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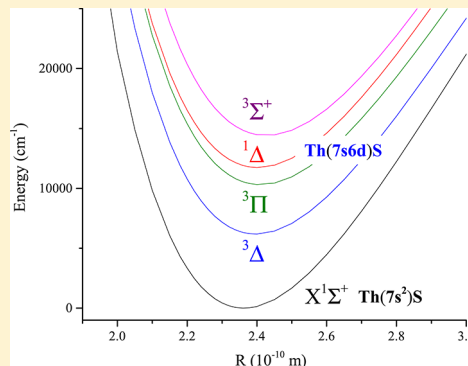
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Spectroscopic and Theoretical Investigations of ThS and ThS<sup>+</sup>

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**ABSTRACT:** Gas-phase ThS has been produced via the reaction of laser ablated Th with H<sub>2</sub>S. Rotationally resolved electronic spectra were recorded by laser-induced fluorescence (LIF) over the range 17500–24000 cm<sup>-1</sup>. Resonance-enhanced multiphoton ionization was used in conjunction with a time-of-flight mass spectrometer to confirm the assignments of nine LIF bands to ThS. Using excitation of a ThS band centered at 22118 cm<sup>-1</sup>, a dispersed fluorescence spectrum revealed a vibrational progression of the X<sup>1</sup>Σ<sup>+</sup> ground electronic state and the term energies of two low-lying excited states (<sup>3</sup>Δ<sub>1</sub> and <sup>3</sup>Δ<sub>2</sub>). Two-color photoionization spectroscopy was used to study ThS<sup>+</sup>. An accurate ionization energy for ThS was obtained (54425(3) cm<sup>-1</sup>); ThS<sup>+</sup> vibronic term energies up to *v* = 7 in the X<sup>2</sup>Σ<sup>+</sup> ground state and *v* = 3 in the <sup>2</sup>Δ<sub>3/2</sub> first excited state were recorded. High-level electronic structure calculations, with inclusion of the spin–orbit interactions yielded predictions that were in good agreement with the experimental data for ThS and ThS<sup>+</sup>. The spectroscopic properties of ThS/ThS<sup>+</sup> are compared with those of the valence isoelectronic pairs ThO/ThO<sup>+</sup>, HfO/HfO<sup>+</sup>, and HfS/HfS<sup>+</sup>.



## ■ INTRODUCTION

Spectroscopic and theoretical studies of diatomic actinide sulfides (AnS) can provide insights concerning the bonding in materials that involve actinide–sulfur bonds. In addition to being a matter of fundamental interest, actinide–sulfur interactions are of importance for nuclear fuels and the design of chelating ligands used in separation processes.<sup>1,2</sup> Differences between the interactions of actinides with hard and soft donor ligands can be explored through comparisons of oxides and sulfides.

There have been relatively few studies of isolated AnS species. The most notable work is that of Pereira et al.,<sup>3</sup> who investigated the reactivities of a series of AnS and AnS<sup>+</sup> species in the gas phase using mass spectrometry. Ionization and bond dissociation energies were evaluated through studies of the reactions with COS, CO<sub>2</sub>, CH<sub>2</sub>O, and NO. As part of this effort, they carried out systematic theoretical studies of the AnS/AnS<sup>+</sup> and AnO/AnO<sup>+</sup> series using density functional theory (DFT) methods. This was done, in part, to assess the accuracy of DFT methods when applied to actinides. Comparisons to the experimental results for AnO/AnO<sup>+</sup> suggested that DFT predictions were reasonably reliable but that the assessment of the sulfide predictions was limited due to the lack of data.

In the present work, we have initiated gas phase spectroscopic studies of AnS species by examining the electronic excitation and photoionization of ThS. This choice is an extension of our recent spectroscopic studies of the related molecular pairs ThO/ThO<sup>+</sup> (refs 4–6), HfO/HfO<sup>+</sup> (refs 7 and 8), and HfS/HfS<sup>+</sup> (ref 9), permitting direct comparisons between the properties of these valence isoelectronic molecules and cations. There are no previous reports of gas phase spectroscopic data for ThS or ThS<sup>+</sup>. However, the neutral

molecule was observed in the matrix isolation study reported by Liang and Andrews.<sup>10</sup> They obtained a ground state vibrational frequency of 474.7 cm<sup>-1</sup> for Th<sup>32</sup>S isolated in solid Ar at a temperature of 7 K. <sup>32</sup>S/<sup>34</sup>S isotopic substitution and DFT calculations were used to confirm the species assignment. The latter predicted a <sup>1</sup>Σ<sup>+</sup> ground state with a low-lying <sup>3</sup>Δ state (as has been observed for ThO, HfO, and HfS).

Here, we report on the characterization of ThS using laser excitation and dispersed fluorescence spectroscopy. Two-color photoionization techniques have been used to obtain an accurate ionization energy (IE) and vibrationally resolved data for the first two electronic states of the ThS<sup>+</sup> cation. High-level ab initio calculations that include the effects of spin–orbit coupling have been carried out for comparison with the spectroscopic data.

## ■ EXPERIMENTAL METHODS

The apparatus used in this study has been described previously,<sup>11–13</sup> so only a brief description is given here. ThS was produced using a laser ablation source. The 1064 nm output of a pulsed Nd/YAG laser (~20 mJ, pulse duration 6 ns, Continuum Minilite II) was focused onto a Th metal disk that was continuously rotated and translated to expose a fresh surface for each laser shot. A pulsed solenoid valve, located behind the Th foil, produced a gas pulse that entrained the ablated material in a carrier gas consisting of He + 0.2% H<sub>2</sub>S. The mixture was subjected to a supersonic expansion, thereby

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cooling the ablation products. The backing pressure and gas pulse duration were typically 2.7–3.1 bar and 300  $\mu$ s.

Laser induced fluorescence (LIF) spectra were recorded with the excitation laser positioned approximately 5 cm downstream from the expansion nozzle orifice. The output from a Coherent ScanMate Pro dye laser/Nd:YAG laser system was propagated perpendicularly to the direction of the gas expansion. Baffle arms were installed on the windows of the source chamber to reduce the amount of scattered laser light. Fluorescence was collected along an axis that was perpendicular to both the laser beam and gas expansion axes. Low resolution spectra (0.15  $\text{cm}^{-1}$  fwhm) were obtained using just the diffraction grating as the tunable element in the ScanMate Pro. Higher resolution spectra were recorded by using an intracavity etalon to reduce line width to approximately 0.06  $\text{cm}^{-1}$ . Fluorescence was detected by a Photonis XP2020 photomultiplier tube. Dispersed fluorescence spectra were collected using a 0.25 m Ebert monochromator (Jarrell-Ash model 82–410, 1180 line/mm grating, 0.5 mm slit width).

Downstream of the LIF detection region, the core of the jet expansion entered a second differentially pumped chamber via a conical skimmer with a 5 mm orifice. This chamber housed a time-of-flight mass-spectrometer (TOFMS) operating with a 250 V/cm field between the repeller and extractor plates. In the TOFMS, the molecular beam was crossed by two counter-propagating beams from tunable dye lasers (Continuum ND6000 and a Coherent ScanMate Pro). Two-color two-photon ( $1 + 1'$ ) resonantly enhanced multiphoton ionization (REMPI) spectra were recorded by scanning the Coherent ScanMate Pro dye laser to search for resonant intermediate excited states, ionizing the excited molecules with the ND6000 dye laser and recording the resulting mass spectrum. The laser beams were temporally overlapped and synchronized with the pulsed molecular beam using digital delay generators.

Photoionization efficiency (PIE) spectra were recorded to determine the ionization energy of ThS using the same experimental arrangement as that for REMPI. The only difference being that the pump laser wavelength was fixed on a known transition of neutral ThS, and the ionization laser was scanned until the onset of the ThS<sup>+</sup> ion signal was observed in the mass spectrometer.

Pulsed field ionization–zero electron kinetic energy (PFI–ZEKE) spectra<sup>11,14</sup> were recorded for the ThS<sup>+</sup> molecular ion using two-color excitation. For these measurements, the repeller and the extractor electrodes were held at –3.5 V to give field free conditions during photoexcitation. After a 1.7  $\mu$ s time delay, a voltage pulse was applied to the extractor electrode to give an electric field of 1.43 V/cm, causing ionization of the remaining molecules in long-lived high- $n$  Rydberg states, and accelerating the electrons toward the MCP detector located 10 cm below the repeller electrode. Transitions in the PFI–ZEKE spectra were confirmed to belong to ThS by detuning the pump laser from resonance with the intermediate state.

The LIF and REMPI spectra typically displayed a resolution of about 0.10–0.15  $\text{cm}^{-1}$ , while rotationally resolved PFI–ZEKE spectra displayed a resolution of about 1.5  $\text{cm}^{-1}$ . LIF and REMPI spectra were calibrated using the observed atomic Th lines.<sup>15</sup>

**Notation.** In the following, we use standard spectroscopic term symbols for the lower energy states of ThS and ThS<sup>+</sup> (i.e., those lying below 10000  $\text{cm}^{-1}$ ). The higher energy excited states of ThS are labeled using  $\{\nu_0/10^3\}|\Omega|$  where  $\nu_0$  is the band

origin in wavenumbers and  $\Omega$  is the projection of the electronic angular momentum along the diatomic axis.<sup>16</sup> The notation is modified to  $[\nu_0/10^3]|\Omega|$  (the curly brackets are replaced by square brackets) when it is established that the  $\nu = 0$  level for the state is being observed.

**Electronic Structure Calculations.** Calculations were carried out at the CASSCF/MRCI+Q level (complete active space self-consistent field multireference configuration interaction with the Davison size extensive correction) of theory as implemented in the MOLPRO 2010.2 suite of programs.<sup>17</sup> Ground state potential energy curves for both ThS and ThS<sup>+</sup> were also examined using the RCCSD(T) method. Our calculations employed the aug-cc-pVTZ basis set of Woon et al.<sup>18</sup> for the sulfur atom, as taken from the MOLRPO 2010.2 basis set library. The basis set used for Th consisted of a 60-electron effective core potential with the atomic natural orbital basis for the valence electrons (ECP60MWB\_ANO).<sup>19,20</sup> It included parameters for calculating the spin–orbit interaction energy and was optimized to recover scalar relativistic effects. The active space used for the calculations consisted of the S 3s and 3p orbitals with Th 7s, 7p, and 6d (13 orbitals with 10 (ThS) or 9 (ThS<sup>+</sup>) electrons). The Th 6s and 6p orbitals were optimized, while being held fully occupied. To limit the size of the calculations the active space was restricted to configurations that had 7 or 8 electrons in the S 3s and 3p orbital subspace.

Spin–orbit coupling energies were determined using the Breit–Pauli operator evaluated in the basis of MCSCF wave functions (CASSCF/MRCI+Q/SO). Potential energy curves (PEC) were calculated up to about 10000  $\text{cm}^{-1}$  above the minimum for each electronic state. To derive spectroscopic constants, the nuclear Schrödinger equation was solved variationally for each PEC of interest using the program LEVEL 8.0.<sup>21</sup> Predictions of the electronic states and excitation energies for ThS calculations that included the spin–orbit interaction are listed in Table 1. The ground state was found to

**Table 1. Calculated Molecular Constants for ThS**

state	$T_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$R_e$ (Å)	method
$X^1\Sigma^+$	0	477	0.1074	2.363	<i>a</i>
	0	479	0.1079	2.358	<i>b</i>
	0	489	0.1089	2.347	<i>c</i>
	0	481	0.1087	2.349	<i>d</i>
$^3\Delta_1$	3940	454	0.1047	2.394	<i>a</i>
$^3\Delta_2$	4856	453	0.1048	2.393	<i>a</i>
	4923	457	0.1052	2.388	<i>b,e</i>
	3220	450	0.1050	2.390	<i>d</i>
$^3\Delta_3$	5811	455	0.105	2.391	<i>a</i>

<sup>a</sup>CASSCF/MRCI/SO calculations. See text for details. <sup>b</sup>CCSD(T).

<sup>c</sup>Density functional theory calculations without spin–orbit coupling. B3LYP/ECP/pVTZ results from ref 3. <sup>d</sup>Density functional theory calculations without spin–orbit coupling. B3LYP/ECP/6-311+G\* results from ref 10. <sup>e</sup>Obtained from a RCCSD(T) calculation for the lowest energy triplet state of  $a_2$  symmetry ( $C_{2v}$ ).

be  $X^1\Sigma^+$ , as it is for the valence isoelectronic species ThO, HfO, and HfS. Molecular constants of  $\omega_e = 477.2$ ,  $\omega_e x_e = 0.92$ ,  $B_0 = 0.1074 \text{ cm}^{-1}$ , and  $R_e = 2.363 \text{ Å}$  were derived from the PEC. The permanent electric dipole moment at the equilibrium distance was predicted to be 4.1 D.

Examination of the wave function at the equilibrium distance indicated that this state has appreciable multireference character. The leading contributions were 56%  $\text{Th}^{2+}(7s^2)S^{2-}$

( $3s^23p^6$ ) and 17%  $\text{Th}^+(7s\sigma^26d\pi)S^-(3s^23p\sigma^23p\pi^3)$ . CCSD(T) calculations yielded molecular constants (also listed in Table 1) that were in good agreement with the CASSCF/MRCI+Q/SO results, but the value of the  $T_1$  diagnostic (0.025 near the equilibrium distance) clearly signaled that the multireference character was potentially problematic.

The lowest energy excited states of ThS are the  $|\Omega| = 1, 2$ , and 3 components of a  $^3\Delta$  state. Calculations without spin–orbit coupling yield a multireference wave function for the  $^3\Delta$  state, with a leading contribution of 74%  $\text{Th}^{2+}(7s5d\delta S^2-(3s^23p^6))$ . The molecular constants derived from the spin–orbit coupled calculations show that promotion of an electron from 7s to the less polarizable 6d orbital causes a slight lengthening of the bond and decrease of the vibrational frequency. A single-point spin–orbit energy calculation, carried out with the inclusion of both singlet and triplet configurations, yielded a vertical excitation energy of  $11504\text{ cm}^{-1}$  for the  $\text{Th}^{2+}(7s5d\delta S^2-(3s^23p^6))\ ^1\Delta_2$  state at the ground state equilibrium distance.

Theoretical predictions for  $\text{ThS}^+$  are presented in Table 2. Following the behavior of the neutral molecule, the low-lying

**Table 2. Calculated Molecular Constants for  $\text{ThS}^+$**

state	$T_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$R_e$ (Å)	method
$X^2\Sigma^+$	0	502	0.1114	2.321	<i>a</i>
	0	508	0.1115	2.318	<i>b</i>
	0	514	0.1123	2.311	<i>c</i>
$^2\Delta_{3/2}$	2499	479	0.1084	2.353	<i>a</i>
$^2\Delta_{5/2}$	4730	487	0.1087	2.350	<i>a</i>
$^2\Pi_{1/2}$	8803	475	0.1063	2.375	<i>a</i>
$^2\Pi_{3/2}$	10313	472	0.1063	2.375	<i>a</i>

<sup>a</sup>CASSCF/MRCI/SO calculations. See text for details. <sup>b</sup>RCCSD(T).

<sup>c</sup>Density functional theory calculations. B3LYP/ECP/pVTZ results from ref 3.

states arise from configurations that are predominantly  $\text{Th}^{3+}(7s)S^2-(3s^23p^6)$   $X^2\Sigma^+$  and  $\text{Th}^{3+}(6d)S^2-(3s^23p^6)$  ( $^2\Delta$ ,  $^2\Pi$ ,  $^2\Sigma^+$ ). These states all show significant configurational mixing, but to a lesser degree than the corresponding states of the neutral molecule. For example, the leading contribution to the  $X^2\Sigma^+$  eigenvector was 70%  $\text{Th}^{3+}(7s)S^2-(3s^23p^6)$ . Ground state molecular constants of  $R_e = 2.318\text{ Å}$ ,  $\omega_e = 508.0$ , and  $\omega_e x_e = 0.99\text{ cm}^{-1}$  were obtained.

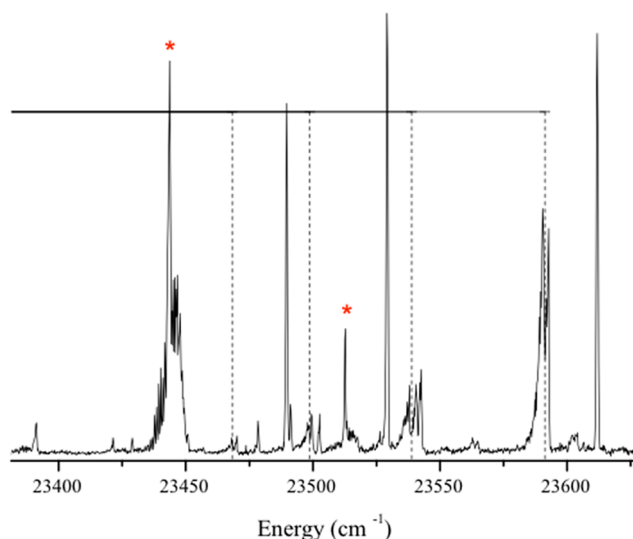
RCCSD(T) calculations for  $\text{ThS}^+(X)$  yielded constants that were comparable to those obtained from the multireference calculations, but again the  $T_1$  diagnostic was significant (0.026). Molecular constants for the  $^2\Delta$  and  $^2\Pi$  states exhibited the characteristic reduction in  $\omega_e$  and increase in  $R_e$  (relative to the ground state) resulting from the lower polarizability of the 6d orbital (cf., Table 2).

Adiabatic ionization energies, obtained using CASSCF/MRCI+Q ( $53709\text{ cm}^{-1}$ ), CCSD(T) ( $53928\text{ cm}^{-1}$ ), and DFT/B3LYP ( $5.33 \times 10^5\text{ cm}^{-1}$ )<sup>3</sup> methods were in good agreement. In Tables 1 and 2, we have also listed results from the density functional theory (DFT) calculations of Pereira et al.<sup>3</sup> and Liang and Andrews.<sup>10</sup> Pereira et al.<sup>3</sup> used the B3LYP and MPW1PW91 functionals in their investigation. There were differences between the results for the two functionals, but neither emerged as being systematically superior. In the following, we quote the results for the more commonly used B3LYP functional. Where comparisons could be made, the DFT results were in good agreement with the predictions of

the present study. Note that the RCCSD(T) and DFT calculations for the  $\text{ThS } ^3\Delta$  state, which did not include spin–orbit coupling, are compared with the experimental and spin–orbit computed values for the  $^3\Delta_2$  component. This choice was based on the expectation that the leading diagonal contribution from the spin–orbit operator will be given by  $A\Lambda\Sigma$ , where  $A$  is the spin–orbit coupling constant,  $\Lambda$  is the body-fixed projection of the electronic orbital angular momentum, and  $\Sigma$  is the projection of the spin. For this Hund's case (a) approximation,  $\Sigma = 0$  for  $^3\Delta_2$ , making this component the least influenced by the spin–orbit interaction. This assumption was supported by the CASSCF/MRCI+Q/SO calculations.

## EXPERIMENTAL RESULTS

Low resolution survey spectra were recorded over the range  $17500\text{--}24000\text{ cm}^{-1}$  using both LIF and  $(1 + 1')$  REMPI detection. The LIF spectrum showed prominent features that were readily assigned to Th, ThO, and ThS. A section of this spectrum is shown in Figure 1. The bands of ThO and ThS



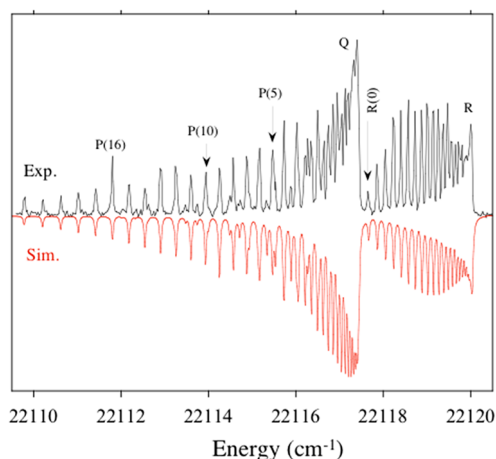
**Figure 1.** Section of a low-resolution LIF spectrum showing bands of ThS that are indicated by the vertical dotted lines. The bands marked with asterisks are from ThO, while the remaining features are Th atomic lines.

could be distinguished on the basis of their characteristic band contours. Data taken using mass-resolved REMPI detection were used to confirm the attribution of specific LIF bands to ThS.

Nine vibronic features of ThS were found that were sufficiently free from overlapping transitions to be good candidates for studies of the rotational structures. The higher resolution spectra were recorded using the LIF detection, as this yielded narrower linewidths (mostly because robust fluorescence signals could be obtained using laser intensities that were low enough to avoid significant power broadening, while the higher intensity needed for REMPI caused some broadening). Figure 2 shows a typically example of the rotational structures observed.

This band has the characteristic features of a  $^1\Pi\text{--}^1\Sigma$  transition, consistent with the theoretical prediction of a  $X^1\Sigma^+$  ground state. The downward-going trace in Figure 2 shows a spectral simulation carried out using the program PGO-





**Figure 2.** Rotationally resolved LIF spectrum of the ThS [22.12]– $X^1\Sigma^+$  band. The upward going trace is the experimental data, and the inverted trace is a simulation with an assumed rotational temperature of 28 K. See text for details.

PHER,<sup>22</sup> with the  $\hat{N}^2$  representation of the Hamiltonian and the assumption of a rotational temperature of 28 K. The rotational structure was fitted by varying the band origin ( $\nu_0$ ), the upper and lower state rotational constants ( $B'$  and  $B''$ ), and the upper state lambda doubling parameter  $q'$ . The line shape was represented by a Lorentzian function with a width (fwhm) of  $0.06\text{ cm}^{-1}$ . Tests showed that the centrifugal distortion constants could not be determined with statistical significance, and they were subsequently set to zero. In fact, all of the bands that were rotationally resolved exhibited  $^1\Pi-X^1\Sigma^+$  structures. The molecular constants obtained using PGOPHER fits to the rotational structures are listed in Table 3. Note that it is

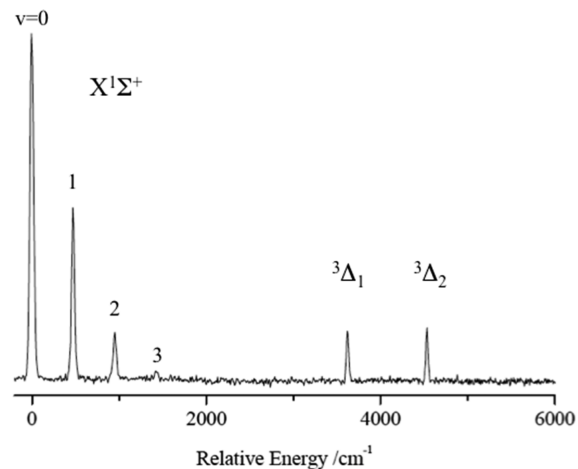
**Table 3. Molecular Constants Derived from the LIF Spectra for ThS**

state <sup>a</sup>	origin ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$q$ ( $\text{cm}^{-1}$ )
$X^1\Sigma^+$	0.0	0.111(2)	0
{18.26}1	18259.0(3)	0.104(2)	0
{18.53}1	18529.4(3)	0.106(2)	$1.6(1) \times 10^{-3}$
{18.69}1	18689.5(3)	0.104(2)	$1.9(2) \times 10^{-3}$
{21.54}1	21542.0(3)	0.103(2)	$2.1(3) \times 10^{-4}$
{21.94}1	21938.8(3)	0.103(2)	$8(3) \times 10^{-4}$
{22.02}1	22024.8(3)	<sup>b</sup>	
[22.12]1	22117.5(3)	0.105(2)	$1.6(7) \times 10^{-4}$
{23.15}1	23148.7(3)	<sup>b</sup>	
{23.59}1	23585.9(3)	0.105(2)	$8(4) \times 10^{-4}$

<sup>a</sup>The values given in curly brackets are vibronic band origins, in units of  $10^3\text{ cm}^{-1}$ . Values given in square brackets are for the electronic origin, in units of  $10^3\text{ cm}^{-1}$ . <sup>b</sup>Rotationally resolved spectra were not obtained due to problems with the etalon scanning system.

convenient for simulations to represent the upper electronic states as being  $^1\Pi$ , but it is likely that these states have mixed character. Hence, in the following, the higher excited states are labeled as being  $|\Omega| = 1$ .

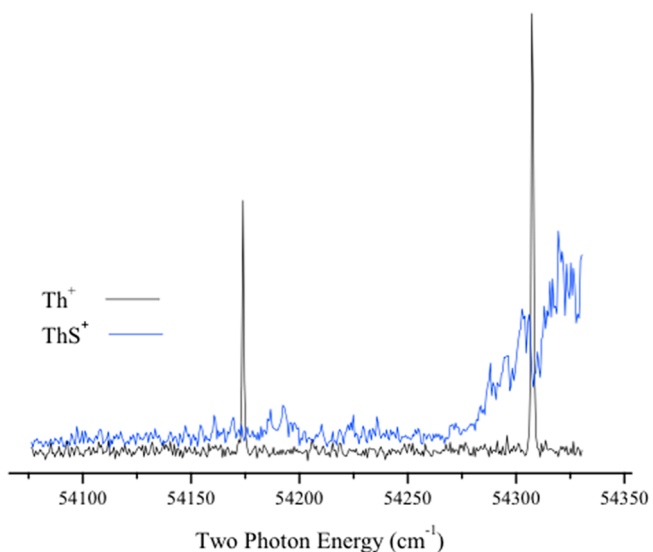
Figure 3 shows a dispersed fluorescence spectrum that was recorded using excitation of the Q-branch band head of the [22.12]1– $X^1\Sigma^+$  transition. The structure on the low energy side of this spectrum is a short progression in the ground state vibration, while the two bands at higher energies may be ascribed to electronically excited states (see below). The



**Figure 3.** Dispersed fluorescence spectrum for ThS recorded using excitation of the [22.12]1– $X^1\Sigma^+$  band.

ground state vibrational intervals defined an approximate value for the harmonic vibrational constant of  $\omega_e = 479(1)\text{ cm}^{-1}$ .

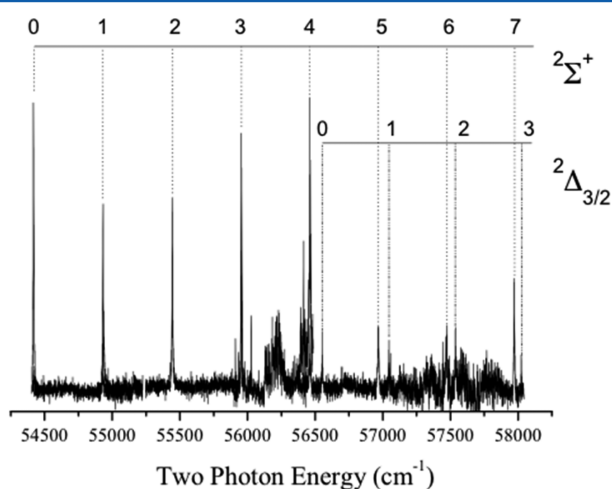
As a preliminary for PFI–ZEKE studies of the ion, two-color photoionization efficiency measurements were used to locate the ionization threshold. The advantage of this low-resolution survey technique is that it provides the fastest way to locate the lowest energy ionization feature. In this experiment, that first laser was set to excite the Q-branch band head of the {18.53}1– $X^1\Sigma^+$  transition. Figure 4 shows the photoionization



**Figure 4.** Two-color PIE spectrum recorded with the first laser set to excite the {18.53}1– $X^1\Sigma^+$  transition. The lower trace shows the spectrum obtained by monitoring the  $\text{ThS}^+$  ion channel. This calibration signal was produced by one-color, two-photon ionization.

efficiency curve recorded by scanning the wavelength of the second dye laser, with detection of the  $\text{ThS}^+$  and  $\text{Th}^+$  ion currents using the TOFMS. The atomic ion signal, resulting from one-color two-photon ionization, provided wavelength calibration points. The trace for  $\text{ThS}^+$  yielded a reasonably well-defined threshold energy. After correction for the effect of the electric field in the mass spectrometer (F) using the approximation  $\Delta E(\text{cm}^{-1}) = 6(F(\text{Vcm}^{-1}))^{1/2}$ , this measurement provided an ionization energy of  $54415(20)\text{ cm}^{-1}$ .

A PFI–ZEKE survey scan for ThS is shown in Figure 5. This trace was recorded with the first laser set to excite the Q-branch



**Figure 5.** PFI–ZEKE scan of ThS. This trace was recorded with the first photon tuned to excite the  $\{23.59\}1-X^1\Sigma^+$  band. This spectrum comprises several dye ranges for the ionizing laser. The baseline noise at  $57500\text{ cm}^{-1}$  is due to background electrons in the apparatus generated from multiphoton processes. A functional fit to the dye laser power curve has been subtracted from the data in the range  $57250$ – $58250\text{ cm}^{-1}$ .

band head of the  $\{23.59\}1-X^1\Sigma^+$  transition. Two vibrational progressions are evident in this trace, along with broad interference features centered near  $56200$  and  $57500\text{ cm}^{-1}$  that were not part of the  $\text{ThS}^+$  spectrum. The interfering features were still present when the first laser was tuned away from the  $\text{ThS}$  resonant excitation. Other than verifying that they did not originate from  $\text{ThS}^+$ , we did not attempt to identify the source of these signals. Higher resolution spectra, recorded with initial excitation of the  $\{23.59\}1-X^1\Sigma^+$  band head, yielded unstructured vibronic features that were approximately  $6\text{ cm}^{-1}$  wide (fwhm). The width was primarily determined by the simultaneous excitation of multiple rotational states. Attempts were made to improve the resolution by using the first laser to excite individual P-branch lines of the neutral molecule transition. However, the signal-to-noise ratio for these measurements was low, and we were unable to resolve the rotational states of the  $\text{ThS}^+$  ion. The blue edge of the PFI–ZEKE origin band was used to obtain a refined value for the IE of  $54425(3)\text{ cm}^{-1}$ . Band edges from the two vibrational progressions are listed in Table 4.

Vibrational constants were determined by fitting the band edges to the standard anharmonic oscillator expression

**Table 4.** Measured Vibronic Energies for  $\text{ThS}^{+a}$

$\nu$	$X^2\Sigma^+$	$^2\Delta_{3/2}$
0	0	2136
1	523	2627
2	1030	3115
3	1537	3603
4	2048	
5	2554	
6	3059	
7	3556	

<sup>a</sup>Energies in  $\text{cm}^{-1}$  with uncertainties of  $\pm 3\text{ cm}^{-1}$ .

$$T_v = T_e + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$$

This procedure yielded vibrational constants of  $\omega_e = 517(2)$  and  $\omega_e x_e = 1.2(3)\text{ cm}^{-1}$  for the ground state and  $\omega_e = 489(4)\text{ cm}^{-1}$  for the excited state (the data did not yield a statistically significant value for  $\omega_e x_e$ ).

## DISCUSSION

The theoretical predictions for the ground state of ThS were found to be in reasonably good agreement with the spectroscopic data. The expected singlet multiplicity and  $X^1\Sigma^+$  symmetry was confirmed. The measured rotational constant was larger than the calculated values, indicating that the equilibrium bond lengths were slightly overestimated. Because of the limited resolution of the dispersed fluorescence spectrum (Figure 3), the ground state vibrational constant of  $479\text{ cm}^{-1}$  was determined with an error band of  $\pm 1\text{ cm}^{-1}$ . While the CASSCF/MRCI + Q/SO and CCSD(T) results were in good agreement with this value, DFT predictions were further outside of this error range. The gas phase measurement is also in good agreement with the ground state vibrational interval of  $\Delta G_{1/2} = 474.7\text{ cm}^{-1}$  determined by matrix isolation spectroscopy,<sup>10</sup> considering the shift expected for the perturbing effect of the Ar host.

Note that the intensity pattern of the ground state progression in the dispersed fluorescence spectrum was consistent with emission from the zero-point vibrational level of the electronically excited state. The pattern indicates a slight shift between the upper and lower state equilibrium distances. This is confirmed by the difference between the rotational constants, which show that the bond length is greater for the excited state. The dispersed fluorescence spectrum also shows transitions that terminate on two low-lying electronically excited states. Only the origin bands are detected for these transitions, indicating that the equilibrium bond lengths for the lower states are close to that of the emitting state. This pattern is consistent with the assignment of the lower states as  $^3\Delta_1$  and  $^3\Delta_2$ . As can be seen in Table 1, these states are predicted to have a larger equilibrium distance, relative to that of the ground state. Note also that the emitting state was  $|\Omega| = 1$ . Hence, the  $\Delta\Omega = 0, \pm 1$  selection rule explains why a transition to the  $^3\Delta_3$  component was not observed. Measured term energies for the  $^3\Delta_1$  and  $^3\Delta_2$  states were  $3623(4)$  and  $4534(4)\text{ cm}^{-1}$ , respectively. The values predicted by the CASSCF/MRCI + Q/SO calculations ( $3940$  and  $4856\text{ cm}^{-1}$ ) were in respectable agreement with both the absolute term energies and the spin–orbit interval. As noted previously, the first-order effects of spin–orbit coupling are minimal for the  $^3\Delta_2$  component, and we found that a CCSD(T) calculation for the energy of this state without spin–orbit coupling was also close to the observed value.

For  $\text{ThS}^+$ , we have observed the ground state and the first electronically excited state at the level of vibrational resolution. The vibrational constants are consistent with the ground state being  $\text{Th}^{3+}(7s)S^2-X^2\Sigma^+$  and the excited state  $\text{Th}^{3+}(6d\delta)-S^2-^2\Delta_{3/2}$ . As has been noted previously in discussions of  $\text{ThO}^+$  (ref 5),  $\text{HfO}^+$  (ref 8), and  $\text{HfS}^+$  (ref 9), the vibrational frequency is lowered by  $(n - 1)d \leftarrow ns$  excitation because the less polarizable  $(n - 1)d$  orbital is more strongly destabilized by the electrostatic interaction with the ligand.<sup>16</sup> The state ordering, term energy for  $^2\Delta_{3/2}$  and the vibrational frequencies from the calculations reported in Table 2 are in good agreement with the experimental data. As in the two-color

PFI–ZEKE spectra recorded for  $\text{ThO}^+$ ,  $\text{HfO}^+$ , and  $\text{HfS}^+$ , the long vibrational progressions observed for  $\text{ThS}^+$  do not follow the Franck–Condon factors for the second excitation step.<sup>5,8,9</sup> This appears to be a common trait for di- and triatomic molecules that contain Th, U, or Hf (refs 5, 8, 9, and 23–27).

Overall, the findings of the present study are in good agreement with those of Pereira et al.<sup>3</sup> Our DFT and CCSD(T) calculations yielded comparable results, and the CASSCF/MRCI+Q/SO calculations show that the trends deduced from the spin-free calculations are not changed significantly by the inclusion of spin–orbit coupling. The  $\text{ThS}$  IE recommended by Pereira et al.<sup>3</sup> (6.7(2) eV) has an error range that encompasses our measured value of 6.7466(25) eV, and the IEs obtained from the calculations of the present study were also in respectable agreement with the experimental value (cf., Table 1). On the basis of both their calculations and comparisons of reactivities, Pereira et al.<sup>3</sup> concluded that the IE of  $\text{ThS}$  would be approximately 0.2 eV higher than that of  $\text{ThO}$ . This prediction was confirmed by the present measurement and our previous<sup>5</sup> IE for  $\text{ThO}$  of 6.60267(3) eV.

The energies of low-lying states of the valence isoelectronic molecules  $\text{HfS}/\text{ThS}/\text{ThO}$  and their cations are collected for comparison in Table 5. Here, it can be seen that the  $^3\Delta_2$ – $^3\Delta_1$

**Table 5. Comparison of Energies for the Low-Lying States of  $\text{HfS}/\text{ThS}/\text{ThO}$  and  $\text{HfS}^+/\text{ThS}^+/\text{ThO}^{+a}$**

molecule	$^3\Delta_1$	$^3\Delta_2$	interval	ref
HfS	6631.3	7596.6	965.3	28
ThS	3623(4)	4534(4)	911(6)	this work
ThO	5316.6	6127.9	811.3	29
molecule	$^2\Delta_{3/2}$	$^2\Delta_{5/2}$	interval	ref
HfS <sup>+</sup>	5187(3)	7986(3)	2799	9
ThS <sup>+</sup>	2136(3)	[4730]	[2231]	this work
ThO <sup>+</sup>	2933.7	5814.4	2880.7	5

<sup>a</sup>Ionization energies ( $\text{cm}^{-1}$ ): IE( $\text{ThS}$ ) = 54425(3); IE( $\text{ThO}$ ) = 53253.8(2); IE( $\text{Th}$ ) = 50868.71(8); IE( $\text{HfS}$ ) = 61933(3); IE( $\text{Hf}$ ) = 55047.9(3). Energies are  $T_0$  values, given in  $\text{cm}^{-1}$ . The values in square brackets for  $\text{ThS}^+$  are from the CASSCF/MRCI/SO calculations.

spin–orbit intervals of the neutral molecules are similar, falling in the range of 811–965  $\text{cm}^{-1}$ . Similarly, the  $^2\Delta_{5/2}$ – $^2\Delta_{3/2}$  intervals of the ions fall in the range 2231–2881  $\text{cm}^{-1}$ . When the effects of the second-order interactions between the  $^1\Delta_2$ ,  $^3\Pi_2$ , and  $^3\Delta_2$  states are taken into account for the neutrals,<sup>28</sup> the intervals for both the neutrals and cations are consistent with the atomic ion ( $n - 1$ )d spin–orbit coupling constants (the second and higher order interactions were calculated by MOLPRO via diagonalization of the matrix for the spin–orbit operator). In this respect, it seems that the low-lying states of these molecules can be rationalized using a ligand field model for the electronic structure. The fact that the  $^3\Delta/2\Delta$  states of  $\text{ThS}/\text{ThS}^+$  are at a lower energy than the corresponding states of  $\text{ThO}/\text{ThO}^+$  reflects the stronger destabilization of the 6d orbital by oxygen. This can be traced to the shorter bond length and greater charge separation of  $\text{ThO}/\text{ThO}^+$ .

Experimental and theoretical studies of  $\text{ThX}/\text{ThX}^+$  and  $\text{HfX}/\text{HfX}^+$  ( $X = \text{O}, \text{S}, \text{F}$ ) diatomics show that the bond lengths contract and that the vibrational frequencies increase on ionization.<sup>5,8,9,24,26</sup> Paradoxically, the bond dissociation energies decrease slightly. The DFT calculations of Pereira et al.<sup>3</sup> indicate that this behavior will be exhibited by all of the

diatomic actinide sulfides. For nearly all of the Th and Hf species studied, the vibrational and rotational constants of the low-lying states provide clear indications of the electronic configuration of the metal atom. In Tables 1, 2, and 4, the change in the vibrational frequency that accompanies  $6d \leftarrow 7s$  promotion is an example of this effect. However, there is one notable exception in this group of molecules. The lowest energy  $^1\Sigma^+$  and  $^3\Delta_1$  states of  $\text{ThF}^+$  were found to have closely similar vibration constants, such that high-level theoretical calculations were unable to resolve the question of the energetic ordering of these states.<sup>24</sup> It is likely that interactions between multiple low-lying configurations are responsible for the deviation of  $\text{ThF}^+$  from the simple molecular constant/electronic configuration mapping observed for the other  $\text{ThX}$  and  $\text{HfX}$  species.

One of the motivations for the study of  $\text{AnS}/\text{AnS}^+$  species by Pereira et al.<sup>3</sup> was the question of whether computationally inexpensive DFT models could be used to reliably predict the physical and chemical characteristics of An–S bonds. For  $\text{ThX}/\text{ThX}^+$  ( $X = \text{S}, \text{O}$ ) the experimental data validate the DFT results, and the higher level calculations performed in the present study indicate that the Th atom relativistic pseudopotential of Cao et al.<sup>19,20</sup> yields reliable quantitative predictions in spin–orbit coupled calculations.

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### Notes

The authors declare no competing financial interest.

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