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Matrix Infrared Spectra and Quasirelativistic DFT Studies of ThS and ThS_2

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Laser-ablated thorium atoms react with discharged sulfur vapor during co-condensation in excess argon at 7 K. The ThS fundamental is observed at 474.7 cm^{-1}, and the ν_1 and ν_3 modes for ThS_2 are observed at 451.4 and 431.5 cm^{-1}, respectively, based on sulfur-34 substitution and infrared spectra of sulfur 32, 34 mixtures. Sulfur isotopic ν_3 vibrational frequencies for ThS_2 indicate a 112 ± 5° upper limit for the S−Th−S bond angle. Quasirelativistic DFT calculations performed on ThS and ThS_2 find that ThS has the $^1\Sigma^+$ ground state, and ThS_2 has the $^1A_1$ ground state with a bond angle of 111.6°. Calculated vibrational frequencies are in excellent agreement with the observed values, and support this first identification of molecular thorium sulfides.

I. Introduction

The actinide sulfides have long been the object of investigation because of their potential use as nuclear fuels.[1] Bulk thorium sulfides have been prepared, and their stoichiometries, crystal structures, phase systems, and physical properties have been studied in detail.[2−7] Although a study of isolated molecules is crucial to understanding the intrinsic properties of solid-state thorium sulfide at a molecular level, no research has been reported for the isolated thorium sulfide molecule, in part, because of the refractory nature of thorium metal.

Recently, we have characterized the ThCO, CThO, and NThO molecules in low-temperature argon and neon matrixes by means of laser-ablation and matrix infrared spectroscopy coupled with density functional theoretical (DFT) calculations and found very good agreement between matrix-isolation observed and DFT computed frequencies for these actinide-containing small molecules.[8−10] Here, we apply these techniques to thorium sulfides, and a combined IR and quasirelativistic DFT investigation of ThS and ThS_2 shows equally good agreement between experiment and theory.

II. Experimental and Computational Methods

Sulfur atoms and small molecules were generated by a microwave discharge in argon seeded with sulfur vapor using a quartz discharge tube sulfur source similar to the one employed in earlier experiments.[11] Natural isotopic sulfur (Electronic Space Products, Inc., recrystallized) and enriched sulfur (98% ^{34}S, EG&G Mound Applied Technologies) were used as received; a 50/50 mixture of the two samples was also employed. The vapor pressure of sulfur located in the sidearm was controlled by the resistively heated windings. A microwave discharge was sustained in the argon−sulfur mixture by an Opthos Instruments, 120 W, microwave power supply (operated at 30−50% of the maximum power level) and an Evenson-Broida cavity. The discharge extended from a region about 5 cm downstream of the sulfur reservoir to the end of the discharge tube. The presence of significant quantities of S_2 in the discharge was indicated by its sky-blue emission,[12,13] which is different from the normal pink argon discharge.

The experimental method for laser ablation and matrix isolation has been described in detail previously.[14,15] Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width, 3−5 mJ/pulse) was focused to ablate the rotating thorium metal target (Oak Ridge National Laboratory). Laser-ablated metal atoms were co-deposited with the sulfur-doped argon spray-on stream onto a 7 K CsI cryogenic window at 2−4 mmol/h for 0.5−1.5 h. Infrared spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 550 spectrometer with 0.1 cm^{-1} accuracy using a mercury cadmium telluride (MCTB) detector down to 400 cm^{-1}. Matrix samples were annealed at different temperatures, and selected samples were subjected to irradiation using a medium-pressure mercury lamp ($\lambda > 240$ nm) with the globe removed.

DFT calculations were performed on thorium sulfide and disulfide molecules using the GAUSSIAN 98 program[16] and the BPW91[17] or hybrid B3LYP[18] density functional. The 6-311+G* basis set was used for sulfur,[19] and the SDD quasirelativistic pseudopotential and basis set were employed for thorium[20] using tight SCF convergence.

III. Results

Infrared Spectra. The sulfur-seeded argon discharge produced metal independent infrared bands, which were also observed in other reactions with discharged sulfur. These bands[11] include strong absorptions of S_3 at 679.8 and 676.0 cm^{-1}, S_4 at 661.7 and 642.4 cm^{-1}, CS_2 at 1528.0 cm^{-1}, and a weak S_2O band at 1157.1 cm^{-1}. Co-condensation of laser-ablated Th atoms with the discharged mixture produced several new absorptions. Figure 1 shows the 700−415 cm^{-1} region of the infrared spectra of reaction products between thorium and discharged sulfur; note the S_3 and S_4 absorptions. One strong band at 431.5 cm^{-1}, and two weak bands at 474.7 and 451.4 cm^{-1} were observed on deposition. The 474.7 cm^{-1} band sharpened, and the 451.4 and 431.5 cm^{-1} bands slightly decreased on annealing. All three bands showed little change on ultraviolet irradiation. In the ^{34}S sample experiments (Figure 2c,d), three corresponding bands were observed at 462.3, 439.2, and 420.7 cm^{-1}. In the 50/50 $^{32}S + {}^{34}S$ mixture experiment (Figure 2e,f), the 474.7 cm^{-1} band showed a doublet pattern, and other two bands exhibited triplet splitting patterns. The new absorptions are listed in the Table 1, and their assignments will be discussed in the next section.

DFT Calculations. The ground-state configurations[21,22] of S and Th atoms were reproduced as $[Ne]3s^23p^3$ and $[Rn]6d^2$-

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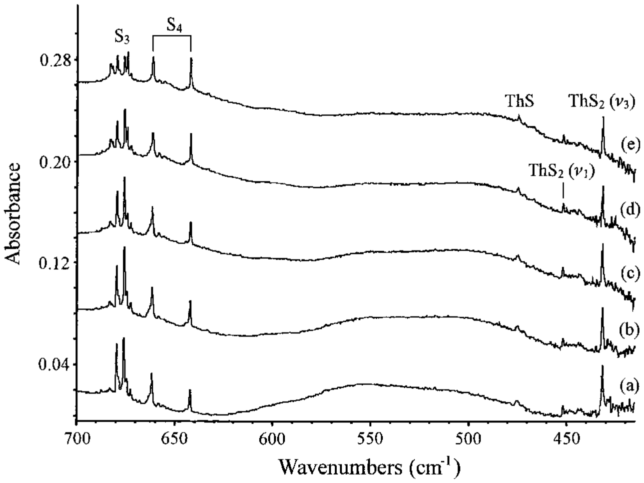

Figure 1. Infrared spectra in the 700−415 cm^{-1} region for laser-ablated Th co-deposited with discharged S in argon at 7 K. (a) Sample deposited for 40 min, (b) after 25 K annealing, (c) after $\lambda > 240$ nm irradiation, (d) after 35 K annealing, (e) after 40 K annealing.

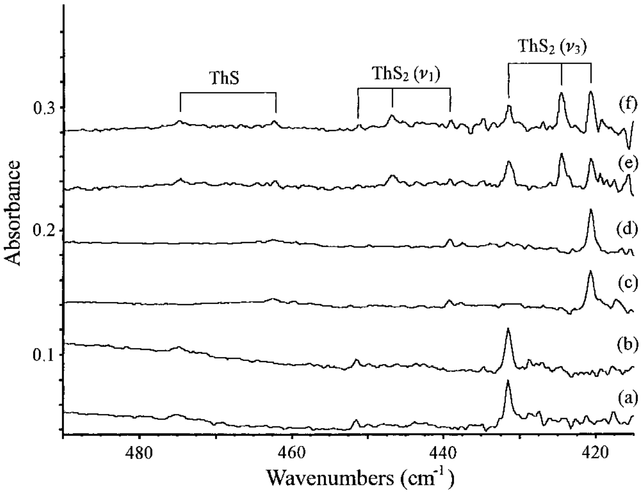

Figure 2. Infrared spectra in the 490−415 cm^{-1} regions for laser-ablated Th co-deposited with discharged S in argon at 7 K. (a, b) ^{32}S, (c, d) ^{34}S, (e, f) 50/50 $^{32}S + ^{34}S$ mixture; (a, c, e) after sample deposition, (b, d, f) after 25 K annealing.

TABLE 1: Infrared Absorptions (cm^{-1}) for ThS and ThS_2 in Excess Argon

^{32}S	^{34}S	$^{32}S + ^{34}S$	R(32/34)	identity
474.7	462.3	474.7, 462.3	1.0268	ThS
451.4	439.2	451.3, 446.8, 439.1	1.0278	ThS_2, ν_1
431.5	420.7	431.4, 424.5, 420.6	1.0257	ThS_2, ν_3

$7s^2$, respectively, using the B3LYP and BPW91 functionals. Calculations for S_2 and S_3 gave ground states of $^3\Sigma_g^-$ and $^1A_1$, respectively.[23,24] The B3LYP calculation finds the S−S bond length in the S_2 molecule to be 1.927 Å, which may be compared to the observed value (1.889 Å).[23] For the S_3 molecule, the B3LYP bond length is 1.952 Å, and bond angle is 118.2°, in excellent agreement with the MCSCF angle (117.0°),[24] and an experimental measurement[11] of 116 ± 2°. Of more importance the B3LYP value of the strong b_2 frequency (638.8 cm^{-1}) is near the matrix value (674.5 cm^{-1}).[11] For thorium sulfide and disulfide, calculations were performed on both singlet and triplet spin multiplicities. For thorium disulfide, both linear and bent starting geometries were employed. Analytical second-derivatives were used to obtain the harmonic frequencies. The calculations for thorium sulfide and disulfide are summarized in Table 2, which will be discussed in the next section. Similar results were obtained in B3LYP and BPW91 calculations.

IV. Discussion

The ThS and ThS_2 molecules will be identified from infrared spectra with sulfur isotopic substitution.

ThS. The weak absorption at 474.7 cm^{-1} red-shifted to 462.3 cm^{-1} in the ^{34}S experiment, and the $^{32}S/^{34}S$ isotopic frequency ratio of 1.0268 is very close to the harmonic diatomic ratio of 1.0269 for ThS. The mixed isotopic $^{32}S + ^{34}S$ experiment gave only two pure isotopic absorptions, which confirms that a single sulfur atom is involved in this vibrational mode. This 474.7 cm^{-1} band is assigned to the Th−S fundamental frequency in the ThS diatomic molecule.

In our DFT/B3LYP calculation, the ground state of ThS is predicted as $^1\Sigma^+$, with a σ^2 configuration. The calculation on the triplet spin multiplicity found two excited electronic states: $^3\Sigma^-$ (δ^2) and $^3\Delta$ ($\sigma^1\delta^1$), which are 39.5, 9.2 kcal/mol, respectively, higher in energy than the $^1\Sigma^+$ state. This result is also in accord with an earlier quasirelativistic study on ThO,[20] which determined the ground state for ThO as $^1\Sigma^+$. The Th−S bond length in the $^1\Sigma^+$ state is 2.349 Å, and vibrational analysis predicts the harmonic frequency at 481.4 cm^{-1}. This calculated harmonic frequency agrees with the observed Th−S fundamental very well, and requires only a scale factor of 0.986, which is typical for the B3LYP calculation.[25] For comparison, DFT calculations were also performed using the BPW91 functional, and similar results were produced as listed in the Table 2. The harmonic frequency was predicted at 479.3 cm^{-1}, slightly lower than the B3LYP value as expected.[25]

The ground-state valence electron configuration of Th is $6d^2 7s^2$, which is analogous to $3d^2 4s^2$ for the Ti atom.[22] However, the ground state of TiS is $^3\Delta$,[23,26] which is different from the $^1\Sigma^+$ ground state for ThS. The bonding in the d-block metal monosulfides includes two components, the σ bond between metal hybridized dsσ and sulfur 3pσ orbital electrons, and the π bonds between metal dπ and sulfur pπ orbital electrons, and hence this bonding has a triple bond character. The metal dδ orbitals are nonbonding, and essentially do not affect bonding. The other hybridized dsσ orbital is also nonbonding, but this orbital is very important in the bonding mechanism. The electrons in this orbital are polarized away from the sulfur atom, and to further reduce the σ repulsion, the metal atom usually undergoes s to d electron promotion. In the ionic limit, the bonding is formed between M^+S^- in which the metal cation has $d^{n-2}s^1$ configuration, where n is the number of valence electrons. TiS simply adopts this bonding scheme, and has the ground state $^3\Delta$ ($\sigma^1\delta^1$).[26]

In contrast, the ground state for ThS is $^1\Sigma^+$ (σ^2) where the nonbonding dsσ orbital is doubly occupied. This ground electronic state reversal is attributed to the relativistic effect, which substantially stabilizes the 7s orbital in thorium. As a matter of fact, the ground state[21,22] for Th^+ is $6d^1 7s^2$, whereas Ti^+ has the ground state of $3d^2 4s^1$. In our calculation, a significant amount of charge transfer from thorium to sulfur was found: the Mulliken charge on thorium is +0.40, and +0.42 in the B3LYP and BPW91 functional calculations, respectively. The Mulliken population analysis using the B3LYP method describes the configuration of thorium in ThS as $7s^{1.70} 7p^{0.04} 6d^{1.52} 5f^{0.34}$. The earlier theoretical study[20] on ThO also found that the $^1\Sigma^+$ state is no longer the ground state in the nonrelativistic calculations.

ThS_2. The weak band at 451.4 cm^{-1} and the strong band at 431.5 cm^{-1} have similar profiles. In the experiments with

TABLE 2: Calculated Electronic States, Relative Energies, Geometries, and Frequencies for ThS and ThS$_2$

species	electronic state	relative energy [kcal/mol]	geometry [Å, deg]	frequency (intensity) [cm^{-1} (km/mol)]
		B3LYP		
ThS	$^1\Sigma^+$ (σ^2)	0	2.349	481.4(58)
	$^3\Delta$ ($\sigma^1\delta^1$)	+9.2	2.390	450.2(62)
	$^3\Sigma^-$ (δ^2)	+39.5	2.421	429.6(57)
ThS$_2$	$^1A_1$	0	2.420, 111.6	105.8(4), 424.3(153), 449.7(19)
	$^1\Sigma_g{}^+$	+17.6	2.463, 180.0	94.2i(61 × 2), 406.8(304), 419.2(0)
	$^3B_2$	+33.8	2.472, 85.8	87.1(3), 269.9(3), 417.2(46)
cyclic Th(S$_2$)	$^1A_1$	+54.8	2.576, 49.3	278.3(0), 317.6(22), 476.5(19)
		BPW91		
ThS	$^1\Sigma^+$ (σ^2)		2.341	479.3(47)
ThS$_2$	$^1A_1$		2.414, 110.7	101.7(3), 422.9(129), 444.3(17)

TABLE 3: Comparison of Computed and Experimental Thorium−Sulfur Stretching Modes in ThS and ThS$_2$

method	ThS			ThS$_2$ ν_1			ThS$_2$ ν_3		
	^{32}S	^{34}S	R(32/34)	^{32}S	^{34}S	R(32/34)	^{32}S	^{34}S	R(32/34)
IR	474.7	462.3	1.0268	451.4	439.2	1.0278	431.5	420.7	1.0257
B3LYP	481.4	468.8	1.0269	449.7	437.5	1.0279	424.3	413.6	1.0259
BPW91	479.3	466.8	1.0268	444.3	432.3	1.0278	422.9	412.3	1.0257

different sulfur concentrations and different laser powers, these two bands showed constant relative absorption intensities of 1:8. They are likely due to two different vibrational modes of the same molecule. The 451.4 and 431.5 cm^{-1} bands red-shifted to 439.2 and 420.7 cm^{-1} in the ^{34}S experiment, with ^{32}S/^{34}S isotopic frequency ratios of 1.0278 and 1.0257, respectively. The average of these ratios equals 1.0268, which is the same as the ^{32}S/^{34}S frequency ratio of the ThS diatomic fundamental. Triplet splitting patterns for both absorptions in the mixed ^{32}S + ^{34}S experiments clearly show that two equivalent sulfur atoms are involved in both vibrations. It is important that the two additional bands at 446.8 and 424.5 cm^{-1} for ^{32}STh^{34}S are 1.6 cm^{-1} *higher* and 1.5 cm^{-1} *lower*, respectively, than the medians of their corresponding pure isotopic bands. Thus, these two modes interact in the mixed isotopic molecule of lower symmetry, and these two modes can be assigned to the same molecule. Hence, the ThS$_2$ molecule is identified, and the bands at 451.4 and 431.5 cm^{-1} are assigned to the symmetric, ν_1, and antisymmetric, ν_3, Th−S stretching modes, respectively. The antisymmetric stretching frequencies of ThS$_2$ and Th^{34}S$_2$ provide a basis for calculation of a 112 ± 5° upper limit to the S−Th−S bond angle.[27,28] An earlier argon matrix isolation study[29] determined a 122.5 ± 2° upper limit for the O−Th−O bond angle, and a recent DFT calculation[10] predicted the O−Th−O bond angle as 118.8°.

Since the Th atom only has four valence electrons, the ground-state ThS$_2$ molecule is obviously a singlet state if no sulfur−sulfur bond is involved. The quasirelativistic DFT calculation found the ground state as $^1A_1$ for this C_{2v} symmetry molecule with a Th−S bond length of 2.420 Å and a S−Th−S bond angle of 111.6°. The linear ThS$_2$ structure converged 17.6 kcal/mol higher in energy, and it is a true transition state because imaginary frequencies were found for the doubly degenerate π_u bending mode. For comparison, the lowest triplet state converged as $^3B_2$, which is 33.8 kcal/mol higher in energy than the $^1A_1$ ground state. The calculation on cyclic Th(S$_2$) located the lowest state as a singlet, which is 54.8 kcal/mol higher than the open structure. Vibrational analysis on the $^1A_1$ ground state predicted antisymmetric and symmetric S−Th−S stretching modes at 424.3 and 449.7 cm^{-1}, with infrared intensities of 153 and 19 km/mol, respectively. These results are very close to the observed values: the predicted infrared absorptions are only 7.2 and 1.7 cm^{-1} (or 1.7% and 0.4%) lower than the observed ν_3 and ν_1 bands, respectively, with 8:1 relative intensity. The ^{32}S/^{34}S isotopic frequency ratios for ν_3 and ν_1 modes were calculated as 1.0259 and 1.0279, respectively, in excellent agreement with the observed values. Comparable results using the BPW91 functional are listed in Tables 2 and 3. Finally, the Mulliken charge on Th in the ThS$_2$ molecule is calculated as +0.99 and +0.97 by the B3LYP and BPW91 methods, respectively.

Similar to ThO$_2$, ThS$_2$ adopts a bent geometry, but the S−Th−S angle is 7−10° smaller. The bonding in ThO$_2$ has been explained in detail previously,[30−32] and the involvement of the low-lying 6d orbital of Th in the highest occupied molecular orbital (HOMO) is crucial to the bending of ThO$_2$. In the current calculation on bent ThS$_2$, the HOMO is b$_2$, and this orbital has 14% thorium 6d character, whereas in the high energy linear ThS$_2$ structure, the b$_2$ orbital becomes a σ_u orbital, but no 6d component is found. Apparently, the bonding mechanism in the ThS$_2$ molecule is similar to that for ThO$_2$.

Reaction Mechanisms. Possible reactions for product formation, along with relative energies calculated by the quasirelativistic DFT, using the B3LYP and BPW91 functionals, respectively, are given below.

$$\mathrm{Th} + \mathrm{S} \rightarrow \mathrm{ThS} \qquad (\Delta E = -149, -156\ \mathrm{kcal/mol}) \tag{1}$$

$$\mathrm{Th} + \mathrm{S_2} \rightarrow \mathrm{ThS} + \mathrm{S} \qquad (\Delta E = -55, -53\ \mathrm{kcal/mol}) \tag{2}$$

$$\mathrm{Th} + \mathrm{S_3} \rightarrow \mathrm{ThS} + \mathrm{S_2} \qquad (\Delta E = -103, -99\ \mathrm{kcal/mol}) \tag{3}$$

$$\mathrm{Th} + \mathrm{S_2} \rightarrow \mathrm{ThS_2} \qquad (\Delta E = -172, -182\ \mathrm{kcal/mol}) \tag{4}$$

$$\mathrm{Th} + \mathrm{S_3} \rightarrow \mathrm{ThS_2} + \mathrm{S} \qquad (\Delta E = -126, -125\ \mathrm{kcal/mol}) \tag{5}$$

The ΔE value for reaction 1 is also the $-D_e$ value for ThS. This value is smaller than the reported experimental D_e value for ThO of 207.5 ± 2.1 kcal/mol,[23] indicating a substantially weaker bond for ThS.

In the current experiment, the dominant processes for formation of ThS and ThS$_2$ cannot be determined. All proposed reactions are thermodynamically favorable, but no apparent increase was observed for either ThS or ThS$_2$ on annealing and irradiation in the argon matrix. This suggests that the formation of ThS and ThS$_2$ may require significant activation energy since thorium sulfides are formed only during the sample deposition process where laser-ablated thorium atoms provide enough excess energy[33] to overcome the activation barriers.

V. Conclusions

Laser-ablated thorium atoms react with discharged sulfur vapor during co-condensation in excess argon at 7 K to form thorium sulfide products. The ThS fundamental is observed at 474.7 cm^{-1}, and the ν_1 and ν_3 modes for ThS_2 are observed at 451.4 and 431.5 cm^{-1}, respectively. The isotopic ν_3 vibrational frequencies for ThS_2 determine the upper limit of the S−Th−S bond angle as 112 ± 5°. Quasirelativistic DFT calculations performed on ThS and ThS_2 show that ThS has the $^1\Sigma^+$ ground state, ThS_2 has the $^1A_1$ ground state, and this C_{2v} molecule has a bond angle of 111.6°. As for ThO_2, the Th 6d orbital participation is responsible for the bent structure, and the valence angle is 7−10° smaller in ThS_2 than in ThO_2. Computed vibrational frequencies are in excellent agreement with the observed values, which supports this first identification of molecular thorium sulfides and validates quantum chemical calculations for thorium sulfides.

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