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Sujata Guha

Tennessee State University

Joseph S. Francisco

Tennessee State University

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AN AB INITIO STUDY OF THE STRUCTURES, VIBRATIONAL SPECTRA, AND ENERGETICS OF AlSH^X ($X = -1, 0, +1$)

SUJATA GUHA AND JOSEPH S. FRANCISCO

Department of Chemistry, Tennessee State University, Nashville, TN 37209; and Department of Chemistry and Department
of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-2084; sguha@tinstat.edu

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ABSTRACT

The ground state of aluminum hydrosulfide, AlSH^X (where $X = -1, 0, +1$), has been examined using high-level ab initio electronic structure calculations at the CCSD(T) level with an augmented correlation-consistent basis set. The geometries have been optimized up through the aug-cc-pV5Z level and vibrational frequencies calculated using the aug-cc-pV5Z basis set. The energetic properties of AlSH are also examined. The adiabatic ionization potential and electron affinity of AlSH are calculated to be 198.5 and 7.7 kcal mol⁻¹, respectively. Dissociation of AlSH into AlS + H will require 78.2 kcal mol⁻¹ of energy, and the Al-S bond energy is 91.1 kcal mol⁻¹. Structural and energetic properties of the cation and anion of AlSH are reported for the first time.

Subject headings: circumstellar matter — radiative transfer — stars: abundances — stars: atmospheres — stars: carbon

1. INTRODUCTION

It has been observed that the circumstellar envelopes of carbon-rich late-type asymptotic giant branch (AGB) stars, such as IRC +10216 and CRL 2688, contain metallic substances (Highberger et al. 2003). Identifying the carriers of metal-containing molecules in the interstellar medium, including circumstellar gas, is crucial for the evaluation of dust grain composition, ionization balance, mass loss from evolved stars, and elemental depletions. Nine metal-containing species have been specifically observed that can be separated into the categories of metal cyanides (NaCN, KCN, MgNC, MgCN, and AlNC; Ziurys et al. 1995, 2002) and metal halides (NaCl, KCl, AlF, and AlCl; Cernicharo & Gue'lin 1987). The most commonly appearing metallic element is aluminum, which is present in the envelope of the carbon star IRC +10216 as AlCl, AlF, and AlNC, with fractional abundances of 9×10^8 , 1×10^7 , and 3×10^{10} , respectively, relative to H₂. The cosmic abundance of aluminum/hydrogen is 3×10^6 . These data suggest that less than 10% of the available aluminum is contained in gas-phase molecules, while the remaining fraction could be present in other gas-phase species.

An aluminum-containing molecule that may be present in circumstellar gas is aluminum hydrosulfide, AlSH, formed due to the reaction of Al or AlCl with H₂S. AlSH, being a closed-shell species, is a likely product of local thermodynamic equilibrium (LTE) radiative transfer chemistry in the circumstellar inner envelope and, thus, a competitive sink for available aluminum (Glassgold 1996). Theoretical calculations by Chen et al. (2001) at the MP2/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-31+G(2df,p) levels suggested that neutral AlSH had a bent structure and, therefore, a spectrum consisting of *a*-type transitions. They also calculated its harmonic vibrational frequencies at the HF/6-31G(d) theory level (Chen et al. 2001).

The pure rotational spectrum of AlSH was experimentally measured (Janczyk & Ziurys 2006) in the range 319–472 GHz, using millimeter and submillimeter direction absorption techniques. Nine transitions of AlSH were recorded for symmetry components $K_\alpha = 0-6$, with the $K_\alpha = 5$ and 6 components being attributed to vibration-rotation interactions. The appearance of *K*-ladder structure indicated that AlSH is a bent species with an \tilde{X}^1A'

electronic state. The structure of neutral AlSH was determined, and its rotational constants as well as ω for the lowest-frequency bending vibration estimated (Janczyk & Ziurys 2006). It was concluded that AlSH is likely to be present in the hot, dense inner envelope of carbon-rich stars where other aluminum-bearing compounds have been detected, in particular IRC +10216 and CRL 2688 (Janczyk & Ziurys 2006).

There is no report available in the literature regarding the structural, spectroscopic, and energetic properties of the cation and anion forms of AlSH. In our present work, high level quantum chemical calculations have been performed at the coupled cluster level of theory on AlSH neutral, cation, and anion forms, in order to achieve a better understanding of the electronic structure of the AlSH species. The spectral as well as energetic properties of the AlSH forms have also been examined.

2. COMPUTATIONAL METHODS

Ab initio electronic structure calculations of the AlSH species have been performed using the GAUSSIAN 03 program (Frisch et al. 2003). Coupled cluster theory (Raghavachari et al. 1989) with single and double excitations along with a perturbative estimate of connected triples, CCSD(T), has been employed in the present work. The equilibrium geometrical parameters of the AlSH species were fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles with a self-consistent field convergence of at least 10^{-9} on the density matrix. The correlation-consistent polarized valence basis sets of Dunning (1989), Kendall et al. (1992), and Woon & Dunning (1993) have been used. The augmented double, triple, quadruple, and quintuple zeta sets, denoted by aug-cc-pVnZ, where *n* is the cardinal number of the basis set ($n = D, T, Q$, and 5) has been utilized. Such augmentation refers to the addition of extra diffuse functions for each angular momentum symmetry. The aug-cc-pVnZ ($n = D, T, Q$, and 5) basis sets correspond to the generally contracted (Raffenetti 1973) basis sets of [2s1p], [3s2p1d], [4s3p2d1f], and [5s4p3d2f1g], respectively, for first-row atoms. The harmonic vibrational frequencies and infrared intensities of all species were obtained numerically at the CCSD(T)/aug-cc-pVnZ level of theory, where $n = D, T, Q$, and 5. The CCSD(T) energetics were extrapolated

to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\text{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2], \quad (1)$$

where $n = 2$ (DZ), 3 (TZ), 4 (QZ), and 5 (SZ) as proposed by Peterson et al. (Peterson et al. 1994).

3. RESULTS AND DISCUSSION

3.1. Geometries for Neutral, Cation, and Anion Forms of AISH

The ground electronic state of neutral AISH has C_s symmetry. The highest occupied molecular orbital (HOMO) of AISH reveals considerable overlap between the p -orbitals of aluminum and sulfur. The p -orbitals of aluminum and sulfur are involved in π -bonding in the AISH neutral form, leading to an Al-S triple bond (Al \equiv S). In hydrogen there is only the σ -orbital, which does not interact with the p -orbitals of sulfur, so there is little conjugation effect on the S-H bond. For neutral AISH, illustrated in Figure 1a, the optimized geometrical parameters are provided in Table 1. The optimizations are carried out with four different Dunning correlation-consistent basis sets. We note the trends of decreasing bond distance with the improvement of basis set size. A comparison of the S-H distance with the theoretical and experimental estimates in literature shows reasonable agreement. The rotational analysis of AISH from absorption studies (Janczyk & Ziurys 2006) determined the S-H distance to be 1.36 ± 0.04 Å, in good agreement with our CCSD(T)/aug-cc-pV5Z results. Our result also agrees fairly well with the range of theoretical estimates of Chen et al. (2001; between 1.3481 and 1.3511 Å) depending on the method of calculation used. The Al-S distance is estimated to be 2.240 ± 0.006 Å (Janczyk & Ziurys 2006) and between 2.2362 and 2.2716 Å (Chen et al. 2001). In our best ab initio result, the Al-S bond is longer than that obtained from the experiments by ca. 0.009 Å. The AISH angle, predicted from our calculations at the CCSD(T)/aug-cc-pV5Z level of theory, differs from experimental results (Janczyk & Ziurys 2006) by 0.7° , and this falls within the experimental uncertainty of $\pm 5.8^\circ$. A comparison of the experimental (Janczyk & Ziurys 2006) and our calculated geometries for AISH shows that the CCSD(T)/aug-cc-pV5Z structural parameters are within 1% (rms error) of the experiments. Since there are no structural determinations for the AISH⁺ cation and AISH⁻ anion in the literature, this uncertainty estimate provides some structural reliability limits to the CCSD(T)/aug-cc-pV5Z structure parameters for the cation and anion forms of AISH, also provided in Table 1.

To aid in the experimental characterization of AISH, rotational constants are presented in Table 2. As a calibration of the rotational constants, a comparison of the experimental rotational constants for AISH (Janczyk & Ziurys 2006) shows that the rms error in our CCSD(T)/aug-cc-pV5Z results is less than 1%.

The structures of the cation and anion of AISH are illustrated in Figures 1b and 1c, respectively. The geometries of these species, presented in Table 1, have been fully optimized to give the best estimation of the equilibrium geometry. The HOMO of the cation has the same character as that of the neutral, suggesting that the HOMO of AISH⁺ is formed by removal of an electron from the HOMO of neutral AISH. Because of this electron removal, an unpaired electron is left in the π -bonding orbitals between aluminum and sulfur. The AISH⁻ anion is formed due to electron acceptance by the $3p$ orbital of aluminum. An examination of the geometries for the AISH⁺ cation shows

similar trends in convergence in the basis set size, that is, a decrease in bond distances in the AISH⁺ species with increasing basis set size. A comparison of the structures of AISH⁺ with that of neutral AISH shows that there is a difference in geometry between the AIS bonds in the two species. In the cation, the AIS bond contracts. At the CCSD(T)/aug-cc-pV5Z level of theory, the AIS bond contracts by 0.098 Å in AISH⁺. The S-H single bond in the cation is longer than the S-H bond in the neutral AISH by 0.007 Å.

Rotational constants that can aid in the structural characterization of AISH⁺ are provided in Table 2. If we use the rms error between CCSD(T)/aug-cc-pV5Z and experimental millimeter absorption spectroscopic results for AISH as a calibration, the predicted rotational constants for AISH⁺ should be reliable to within the 1% uncertainty range.

Our best estimate of the Al-S bond in AISH⁻ is 2.346 Å. Note that there is 0.097 Å elongation of the Al-S bond in AISH with the addition of an electron. Rotational constants for AISH⁻ are provided in Table 2.

3.2. Vibrational Frequencies for Neutral, Cation, and Anion of AISH

Vibrational frequencies for AISH are provided in Table 3. The AISH neutral species has three normal vibrational modes: two stretching modes and one bending mode, all of which are infrared active. For the AISH species, the predicted vibrational frequencies are all positive and real, confirming that the optimized geometries used in the frequency calculations represent the minimum energy structures of AISH. An asymmetric top pattern exists for AISH, indicating a bent structure. This is consistent with experimental predictions (Janczyk & Ziurys 2006). The structural changes are manifested in the vibrational frequencies. From their experimental work, Janczyk & Ziurys provided an estimate of ω as 430 cm^{-1} for the lowest frequency vibration of AISH (Janczyk & Ziurys 2006). The AISH bending mode, reported in the work of Chen et al. (2001) at the HF/6-31G(d) theory level, is located at 432.5 cm^{-1} . Our best calculated value of 426 cm^{-1} for the AISH vibrational motion agrees well with the literature values.

For the cation and anion of AISH, there are no experimental determinations of any normal vibrational modes. Predictions for these modes are also listed in Table 3. For AISH⁺, all positive real vibrational frequencies are found, indicating a true minimum energy structure. The structural changes in between neutral AISH and its cation are also manifested in the vibrational frequencies. The decrease in the Al-S bond length in AISH⁺ is reflected in an increase in its Al-S stretching frequency by 125 cm^{-1} . Thus, there is a shift to higher frequency with the ionization of AISH, consistent with the changes in the Al-S bonding. The Δr change in the S-H bond length for AISH-AISH⁺ of 0.007 Å, at the CCSD(T)/aug-cc-pV5Z theory level, would suggest a redshift in the S-H stretching mode in the cation from that in its corresponding neutral. In the assignments in Table 3, the S-H vibrational mode is indeed redshifted from that of the corresponding neutral species by 43 cm^{-1} . The redshift suggests a weaker bond consistent with the elongation of the S-H bond with the removal of an electron from neutral AISH. In the case of AISH/AISH⁻, the Al-S and S-H vibrational motions are clearly distinguishable.

3.3. Adiabatic Ionization Potential for AISH

An important objective of our study is to determine the adiabatic ionization potential for the AISH species. To our knowledge, there have been no previous determinations of its adiabatic

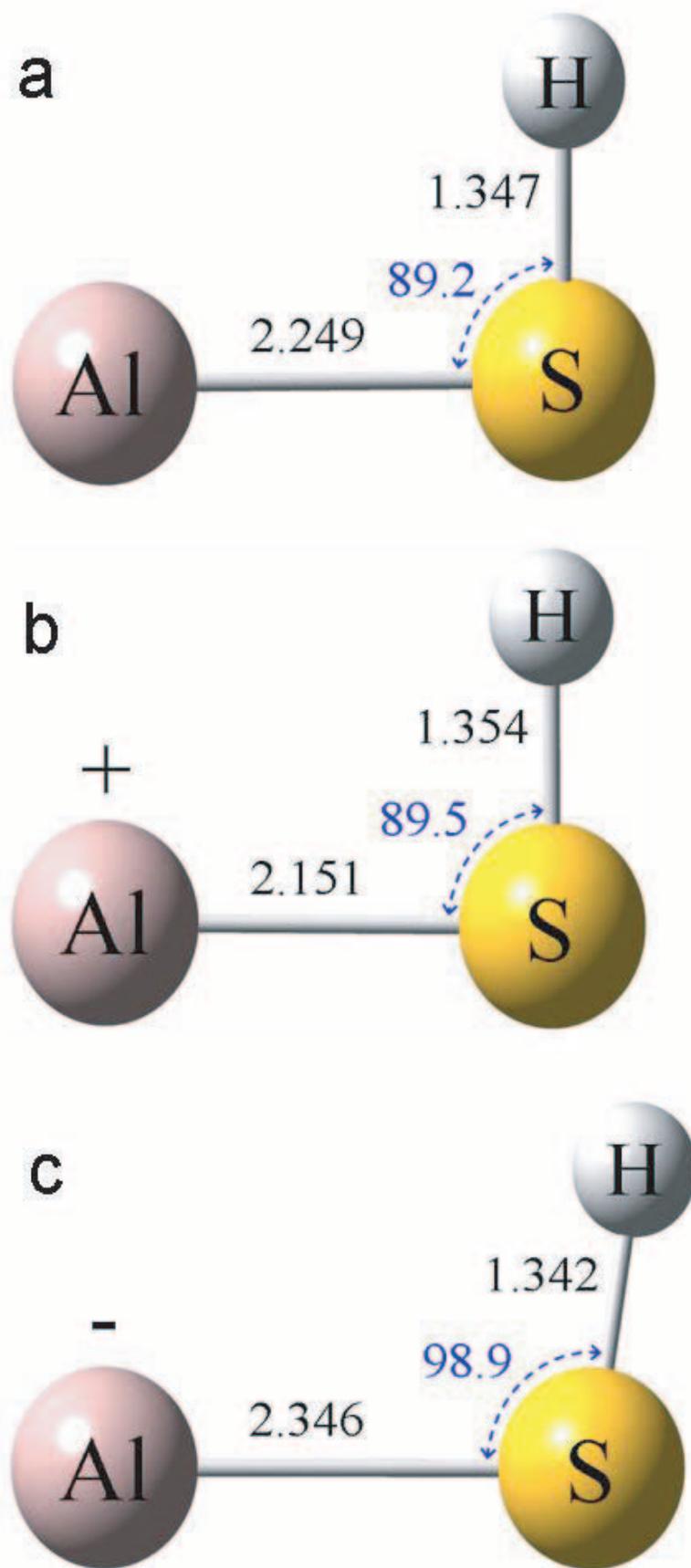


FIG. 1.—Optimized structures for the (a) AlSH neutral, (b) AlSH cation, and (c) AlSH anion.

TABLE 1
GEOMETRIES FOR AISH NEUTRAL, CATION, AND ANION

SPECIES	BASIS SET	GEOMETRIES			REFERENCE
		$r(\text{Al-S})$ (Å)	$r(\text{S-H})$ (Å)	$\theta(\text{AISH})$ (deg)	
AISH	MP2/6-31G(d)	2.2362	1.3481	92.4	1
	B3LYP/6-31G(d)	2.2811	1.3558	92.8	1
	B3LYP/6-31+G(2df,p)	2.2716	1.3511	90.0	1
	CCSD(T)/aug-cc-pVDZ	2.308	1.363	90.4	
	CCSD(T)/aug-cc-pVTZ	2.267	1.350	89.2	
	CCSD(T)/aug-cc-pVQZ	2.254	1.348	89.3	
	CCSD(T)/aug-cc-pV5Z	2.249	1.347	89.2	
	Experiment	2.240 ± 0.006	1.36 ± 0.04	88.5 ± 5.8	2
AISH ⁺	CCSD(T)/aug-cc-pVDZ	2.216	1.370	90.3	
	CCSD(T)/aug-cc-pVTZ	2.147	1.357	89.5	
	CCSD(T)/aug-cc-pVQZ	2.157	1.355	89.6	
	CCSD(T)/aug-cc-pV5Z	2.151	1.354	89.5	
AISH ⁻	CCSD(T)/aug-cc-pVDZ	2.425	1.360	98.2	
	CCSD(T)/aug-cc-pVTZ	2.369	1.346	98.5	
	CCSD(T)/aug-cc-pVQZ	2.353	1.344	98.9	
	CCSD(T)/aug-cc-pV5Z	2.346	1.342	98.9	

REFERENCES.—(1) Chen 2001; (2) Janczyk 2006.

TABLE 2
ROTATIONAL CONSTANTS FOR AISH NEUTRAL, CATION, AND ANION

SPECIES	METHOD	ROTATIONAL CONSTANTS (GHz)		
		A	B	C
AISH	CCSD(T)/aug-cc-pVDZ	278.564	6.387	6.244
	CCSD(T)/aug-cc-pVTZ	284.006	6.626	6.475
	CCSD(T)/aug-cc-pVQZ	284.831	6.703	6.549
	CCSD(T)/aug-cc-pV5Z	285.245	6.732	6.577
	Experiment ^a	287.615(62)	6.7969905(59)	6.6264144(56)
AISH ⁺	CCSD(T)/aug-cc-pVDZ	275.925	6.932	6.762
	CCSD(T)/aug-cc-pVTZ	281.020	7.208	7.027
	CCSD(T)/aug-cc-pVQZ	281.786	7.316	7.131
	CCSD(T)/aug-cc-pV5Z	282.227	7.363	7.176
AISH ⁻	CCSD(T)/aug-cc-pVDZ	287.266	5.759	5.646
	CCSD(T)/aug-cc-pVTZ	293.793	6.030	5.909
	CCSD(T)/aug-cc-pVQZ	295.267	6.114	5.990
	CCSD(T)/aug-cc-pV5Z	296.178	6.148	6.023

^a Values from Janczyk (2006).

TABLE 3
HARMONIC VIBRATIONAL FREQUENCIES FOR AISH NEUTRAL, CATION, AND ANION

Species	Method	$\nu(\text{Al-S})$ (cm ⁻¹)	$\nu(\text{S-H})$ (cm ⁻¹)	$\nu(\text{AISH})$ (cm ⁻¹)
AISH	HF/6-31G(d) ^a	541.1	2856.0	432.5
	CCSD(T)/aug-cc-pVDZ	478	2643	405
	CCSD(T)/aug-cc-pVTZ	486	2657	422
	CCSD(T)/aug-cc-pVQZ	488	2661	425
	CCSD(T)/aug-cc-pV5Z	491	2662	426
AISH ⁺	CCSD(T)/aug-cc-pVDZ	608	2608	437
	CCSD(T)/aug-cc-pVTZ	612	2616	475
	CCSD(T)/aug-cc-pVQZ	613	2618	489
	CCSD(T)/aug-cc-pV5Z	616	2619	494
AISH ⁻	CCSD(T)/aug-cc-pVDZ	479	2638	316
	CCSD(T)/aug-cc-pVTZ	489	2654	341
	CCSD(T)/aug-cc-pVQZ	495	2655	345
	CCSD(T)/aug-cc-pV5Z	494	2663	348

^a Values from Chen (2001).

TABLE 4
TOTAL ENERGIES FOR AISH NEUTRAL, CATION, AND ANION

Species	Basis Set	Energy (hartrees)
AISH	aug-cc-pVDZ	-640.29251
	aug-cc-pVTZ	-640.36425
	aug-cc-pVQZ	-640.38472
	aug-cc-pV5Z	-640.39193
AISH ⁺	aug-cc-pVDZ	-639.97944
	aug-cc-pVTZ	-640.04919
	aug-cc-pVQZ	-640.06903
	aug-cc-pV5Z	-640.07611
AISH ⁻	aug-cc-pVDZ	-640.30305
	aug-cc-pVTZ	-640.37602
	aug-cc-pVQZ	-640.39673
	aug-cc-pV5Z	-640.40392
H.....	aug-cc-pVDZ	-0.49933
	aug-cc-pVTZ	-0.49982
	aug-cc-pVQZ	-0.49995
	aug-cc-pV5Z	-0.49999
AIS	aug-cc-pVDZ	-639.66415
	aug-cc-pVTZ	-639.73298
	aug-cc-pVQZ	-639.75382
	aug-cc-pV5Z	-639.76103
Al.....	aug-cc-pVDZ	-241.92269
	aug-cc-pVTZ	-241.93150
	aug-cc-pVQZ	-241.93375
	aug-cc-pV5Z	-241.93453
SH	aug-cc-pVDZ	-398.23801
	aug-cc-pVTZ	-398.29134
	aug-cc-pVQZ	-398.30572
	aug-cc-pV5Z	-398.31066

NOTE.—The CCSD(T) method is used for basis sets.

ionization potential. Ionization of AISH to its cation form involves the removal of an electron from the π -molecular orbital, which is composed of the p -orbitals of aluminum and sulfur atoms. The total energies of the AISH species are provided in Table 4, and ionization potentials are provided in Table 5. The ionization potential is calculated as the difference in total energy, at 0 K, of the cation and the corresponding neutral at their respective levels of theory,

$$IP = E_0(\text{cation}) - E_0(\text{neutral}). \quad (2)$$

There are some interesting trends in the ionization potential data. As expected, improvement in the basis sets increases the adia-

TABLE 5
IONIZATION POTENTIAL, ELECTRON AFFINITY, AND BOND DISSOCIATION ENERGY FOR AISH

Basis Set ^a	IP ^b (kcal mol ⁻¹)	EA ^b (kcal mol ⁻¹)	BDE(AIS-H) ^b (kcal mol ⁻¹)	BDE(Al-SH) ^b (kcal mol ⁻¹)
aug-cc-pVDZ.....	196.6	6.7	76.8	81.4
aug-cc-pVTZ.....	197.9	7.5	78.3	87.4
aug-cc-pVQZ.....	198.3	7.6	77.9	89.8
aug-cc-pV5Z.....	198.4	7.6	77.9	90.8
CBS-limit	198.5	7.7	78.2	91.1

^a The CCSD(T) method is used for basis sets.

^b Zero-point energy corrections included.

batic ionization potential values for the AISH species. For AISH, there is a 1.8 kcal mol⁻¹ difference between the aug-cc-pVDZ and aug-cc-pv5Z ionization potential values.

Table 5 also contains estimations for the adiabatic electron affinity of AISH. The adiabatic electron affinities are calculated as the difference in total energies, at 0 K, of the anion and the corresponding neutral at the respective levels of theory,

$$EA = E_0(\text{neutral}) - E_0(\text{anion}). \quad (3)$$

The electron affinity for AISH is estimated to be 7.6 kcal mol⁻¹ at our highest level of theory. The estimated bond dissociation energies (BDE) listed in Table 5 show that AISH is stable toward dissociation into AIS + H by 77.9 kcal mol⁻¹ and into Al + SH by 90.8 kcal mol⁻¹ at the CCSD(T)/aug-cc-pV5Z level of theory. All complete basis set limit results are included in Table 5.

4. CONCLUSIONS

Structural and energetic calculations on ground state AISH and its cation and anion forms have been performed using the coupled cluster method. The calculations of the structure of neutral AISH at the CCSD(T)/aug-cc-pV5Z level of theory are found to be in excellent agreement with the experimental millimeter/submillimeter measurements as well as theoretical results available in literature. The vibrational frequencies calculated at the CCSD(T)/aug-cc-pV5Z level of theory are also in good agreement with the literature measurements for neutral AISH. We have calculated the adiabatic ionization potential and electron affinity for AISH, for its first ionization. They are, so far, the only reported values for ionization of the AISH species.

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