

On the electronic structure of AlS_2 and AlS_2^-

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Abstract

The ground and low-lying excited states of AlS_2 and AlS_2^- have been studied using density functional theory (DFT) and coupled cluster [CCSD(T)] approximations, in conjunction with the 6-311+G(2df) one particle basis set. AlS_2 is linear with a ${}^2\Pi_g$ ground state. CCSD(T) predicts that the 2A_2 state of the C_{2v} isomer is separated from the ground state by less than 0.1 eV, while the ${}^2\Pi_u$ and ${}^2\Sigma_u^+$ states in $D_{\infty h}$ symmetry are located at 0.67 eV and 1.40 eV, respectively, above the ${}^2\Pi_g$ state. The AlS_2^- anion possesses a ${}^1\Sigma_g^+$ ground state with a very similar geometry with the neutral molecule. At the CCSD(T) level, adiabatic electron detachment energies for the [$\text{AlS}_2({}^2\Pi_g) \leftarrow \text{AlS}_2^-({}^1\Sigma_g^+)$] transition is 4.03 eV.

Keywords: AlS_2 , AlS_2^- , Electronic structure, detachment energies, DFT, CCSD(T).

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1 Introduction

Identification of the ground state geometry of the AlO_2 and GaO_2 molecules posed a fascinating challenge to both experiment and theory for a period of time [1-15]. Earliest isolation and characterization of these group 13 oxides involved matrix isolation techniques and the use of vibrational spectroscopy. And similar to many important molecular systems that enjoy fleeting existence, unambiguous determination of the properties of the MO_2 ($M = \text{Al, Ga, In}$) molecules from experimental data has not been an easy task [1-4, 12-14]. Several of the earlier experimental work identified the triatomics as cyclic MO_2 in inert matrices [1-3]. Subsequently, the use of laser ablation as a source of metal atoms afforded the identification of the linear O-M-O species [4]. While the cyclic MO_2 (2A_2) and the linear O-M-O (${}^2\Pi_g$) have

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been identified as significant products in low-temperature matrix experiments [1-4], only the linear molecules have been detected in the gas phase [12,13]. After years of laborious and meticulous experimental and theoretical efforts, linear O-M-O($^2\Pi_g$) is now established as the ground state geometry for both AlO_2 and GaO_2 molecules [12-15].

Report of experimental studies on AlS_2 is very scarce. However, there are theoretical studies on the geometry, bonding, and harmonic vibrational frequencies of the cyclic form of the molecules. Bu and coworkers studied doublet and quartet states of cyclic AlS_2 using different theoretical approximations, including density functional theory (DFT), quadratic configuration interaction [QCISD(T)] and coupled cluster [CCSD(T)] approach [16]. They found a 2A_2 lowest state for the cyclic form of AlS_2 akin to valence isoelectronic AlO_2 . Using DFT and CCSD(T), Bu et al. also investigated the potential energy surface of cyclic GaS_2 and concluded that the species has a 2A_2 lowest state. To our knowledge, no information is available in the literature on the linear form of AlS_2 . Further, the relative energies of the cyclic and the linear species of these triatomic sulfides have not been reported.

The cardinal objective of this article is to report the geometry and the electron detachment energies of AlS_2^- using B3LYP and CCSD(T) theoretical approximations. En-route, the potential energy surfaces of neutral AlS_2 is revisited and an attempt is made to establish the ground electronic state of the triatomic molecule.

2 Computational methods

The 6-311+G(2df) one-particle basis set stored in the GAUSSIAN 03 program [17] was used for all calculations. Using B3LYP density functional and the CCSD(T) ab-initio method, geometries of several states were fully optimized. Harmonic vibrational frequencies were computed for the low-lying states with B3LYP and in some cases at the CCSD(T) level. For the CCSD(T) computations, the 15 lowest molecular orbitals (MO) were frozen for $\text{AlS}_2/\text{AlS}_2^-$ and no virtual orbitals were deleted. The vertical electron detachment energy (VEDE) and the adiabatic electron detachment energy (AEDE) were computed as follows:

$$VEDE = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion})$$

$$AEDE = E(\text{optimized neutral}) - E(\text{optimized anion})$$

All computations were performed with GAUSSIAN 03 [17].

Table 1: Geometries (\AA , degrees), harmonic vibrational frequencies (cm^{-1}), adiabatic energy separations (ΔE , eV), VEDE (eV) and the AEDE (eV) for the $\text{AlS}_2^-/\text{AlS}_2$ system.

Method	State	$r(\text{Al}-\text{S})$	$R(\text{S}-\text{S})$	$\Theta(\text{SAlS})$	ω_1	ω_2	ω_3	ΔE	VEDE	AEDE
AlS_2										
B3LYP	$^2\Sigma_u^+$	2.058			401	145	676	1.22		
CCSD(T)		2.069						1.35		
B3LYP	$^2\Pi_u$	2.093			400	156	‡	0.36	4.56	4.54
CCSD(T)		2.105						0.62	4.73	4.70
B3LYP	$^2\Pi_g$	2.072			414	132	594	-0.25	3.93	3.93
CCSD(T)		2.082						-0.05	4.03	4.03
B3LYP	2A_1	2.172	2.259	62.7	563	371	413	0.39		
CCSD(T)		2.172	2.258	62.6				0.32		
B3LYP	2A_2	2.448	2.015	48.6	592	338	215	0.00		
CCSD(T)		2.424	2.022	49.3				0.00		
AlS_2^-										
B3LYP	3B_1	2.335	2.666	69.6	407	225	227	3.28		
B3LYP	1A_1	2.317	2.173	55.9	485	384	268	1.75		
CCSD(T)		2.306	2.177	56.3				1.66		
B3LYP	$^1\Sigma_g^+$	2.064			419	175	743	0.00		
CCSD(T)		2.067						0.00		

‡unphysical frequencies.

3 Results and discussion

3.1 AlS_2 and AlS_2^-

Earlier, a 2A_2 state was computed as the lowest state for cyclic AlS_2 and the latter was classified as a supersulfide [16]. Theoretical calculations on the linear form are not available. In Table 1, we present the energies, geometrical parameters, and harmonic vibrational frequencies for the low-lying electronic states of AlS_2 in the linear and cyclic geometries. The results in Table 1 show that the lowest-lying ${}^2\Pi_g$ and 2A_2 states are within 0.25 eV of each other. Specifically, B3LYP places the ${}^2\Pi_g$ state at 0.25 eV below the 2A_2 state. A more complete account of dynamic electron correlation via the CCSD(T) approach favors the cyclic isomer with concomitant lowering of the energy difference between the two states to 0.05 eV. Thus, the two lowest-lying states of AlS_2 are nearly isoenergetic. Taking into account the margin of errors in our CCSD(T) calculations, we can only infer that the ${}^2\Pi_g$ and 2A_2 states are within 0.1 eV of each other with the linear isomer slightly more stable than the cyclic form. At the CCSD(T) level, adiabatic excitation energies are 0.62 eV and 1.35 eV for the ${}^2\Pi_u$ and ${}^2\Sigma_g^+$ states, respectively. The CCSD(T) fragmentation energies are 7.2 eV for the $\text{SAIS}({}^2\Pi_g) \rightarrow \text{Al}({}^2P) + 2\text{S}({}^3P)$ process, 3.08 eV for $\text{SAIS}({}^2\Pi_g) \rightarrow \text{Al}({}^2P) + \text{S}_2({}^3\Sigma_g^-)$ and 3.20 eV for $\text{SAIS}({}^2\Pi_g) \rightarrow \text{AlS}({}^2\Sigma^+) + \text{S}({}^3P)$.

Harmonic vibrational frequency analysis confirm the states computed for AlS_2 as minima with the exception of ${}^2\Pi_u$ that exhibits unphysical frequency for the $\omega_3(\sigma_u)$ antisymmetric stretching mode. It is noteworthy that the geometric parameters and relative energies predicted by B3LYP and CCSD(T) for all the states agree quite well. The B3LYP bond distances deviate from those of CCSD(T) by less than 0.03 Å and the bond angles by less than 1°. As for the relative energies, the B3LYP predictions differ by not more than 0.3 eV from the corresponding CCSD(T) values, and may be larger or smaller as presented in Table 1.

Both the linear and cyclic geometries were optimized for AlS_2^- . The results of geometry optimization and harmonic vibrational frequency calculations are included in Table 1. Accommodation of an extra electron by the π_g highest occupied MO (HOMO) of the ${}^2\Pi_g$ state yields the ${}^1\Sigma_g^+(7\sigma_u^2 3\pi_u^4 2\pi_g^4)$ state of AlS_2^- . A positive vertical electron affinity (VEA) of 3.93 eV at the B3LYP level and 4.02 eV using CCSD(T) is calculated for the process. Optimization of the geometry yields a B3LYP bond length of 2.064 Å and corresponding CCSD(T) bond length of 2.067 Å. Similarly for the cyclic isomer, addition of one electron to the a_2 HOMO of the 2A_2 state results in ${}^1A_1(7b_2^2 1a_1^2 2a_2^2)$ state of the anion with VEA of 2.12 eV and 2.13 eV at the B3LYP and CCSD(T) levels, respectively. Optimized geometry of the ${}^1\Sigma_g^+$ and 1A_1 states possess zero Hessian index. The electronic ground state of the anion is found to be the ${}^1\Sigma_g^+$ state with the 1A_1 state higher in energy by 1.66 eV at the CCSD(T) level. Again, similar to the neutral molecule, geometries and relative energies computed by B3LYP and CCSD(T) for the anion agree quite well. As presented for the anion in Table 1, the two theoretical approaches predicted bond lengths that differ by less than 0.02 Å, the angles agree to within 0.5° and the relative energies differ by less than 0.1 eV.

3.2 AlS_2^- electron detachment transitions

Electron photodetachment spectrum of AlS_2^- is expected to exhibit the following electron detachment processes from the ${}^1\Sigma_g^+(7\sigma_u^2 3\pi_u^4 2\pi_g^4)$ ground electronic state of AlS_2^- to neutral AlS_2 .

Detachment of an electron from the $2\pi_g$ highest occupied molecular orbital (HOMO) of the anion yields the ${}^2\Pi_g$ ground electronic state of the AlS_2 . From the results presented in Table 1, the VEDE for this process is 3.93 eV at the B3LYP level. The latter agrees quite well with the CCSD(T) prediction of 4.03 eV. The AEDE, which in this case is equivalent to the adiabatic electron affinity (AEA), is identical with the VEDE at both levels of theory. The $2\pi_g$ molecular orbital (MO) is nonbonding in character and the detachment of electron from the orbital changes the bond length by less than 0.01 Å (B3LYP) or 0.02 Å [CCSD(T)]. The similar geometry between the anion and the neutral molecule explains the nearly identical values for the AEDE and the VEDE. At the CCSD(T) level, the VEDE for the $[\text{AlS}_2({}^2\Pi_u) \leftarrow \text{AlS}_2^-({}^1\Sigma_g^+)]$ is 4.73 eV.

4 Conclusions

In this work, density functional theory (DFT) and ab initio coupled cluster method [CCSD(T)] have been used to calculate the ground and low-lying electronic states of AlS_2 and AlS_2^- . The ground electronic state of AlS_2 computed in this work is ${}^2\Pi_g$ in $D_{\infty h}$ symmetry. The geometry of AlS_2^- is similar to that of the neutral molecule. Electron detachment energies associated with the transitions from the ${}^1\Sigma_g^+$ ground electronic state of the anion to the lowest lying states of the neutral molecule have been presented and discussed.

Similar to valence isoelectronic AlO_2 , the 2A_2 state of the cyclic C_{2v} isomer of AlS_2 is nearly isoenergetic with the ${}^2\Pi_g$ ($D_{\infty h}$) ground state. On the other hand, the ${}^1\Sigma_g^+$ ground electronic of the anion is well separated from the 1A_1 and 3B_1 states with the C_{2v} symmetry.

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