ furnace. Gaseous $H_2S$ is passed over the heated Ge (about 1500 K) in order to produce a continuous stream of gaseous GeS. Simultaneously with the high temperature species, $CH_4$-gas containing about 2% COS is condensed on the cold copper block. The gases are handled and measured with conventional vacuum techniques. The gas flow is controlled via the decrease of the pressure with a difference capacity manometer (MKS Instruments Deutschland GmbH).

## QUANTUM CHEMICAL CALCULATIONS

Quantum chemical calculations are performed on an IBM 390 workstation using the GAUSSIAN94

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program package [6]. Unless stated otherwise, for MP2 calculations basis sets of TZVP quality [7] and for DFT calculations (with either B3-LYP or BP-86 functionals), SVP basis sets [8] are used.

## *RESULTS*

When the high temperature molecule GeS, which is generated at 1500 K by passing a stream of gaseous $H_2S$ over fluid Ge, has been condensed and put together with an excess of $CH_4$ [9] on a 15 K cold copper block, the Raman spectrum presented in Figure 1 is observed. The accurate positions of the vibrations in wavenumbers of the following isotopic isomers of GeS are presented in Table 1, the intensities are in line with the isotopic distribution of Ge and S:

$$^{70}Ge,\ 20.5\%;\ ^{72}Ge,\ 27.4\%;\ ^{73}Ge,\ 7.8\%;\ ^{74}Ge,\ 36.5\%;\ ^{76}Ge,\ 7.8\%;\ ^{32}S,\ 95.0\%;\ ^{34}S,\ 4.2\%.$$

After cocondensation of GeS with COS in $CH_4$, the Raman spectrum presented in Figure 2 is measured. Besides the absorption of GeS, the deformation vibration of COS is observed. After photolysis with a Hg medium-pressure lamp (for 10 minutes), a new sharp signal at 474.7 cm$^{-1}$ is detected, which is presented in Figure 2 b. This new signal increases while the intensities of the bands of GeS and COS decrease. In contrast to the large half width of the band of GeS, the signal of $GeS_2$ is sharp, which is plausible because the different Ge isotopes do not move within this symmetric vibration, and therefore the frequencies for all isomers containing different Ge isotopes are identical. However, the species $Ge^{32}S^{34}S$, which is expected to have its symmetric stretching vibration at about 467.5 cm$^{-1}$, is not observed because the signal-to-noise ratio does not allow us to detect bands of small intensities.

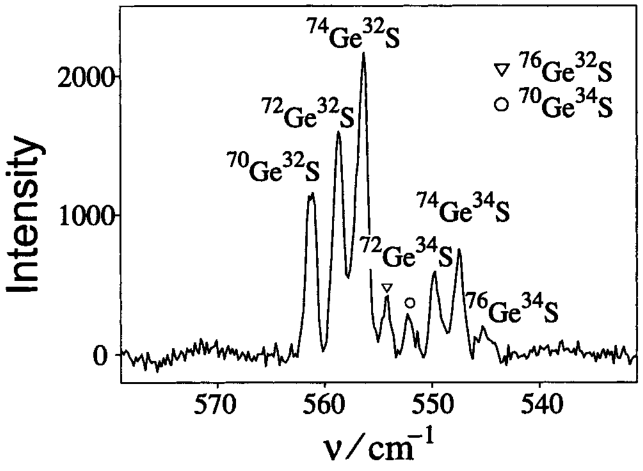

**FIGURE 1** Raman spectrum of matrix isolated molecular GeS in solid methane ($\nu_{excitation}$ = 514.5 nm; L = 200 mW; resolution, $\Delta\nu$ = 2.2 cm$^{-1}$).

**TABLE 1** Observed Vibrational Frequencies of the Different Isotopic Isomers of Molecular GeS in Solid Methane

| *Ge/S* | *70/32* | *72/32* | *74/32* | *76/32* | *70/34* | *72/34* | *74/34* | *76/34* |
|---|---|---|---|---|---|---|---|---|
| $\nu$/cm$^{-1}$ | 561.3 | 558.7 | 556.1 | 554.3 | 552.3 | 550.1 | 547.7 | 545.3 |

## *AB INITIO CALCULATIONS AND DISCUSSION*

In order to compare the experimentally detected frequencies with those from ab initio calculations, the observed positions have to be corrected with respect to anharmonicity and matrix shift. As discussed earlier, a simple procedure was applied. The measured frequencies are multiplied by a factor, which is the quotient of the harmonic gas-phase value $\omega$

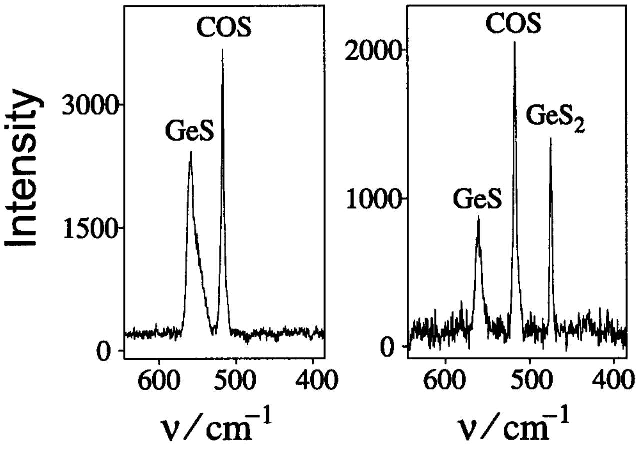

**FIGURE 2** Raman spectra after cocondensation of monomer GeS with COS before (left) and after (right) a 254 nm photolysis in solid methane ($\nu_{excitation}$ = 514.5 nm; L = 200 mW; resolution, $\Delta\nu$ = 2.2 cm$^{-1}$).

**TABLE 2** Comparison of Experimental, Corrected Experimental, and Calculated (on a DFT- and MP2-Level) Data of $GeS_2$

| | *Exp.* | *Corr. [10]* | *DFT* | *MP2* |
|---|---|---|---|---|
| d (GeS)/pm | – | – | 201.8 | 200.8 |
| $\nu(\Pi_u)$/cm$^{-1}$ | – | – | 128.2 | 117.2 |
| $\nu(\Sigma_g^+)$/cm$^{-1}$ | 474.7[11] | 494.2 | 474.7 | 496.3 |
| $\nu(\Sigma_u^-)$/cm$^{-1}$ | 653.4 [12] | 663.9 | 647.5 | 676.2 |

**TABLE 3** Experimental and Calculated Mulliken Charges $Q_M$, Force Constants, and Thermochemical Data for the Different Couples $CS/CS_2$, $SiS/SiS_2$, and $GeS/GeS_2$

| | $d_{exp.}$(M-S) $pm^{-1}$ [13] | $d_{theor.}$(M-S) $pm^{-1}$ [14] | $Q_M$ [14] | $f_r$/mdyn $Å^{-1}$ [15] | $f_{rr}$/mdyn $Å^{-1}$ | BE/kJ $mol^{-1}$ [16] |
|---|---|---|---|---|---|---|
| CS | 153.5 | 154.2 | −0.08 | 8.49 | – | 709 |
| $CS_2$ | 155.5 | 156.4 | 0.11 | 7.67 [17] | 0.70 | 572 |
| SiS | 192.9 | 196.2 | 0.50 | 4.94 | – | 616 |
| $SiS_2$ | – | 195.2 | 0.95 | 5.09 | 0.07 | 458 |
| GeS | 201.2 | 202.6 | 0.43 | 4.41 | – | 535 |
| $GeS_2$ | – | 200.8 | 0.71 | 4.53 | 0.07 | 401 |

$[\omega(^{74}Ge^{32}S) = 578.8\ cm^{-1}]$ and the observed frequency in matrix material $\nu[^{74}Ge^{32}S]$. For methane and argon matrices, values of 1.041 and 1.016 are obtained. In Table 2 the corrected vibrational modes are presented together with the results from DFT (B3-LYP, SVP-basis) and MP2 (TZVP-basis) calculations.

With the help of the corrected frequencies, stretching and interaction (stretch–stretch) force constants ($f_r$ and $f_r$, respectively) are calculated. These values are listed together with the corresponding constants of $CS/CS_2$ and $SiS/SiS_2$ in Table 3.

In order to compare bonding of monosulfide and disulfide of different elements of group XIV, some other molecular data have been calculated at the same level: Mulliken charges and bond distance. In addition to the bond energy values from the literature, bond energy has been obtained from a combined method using quantum chemical results and experimental data. With the help of MP2 calculations (TZVP basis), the energy for the reaction.

$$GeS_{(g)} + COS_{(g)} \rightarrow GeS_{2(g)} + CO_{(g)}$$

has been calculated to be $-43.8$ kJ $mol^{-1}$.

Based on this value and the well-known thermodynamic data of GeS, CO, and COS, the $\Delta H_f^{298}$ value for $GeS_{2(g)}$ is calculated to be 113 kJ $mol^{-1}$ [18]. From this result, the bond energy of $GeS_{2(g)}$ is found to be 407.8 kJ, which is very close to the experimental value of 401 kJ $mol^{-1}$ [16,19].

From Table 2, it is evident that there is a significant difference between the carbon sulfides and the sulfides of Si and Ge. For the couple $CS/CS_2$, all data listed in Table 2 show that CS exhibits a stronger bond than $CS_2$, which is in line with the chemical intuition of a triple bonding of CS and a double bonding of $CS_2$. However, for sulfides of the heavier homolog, force constants and distances favor stronger bonds for the disulfides, and with respect to bond energy, the monosulfides should have stronger interactions. The reason for these unexpected trends may be the changes in polarity from the monosulfides to the disulfides. While there are nearly nonpolar bonds in CS as well as in $CS_2$, there is significant polar bonding within the heavier homologs, with a dramatic increase from the mono- to the disulfides. Thus, in mostly covalent bonded systems (C = C, C-C, CO, $R_2C = O$, CS, $R_2C = S$), there are shorter bonds with larger force constants within the triple bonded systems than for the double bonded ones. On the other hand, nearly similar force constants are obtained for GeS as for $GeS_2$. This trend was already discussed for the couple $SiS/SiS_2$ [20] and $GeO/GeO_2$ [21].

For all of these "polar" molecules, there are different changes of polarity within the mono and disulfide (oxide) during their stretching vibrations; that is, while polarity increases during this vibrational mode of GeS, it decreases for the more polar $GeS_2$. Consequently, the covalent bond strength, which mainly influences the force constant, is lowered for GeS and strengthened for $GeS_2$, which is in line with the observed similarity of both force constants $f_{GeS}$. Obviously, this trend within the force constants corresponds to the changes of GeS distances (this consideration is discussed in detail for the couple $SiS/SiS_2$ in [20]).

However, for the couple $GeS/GeS_2$, only the values for bond energy reflect chemical intuition. This discrepancy to the trends within the force constant and the distances is plausible as a consequence of the definition of bond energy, which is based on the neutral atoms (e.g., $GeS_{(g)} \rightarrow Ge_{(s)} + S_{(g)}$), and therefore any polarity within the starting molecule reduces the value of the bond energy. On this basis, it is evident that the more polar bond of $GeO_2$ is coupled with a lower bond energy than that observed for the more covalent bond of GeO.

## *CONCLUSION*

Matrix-isolation technique supported by Raman spectroscopy and assisted by quantum chemical calculations proved once more to be the proper method to obtain a better understanding of the bonding of small molecules in which elements of higher periods are involved in multiple bonding.

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