

High-level Ab Initio Studies of the Spectroscopic Properties of Triatomic [Al, S, O]² (x = 0, +1) and Its Potential for Detection in Space

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Abstract

Highly reliable molecular properties have been computed for the [Al, S, O]^x (x = 0, +1) molecular system. Spectroscopic parameters are predicted from analysis of each isomer's 3D potential energy surface calculated using the explicitly correlated multireference configuration interaction method, including the Davidson correction (MRCI-F12+Q). These parameters provide an accurate prediction of spectroscopic data that can be used in laboratory and observational studies of these molecules. *Linear*-SAIO is expected to have a large permanent dipole moment suitable for detection in the circumstellar envelopes of large, evolved, oxygen-rich stars such as VY Canis Majoris, IK Tauri, and R Doradus. Frequencies are provided for rotational transitions originating from the most highly populated rotational state based on a Boltzmann distribution. Additionally, both linear isomers exhibit a flat potential along the bending angle and are predicted to have very low bending mode frequencies (<200 cm⁻¹), complicating the spectra of these molecules.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Molecular spectroscopy (2095); Red supergiant stars (1375); Radio spectroscopy (1359); Line positions (2085)

1. Introduction

Large, evolved stars, such as those classified as asymptotic giant branch (AGB) stars and red supergiants (RSGs), continuously eject mass into the region around them, creating chemically complex circumstellar envelopes (CSEs). Stars with the AGB designation are cool, evolved, luminous stars with a progenitor mass of less than 10 M_{\odot} , while the RSG designation is populated with luminous stars having the largest volume and initial main-sequence masses between 10 and 40 M_{\odot} . As age increases, stellar mass loss increases drastically (Willson 2000). Different temperature and pressure regions exist within these CSEs corresponding to different distances from the stellar photosphere. These differing environments allow for various forms of chemistry to take place. Additionally, photochemical processes are initiated as species are bombarded with incoming ultraviolet (UV) light that enters from outside of the CSEs (Ziurys 2006). Depending on the age and characteristics of the central star, these envelopes can contain very different chemical compositions. For example, IRC+10216, an AGB carbon-rich star, has been relatively well explored and shows great chemical complexity with the detection of metal-containing molecules and carbon-chain radicals (Winnewisser & Walmsley 1978; Cernicharo & Guelin 1987; Turner et al. 1994; Ziurys et al. 1994, 2002; Cernicharo et al. 2000; Ziurys 2006; Pulliam et al. 2010). The chemistry around carbon-rich AGB stars is dominated by these long carbon chains, with contributions from silicon and metals such as magnesium and sodium (Ziurys 2006). Conversely, oxygen-rich stars like the RSG star VY Canis Majoris (VY CMa) and AGB stars IK Tauri (IK Tau) and R Doradus (R Dor) exhibit less chemical diversity, with only recent identification of new molecules such as SO₂ (Omont et al. 1993; Adande et al. 2013), NaCl (Ziurys et al. 2007), AlO (De Beck et al. 2017) and AlOH (Tenenbaum & Ziurys 2010). However, it is theorized that oxygen-rich CSEs contain as much chemical diversity as carbon-rich CSEs, but many molecules have simply not been identified yet (Ziurys et al. 2007).

Many aluminum-containing species have been observed in the CSEs of VY CMa, IK Tau, and R Dor, including molecules such as AlO (10^{-8} abundance compared to H₂; Tenenbaum & Ziurys 2009; Decin et al. 2017), AlOH (Tenenbaum & Ziurys 2010; Decin et al. 2017), and AlCl (Kaminski et al. 2013b; Decin et al. 2017); all well studied in all three stars. Formation of these molecules in VY CMa is theorized to happen via photospheric shocks and photochemistry, with shocks playing a more prominent role because of the greater macroturbulent velocities (Ziurys et al. 2009). Aluminum is classified as a refractory element, as it has a relatively high equilibrium condensation temperature, at which it will be found 50% of the time in the form of a solid compound under a pressure of 10^{-4} bar. It is theorized that AlO is an important progenitor of dust particles (Kaminski et al. 2013a), potentially forming large molecular clusters such as $(Al_2O_3)_x$, which act as a dust nucleation site. $(Al_2O_3)_x$ can also condense onto the surface of other dust or ice grains (Lodders 2003). The abundance of AlO, AlOH, and AlCl in the CSEs of both IK Tau and R Dor, derived from a non-LTE radiative transfer model, is approximately 1×10^{-7} relative to H_2 (Decin et al. 2017), meaning only 2% of the total available aluminum [(Al/H] = 3×10^{-6} ; Savage & Sembach 1996; Lodders 2003) is found in these three molecules. This leaves the possibility that some Al may be found in [Al, S, O] triatomic molecules. Sulfur can be found in high abundance in high-energy regions

Sulfur can be found in high abundance in high-energy regions and near large, evolved stars (Danilovich et al. 2017, 2018). Specifically, SO₂ chemistry is prominent in many astronomical features, such as hot cores (Schilke et al. 2001), CSEs of old stars such as IK Tau, R Dor, and VY CMa (Tenenbaum et al. 2010; Kaminski et al. 2013b; Danilovich et al. 2016, 2020), and cold, dense molecular clouds (Turner 1994). In the envelope of VY CMa, SO₂ is found to be the sulfur "parent" molecule, originating in the stellar photosphere before flowing out and participating in chemical and photochemical reactions farther from the surface, where the abundance is observed to drop drastically (Adande et al. 2013). At distances of up to 30 R_* , where chemical reactions are known to take place and photochemical activity is high, S, O, and Al will all be available for reaction in the form of molecules such as SO, SO₂, AlO, AlOH, and other aluminum-containing molecules (Ziurys et al. 2007; Kaminski et al. 2013b; Decin et al. 2017; Danilovich et al. 2020). Additionally, observation of the molecules AlO and AlOH past the dust condensation region of IK Tau and R Dor indicates that the aluminum oxide condensation cycle is not efficient (Decin et al. 2017), and the relevant molecules required for formation of triatomic [Al, S, O] may be present throughout the CSEs.

The neutral species may be formed mainly via three mechanisms: (i) the gas-phase chemical reactions $AIS + O_2$, AIO + SO, and $AI + SO_2$, (ii) the radiative association between atom + diatom whether AI + SO or AIO + S, and (iii) the reaction of sulfur-bearing species, such as SO or SO₂, at the dust surface of AI_2O_3 . In fact, the presence of AI_2O_3 clusters in the oxygen-rich regions of AGB stars (Decin et al. 2017) increases the likelihood of aluminum-bearing molecules forming on the surface of said clusters. Kim et al. (2007) demonstrated a similar mechanism for the formation of AICN and AINCO on the surface of AI_2O_3 . The cation may form through the photoionization of the neutral species or via collision.

Previously, a few computational studies have been performed on the [Al, S, O] group of isomers. Using various density functional theory (DFT) methods, Bu found five different isomeric forms for the [Al, S, O] triatomic molecular group with linear-SAIO as the ground state minimum (Bu 2000, 2001). Isomerization pathways were found that connect the two linear isomers by two transition state structures and an intermediate (Bu 2001). A follow-up study by Bu looked at the bonding character of the [Al, S, O] quartet excited states using coupled-cluster (CCSD(T)) and DFT methods (Bu 2002). As will be explained in this paper, coupled-cluster methods are not suitable for accurate characterization of the [Al, S, O] group of molecules because of their radical character. which causes a large T1 diagnostic value. Nonetheless, Bu found four minimum structures with the lowest energy state being cyc-AlSO (${}^{4}A''$).

Many high-level theoretical studies have been performed on aluminum-bearing molecules (Ma et al. 1995; Alikhani 2003; Trabelsi & Francisco 2018; Yousefi & Bernath 2018; Yurchenko et al. 2018; Trabelsi et al. 2019a, 2019b, 2019c; Xu et al. 2020). These publications have set a benchmark for the computational study of aluminum-bearing species, and many of the methods are adapted for the current work.

In this paper, accurate high-level calculations of the electronic structure and spectroscopic parameters of the [Al, S, O] triatomic isomers are presented for the first time. The electronic structure calculations were performed using explicitly correlated multireference configuration interaction methods with large basis sets. Following identification of the stable isomers, a 3D potential energy surface (3D-PES) is generated around the equilibrium geometry of each isomer, and a set of spectroscopic constants were produced. From these constants, rotational transition frequencies were derived. These predictions will help drive detection and identification of the [Al, S, O] triatomic isomers in laboratory experiments and observational studies of oxygen-rich CSEs surrounding large, cool stars.

2. Computational Methods

First, calculations were performed with the complete active space self-consistent field (CASSCF) method (Knowles & Werner 1985; Werner & Knowles 1985) to investigate the electronic wave functions of each of the [Al, S, O] isomers. Then geometries were optimized using the standard coupledcluster theory with single and double excitations, including a perturbative treatment of triples (CCSD(T); Knowles et al. 1993, 2000), and the aug-cc-pV(X+d)Z basis sets of increasing size (X = D, T, Q, 5) (Dunning 1989; Dunning et al. 2001). Additionally, the explicitly correlated (CCSD(T)-F12) method (Adler et al. 2007; Knizia et al. 2009) is also used with the augcc-pVQZ and explicitly correlated cc-pVXZ-F12 (X = D, T, Q) basis sets (Peterson et al. 2008) for comparison. An accurate description of the electronic structure and spectroscopic parameters of these species is achieved using CASSCF followed by the internally-contracted multireference configuration interaction (MRCI) method (Knowles & Werner 1988; Werner & Knowles 1988; Shamasundar et al. 2011) in conjunction with the aug-cc-pV(X+d)Z basis sets (X = T, Q), which add tight d functions to the aluminum and sulfur atoms. This is an addition that is important for proper characterization of sulfur-bearing molecules (Dunning et al. 2001). Additionally, calculations were performed with the contracted relativistic Douglas-Kroll aug-cc-pwCVTZ-DK basis set to correct for scalar relativistic and core-correlation effects (Jorge et al. 2009). Geometry optimizations were also performed with the MRCI+Q method, including Davidson corrections to further account for electron correlation to the energy (Szalay & Bartlett 1993) and the explicitly correlated MRCI-F12 method (Shiozaki et al. 2011).

In this study, optimized geometries, harmonic frequencies, and rotational constants were calculated using CCSD(T) as well as the CASSCF and MRCI methods. The permanent dipole moments at equilibrium geometry (μ_e) are calculated in the center of mass of the molecule using the finite field procedure as implemented in MOLPRO. All electronic structure calculations were performed using the MOLPRO2019 software (Werner et al. 2019).

The 3D-PESs of the ground electronic state for the linear isomer were calculated at the MRCI-F12+Q/aug-cc-pVQZ level of theory. The resulting 3D-PESs were used to compute a set of spectroscopic constants using the derivatives of the potentials at equilibrium and perturbation theory (Mills 1972) as implemented in the SURFIT (Senekowitsch 1988) program. Vibrationally corrected rotational constants (Kroto 1975) were then calculated using the following formula:

$$X_o = X_e + \Delta X_o, \tag{1}$$

where X_e is the equilibrium rotational constants corresponding to the molecular geometry at the minimum of the Born– Oppenheimer PES. ΔX_o is the vibrational correction obtained from the following formula:

$$\Delta X_o = -\sum_r - \alpha_r^i \left(\nu_r + \frac{1}{2} \right), \tag{2}$$

where the sum is over all normal coordinates, r, and α_r is the vibration–rotation interaction constant. ν_r is the vibrational quantum number of the normal mode. Including the vibrational correction to the equilibrium rotational constants accounts for



Figure 1. MRCI-F12+Q/aug-cc-pVQZ 1-D PES of the electronic ground state of (a) AlOS and (b) SAIO along the bending angle. Molecular structures are included for visualization of the different bending angles along the lowest energy potential energy surface with A'' being the ground state in both cases.

the presence of zero-point vibrational motion in the ground vibrational state of the molecule.

3. Results and Discussion

3.1. Equilibrium Geometries

3.1.1. Neutral-[Al, S, O]

All possible triatomic isomers that may be formed with the three atoms Al, S, and O are explored. Structural and bonding analysis is performed to deduce which isomers may be expected to occur in the CSEs of evolved, oxygen-rich stars. At first glance, the existence of three isomers is expected: AlSO, AlOS, and SAlO that may be formed through Al+SO, AIO+S, or AIS + O entrance channels. All levels of theory show that only AlOS and SAlO form a true minimum in their PES. When the sulfur atom is in the middle (e.g., AlSO), no stability is found, and the potential is characterized by an imaginary frequency. Both AlOS and SAlO are linear with an X²Π electronic ground state and form a Renner-Teller pair when the bending angle (θ) = 180°. When θ varies from 0° to 180°, a splitting of the Π state into A' and A" states occurs, and the third isomer, *cyc*-AlOS, appears with an X^2A'' ground state. The evolution of the ground state along the bending angle for AlOS and SAlO is depicted in Figure 1. Extensive calculations at various levels of theory were done on each isomer, and total energies, relative energies, and optimized equilibrium geometries are listed in Table 1 for the three neutral isomers in their ground electronic state.

Close inspection of Table 1 shows that at the MRCI/aug-ccpV(Q+d)Z level of theory, *linear*-AlOS ($X^2\Pi$) is the most stable isomer and is located only 0.06 eV and 0.95 eV below *cyc*-AlOS (A^2A'') and *linear*-SAlO ($X^2\Pi$), respectively. Increasing basis set size and including various corrections consistently shortens both AlO and SO bond lengths and elongates the AlS bond length, along with changing the order of stability. When including the Davidson correction (MRCI+Q), the cyclic isomer is more stable and located 0.20 eV below *linear*-AlOS. The scalar relativistic and core-correlation correction at the MRCI/aug-cc-pwCVTZ-DK level shows that *linear*-AlOS is more stable by 0.54 eV compared to *linear*-SAlO, with the cyclic isomer being the least stable at this level of theory. An explicit treatment of the electron correlation at the MRCI-F12/ aug-cc-pVOZ level shows that *linear*-AlOS is more stable and located 0.47 eV below the cyc-AlOS isomer. Convergence is not reached for the MRCI-F12 level of theory for linear-SAIO. As one can see, multireference treatment of this system shows some disagreement regarding the stability of the isomers and the SO equilibrium distance. In fact, throughout the multireference methods, the AlO equilibrium distance stays relatively consistent, even with the Davidson correction and inclusion of the electron correlation. Alternatively, the SO equilibrium distance does show some fluctuation for linear-AlOS, where the smallest value calculated at MRCI-F12/augcc-pVQZ is predicted to be 1.5758 Å, approximately 0.015 Å less than at the MRCI/aug-cc-pV(Q+d)Z level. Given the strong scatter of results among the multireference levels of theory, it would be interesting to know how single reference treatment using coupled-cluster theory would compare. For linear-AlOS and the cyclic isomer, the diagnostic T1 is calculated to be 0.022 and 0.024, respectively, while that for linear-SAIO is greater than 0.03 at the CCSD(T)/aug-cc-pV(5 +d)Z level of theory. This indicates the multireference character of the neutral ground state. All CCSD(T) levels predict linear-SAIO as the more stable isomer, displaying the problems that occur when the multireference character of these molecules is ignored.

The AlO bond is present in all three isomers, and the length is predicted to be the shortest in *linear*-SAIO, with a value of 1.6055 Å at the MRCI/aug-cc-pV(Q+d)Z level of theory, compared to 1.7228 Å and 1.7190 Å for *linear*-AlOS and *cyc*-AlOS, respectively. Inclusion of scalar relativistic effects does not change the AlO bond length in *linear*- or *cyc*-AlOS, but elongates it in *linear*-SAIO to a value of 1.6128 Å. There is a similar pattern with inclusion of the Davidson correction. The AlO bond length in the free diatomic molecule AlO ($X^2\Sigma^+$) has been experimentally determined to be 1.6179 Å (Huber & Herzberg 1979), similar to *linear*-SAIO, but much shorter than in *linear*- and *cyc*-AlOS by over 1 Å. CCSD(T) methods consistently predict a shorter AlO bond length in *linear*-AlOS than MRCI methods. In *cyc*-AlOS and *linear*-SAIO, CCSD(T) predicts a similar AlO bond length to MRCI using all basis sets. Table 1

Equilibrium Geometry, Rotational Constants, Total Energy $(E_{\rm T})$, and Relative Energy $(E_{\rm r})$ for *linear*-AlOS, cyc-AlOS and *linear*-SAlO Neutral Doublet Isomers

| | | | lin | ear-AlOS (X | ² Π) | | | | |
|-------------|------------------|-------------------------|------------------------|-------------------------|------------------|------------|------------|-----------------------------|------------------------|
| Method | Basis | R _{AlO} (Å) | R _{OS} (Å) | θ (deg) | A (MHz) | B (MHz) | C (MHz) | E _T (Hartree) | E _r (eV) |
| MRCI | aug-cc-pV(Q+d)Z | 1.7228 | 1.5883 | 180.0 | 3144 | 3144 | 0 | -714.84257247 | 0.00 |
| | aug-cc-pwCVTZ-DK | 1.7259 | 1.5793 | 180.0 | 3156 | 3156 | 0 | -716.40154967 | 0.00 |
| MRCI+Q | aug-cc-pV(Q+d)Z | 1.7251 | 1.5888 | 180.0 | 3139 | 3139 | 0 | -714.87034821 | 0.00 |
| MRCI-F12 | aug-cc-pVQZ | 1.7276 | 1.5758 | 180.0 | 3159 | 3159 | 0 | -714.87222151 | 0.00 |
| CCSD(T) | CBS | 1.7183 | 1.6024 | 180.0 | 3126 | 3126 | 0 | -714.91760205 | 0.00 |
| | aug-cc-pwCVTZ-DK | 1.7210 | 1.6118 | 180.0 | 3103 | 3103 | 0 | -716.44057155 | 0.00 |
| CCSD(T)-F12 | aug-cc-pVQZ | 1.7182 | 1.6030 | 180.0 | 3125 | 3125 | 0 | -714.91107657 | 0.00 |
| | CBS | 1.7155 | 1.6021 | 180.0 | 3132 | 3132 | 0 | -714.92218701 | 0.00 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 1.7143 | 1.6086 | 180.0 | 3121 | 3121 | 0 | -717.07245656 | 0.00 |
| | | | c | yc-AlOS (A ² | A″) | | | | |
| Method | Basis | R _{AlO} | R _{OS} | θ | Α | В | С | E_{T} | $E_{\rm r}$ |
| MRCI | aug-cc-pV(Q+d)Z | 1.7190 | 1.8375 | 73.2 | 20006 | 7569 | 5491 | -714.84051360 | 0.06 |
| | aug-cc-pwCVTZ-DK | 1.7190 | 1.8487 | 73.2 | 19915 | 7512 | 5455 | -716.38009879 | 0.58 |
| MRCI+Q | aug-cc-pV(Q+d)Z | 1.7223 | 1.8451 | 73.3 | 19913 | 7507 | 5452 | -714.87772776 | -0.20 |
| MRCI-F12 | aug-cc-pVQZ | 1.7215 | 1.8381 | 73.2 | 19956 | 7564 | 5485 | -714.85232974 | 0.47 |
| CCSD(T) | CBS | 1.7213 | 1.8279 | 73.9 | 20225 | 7492 | 5467 | -714.90485106 | 0.34 |
| | aug-cc-pwCVTZ-DK | 1.7242 | 1.8425 | 74.0 | 20098 | 7385 | 5400 | -716.42364886 | 0.46 |
| CCSD(T)-F12 | aug-cc-pVQZ | 1.7217 | 1.8275 | 73.9 | 20229 | 7488 | 5465 | -714.89824158 | 0.35 |
| | CBS | 1.7204 | 1.8264 | 73.9 | 20251 | 7503 | 5474 | -714.90979034 | 0.33 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 1.7171 | 1.8385 | 74.0 | 20220 | 7438 | 5437 | -717.05422865 | 0.50 |
| | | | lin | ear-SAlO (X | ⁻² Π) | | | | |
| Method | Basis | R _{AlO} | R _{AIS} | θ | Α | В | С | E_{T} | $E_{\rm r}$ |
| MRCI | aug-cc-pV(Q+d)Z | 1.6055 | 2.1667 | 180.0 | 3040 | 3040 | 0 | -714.80771532 | 0.95 |
| | aug-cc-pwCVTZ-DK | 1.6128 | 2.1505 | 180.0 | 3061 | 3061 | 0 | -716.38171921 | 0.54 |
| MRCI+Q | aug-cc-pV(Q+d)Z | 1.6095 | 2.1714 | 180.0 | 3026 | 3026 | 0 | -714.82934517 | 1.12 |
| CCSD(T) | CBS | 1.6062 | 2.1661 | 180.0 | 3040 | 3040 | 0 | -714.92354060 | -0.16 |
| | aug-cc-pwCVTZ-DK | 1.6115 | 2.1703 | 180.0 | 3021 | 3021 | 0 | -716.44477056 | -0.11 |
| CCSD(T)-F12 | aug-cc-pVQZ | 1.6090 | 2.1600 | 180.0 | 3048 | 3048 | 0 | -714.91752473 | -0.18 |
| | CBS | 1.6078 | 2.1597 | 180.0 | 3050 | 3050 | 0 | -714.92914930 | -0.18 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 1.6036 | 2.1658 | 180.0 | 3044 | 3044 | 0 | -717.07455236 | -0.06 |

There is an SO bond present in *linear*- and *cyc*-AlOS. Across all levels of theory, the SO bond is predicted to be shorter in *linear*-AlOS by over 0.2 Å. At the MRCI/aug-cc-pV(Q+d)Z level of theory, the SO bond is predicted to be 1.5883 Å in linear-AlOS and 1.8375 Å in cyc-AlOS. Inclusion of scalar relativistic effects proves to shorten this bond in the linear isomer while elongating it in the cyclic isomer. Inclusion of the Davidson correction does not change the SO bond in linear-AlOS, while it elongates the same bond in cyc-AlOS. All CCSD(T) methods predict a longer SO bond in linear-AlOS than MRCI methods. At CCSD(T)/CBS, this value is predicted to be 1.6024 Å. Both isomers are predicted to have a longer SO bond length than the free diatomic SO $(X^3\Sigma^-)$, which was experimentally determined to be 1.481 Å (Huber & Herzberg 1979). Comparing the equilibrium bond lengths in the triatomic molecules to those in the free diatomics, the formation of *linear*-AlOS may occur through the reaction Al + OS due to the much larger AlO bond length in linear-AlOS. Upon AlO bond formation, the SO bond elongates slightly while the aluminum atom finds a potential minimum far away from the diatomic AlO bond length.

Linear-SAIO includes an AIS bond that is predicted to be 2.1667 Å at the MRCI/aug-cc-pV(Q+d)Z level of theory,

slightly longer than that in *cyc*-AlOS, which has an AlS bond length of 2.1229 Å. The Davidson corrected MRCI method predicts a longer AlS bond in both isomers. The AlS bond length in both isomers at all levels of theory is predicted to be larger than the experimentally determined AlS bond length in the diatomic AlS ($X^2\Sigma^+$, $R_{AlS} = 2.0129$ Å) (Huber & Herzberg 1979).

3.1.2. Cation-[Al, S, O]⁺¹

After characterization of the neutral ground state, the cations of each isomer are explored. Following removal of an electron, each isomer can take on a singlet or triplet spin multiplicity. Each isomer is most stable in the triplet configuration, with triplet *linear*-AlOS⁺ ($X^{3}\Pi$) being the global minimum. The stability and equilibrium geometries at many levels of theory are reported in Table 2 and will be explored below as they relate to each other and their neutral counterparts.

All MRCI calculations except MRCI+Q/aug-cc-pV(T+d)Z predict triplet *linear*-AlOS⁺ as the most stable cation isomer. It is predicted to be 0.11 eV and 0.20 eV more stable than the next two closest isomers, triplet *cyc*-AlOS⁺ ($A^{3}A''$) and singlet *cyc*-AlOS⁺ ($A^{1}A''$), respectively, at MRCI/aug-cc-pV(T+d)Z. Increasing basis set size increases this energy gap between triplet

 Table 2

 Equilibrium Geometry, Rotational Constants, Total Energy (E_T), and Relative Energy (E_t) for *linear*-AlOS⁺, *cyc*-AlOS⁺ and *linear*-SAlO⁺ Cation Isomers

| | | | lir | <i>near</i> -AlOS $^+$ (X | ³ П) | | | | |
|---------------------|--|----------------------------|----------------------------|------------------------------------|-------------------------|----------------------|----------------------|---|------------------------|
| Method | Basis | R _{AlO} (Å) | R _{OS} (Å) | θ (deg) | A (MHz) | B (MHz) | C (MHz) | E _T (Hartree) | E _r (eV) |
| MRCI | aug-cc-pV(T+d)Z aug-cc-pV(O+d)Z | 2.1718 | 1.5016 | 180.0 180.0 | 2551 2518 | 2551 2518 | 0 | -714.51870136 -714 56506424 | 0.00 |
| MRCI+Q | aug-cc-pwCVTZ-DK aug-cc-pV(T+d)Z | 2.3076 2.1802 | 1.4927 1.5040 | 180.0 180.0 | 2380 2536 | 2380 2536 | 0 0 | -716.12989930 -714.53837535 | 0.00 |
| MRCI-F12 | aug-cc-pV(Q+d)Z aug-cc-pVQZ CBS | 2.2184 2.3124 2.0372 | 1.4945 1.4915 1.4997 | 180.0 180.0 180.0 | 2495 2375 2754 | 2495 2375 2754 | 0 0 0 | -714.58719745 -714.59667665 -714.62714093 | 0.00 0.00 0.00 |
| CCSD(T)-F12 | aug-cc-pwCVTZ-DK aug-cc-pVQZ | 2.0572 2.0522 2.0398 | 1.5063 1.5004 | 180.0 180.0 | 2721 2749 | 2721 2749 | 0 0 | -716.15368275 -714.62099468 | 0.00 |
| CCSD(T)-AE | CBS aug-cc-pwCVTZ-DK | 2.0381 2.0453 | 1.4986 1.5036 | 180.0 180.0 | 2755 2736 | 2755 2736 | 0 0 | -714.63110325 -716.78548710 | 0.00 0.00 |
| | | | С | yc -AlOS ⁺ ($A^{3}A$ | 4″) | | | | |
| Method | Basis | R _{AlO} | R _{OS} | θ | Α | В | С | E_{T} | $E_{\rm r}$ |
| MRCI | aug-cc-pV(T+d)Z aug-cc-pV(Q+d)Z | 1.7763 1.7727 | 1.6589 1.6497 | 81.0 80.9 | 23619 23772 | 6922 6986 | 5353 5399 | -714.51432378 -714.54945915 | 0.11 0.42 |
| MRCI+Q | aug-cc-pWCVTZ-DK aug-cc-pV(T+d)Z | 1.7726 1.7820 | 1.6563 1.6622 | 81.0 80.9 | 23716 23487 | 6943 6890 | 5371 5327 | -716.09078404 -714.54228853 | 1.06 -0.11 |
| MRCI-F12 CCSD(T) | aug-cc-pV(Q+d)Z aug-cc-pVQZ CBS | 1.7782 1.7747 1.7791 | 1.6527 1.6516 1.6421 | 80.8 80.8 81.0 | 23638 23704 23857 | 6960 6976 6971 | 5376 5390 5395 | -714.57954185 -714.56013813 -714.60297213 | 0.21 0.99 0.65 |
| CCSD(T)-F12 | aug-cc-pwCVTZ-DK aug-cc-pVQZ | 1.7814 1.7794 | 1.6523 1.6421 | 81.4 81.2 | 23796 23912 | 6872 6946 | 5332 5383 | -716.12428682 -714.59650811 | 0.80 0.66 |
| CCSD(T)-AE | CBS aug-cc-pwCVTZ-DK | 1.7777 1.7811 | 1.6408 1.6524 | 81.2 81.4 | 23966 23795 | 6954 6874 | 5390 5334 | -714.60742034 -716.75402406 | 0.64 0.85 |
| | | | С | yc -AlOS ⁺ (A^1A | A″) | | | | |
| Method | Basis | R _{AlO} | R _{OS} | θ | Α | В | С | E_{T} | $E_{ m r}$ |
| MRCI | aug-cc-pV(T+d)Z aug-cc-pV(Q+d)Z | 1.7758 1.7756 | 1.6609 1.6556 | 80.9 80.4 | 23584 23466 | 6922 7025 | 5351 5406 | -714.51122376 -714.54474714 | 0.20 0.55 |
| MRCI+Q | aug-cc-pwCVTZ-DK aug-cc-pV(T+d)Z | 1.7718 1.7809 | 1.6584 1.6649 | 81.0 80.9 | 23686 23438 | 6942 6893 | 5368 5326 | -716.08765516 -714.53909074 | 1.15 -0.02 |
| MRCI-F12 CCSD(T) | aug-cc-pV(Q+u)Z aug-cc-pVQZ CBS | 1.7800 1.7740 1.6720 | 1.6535 1.9429 | 80.4 80.8 69.3 | 23670 18724 | 6987 6978 8008 | 5379 5389 5609 | -714.57009423 -714.55719274 -714.55280503 | 1.07 2.02 |
| CCSD(T)-F12 | aug-cc-pwCVTZ-DK aug-cc-pVQZ | 1.6921 1.6897 | 1.7418 1.7354 | 82.6 81.5 | 24242 23973 | 6687 6867 | 5241 5338 | -716.07345030 -714.54572884 | 2.18 2.04 |
| CCSD(T)-AE | CBS aug-cc-pwCVTZ-DK | 1.6716 1.6736 | 1.9392 1.8962 | 69.4 72.8 | 19305 20218 | 7791 7449 | 5550 5443 | -714.55731913 -716.70272621 | 1.90 2.25 |
| | | | lir | near-AlOS ⁺ (A | ¹ Π) | | | | |
| Method | Basis | R _{AlO} | R _{OS} | θ | Α | В | С | E_{T} | $E_{\rm r}$ |
| MRCI | aug-cc-pV(T+d)Z aug-cc-pV(Q+d)Z | 1.6185 1.6141 | 1.6663 1.6497 | 180.0 179.9 | 3189 3231 | 3189 3231 | 0 0 | -714.42631309 -714.52017595 | 2.51 1.22 |
| MRCI+Q | aug-cc-pwCVTZ-DK aug-cc-pV(T+d)Z aug-cc-pV(O+d)Z | 1.6154 1.6198 1.6169 | 1.6637 1.6681 1.6604 | 180.0 180.0 180.0 | 3200 3184 3204 | 3200 3184 3204 | 0 0 0 | -716.03893284 -714.43912194 -714.48671751 | 2.47 2.70 2.73 |
| MRCI-F12 CCSD(T) | aug-cc-pVQZ CBS | 1.6179 2.0768 | 1.6597 1.5061 | 180.0 180.0 | 3204 2683 | 3204 2683 | 0 0 | -714.50842568 -714.58783411 | 2.40 1.06 |
| CCSD(T)-F12 | aug-cc-pwCV1Z-DK aug-cc-pVQZ CBS | 2.0932 2.0824 2.0818 | 1.5134 1.5065 1.5052 | 180.0 180.0 180.0 | 2648 2674 2677 | 2648 2674 2677 | 0 0 | -716.11352324 -714.58106562 -714.59186881 | 1.09 1.08 1.07 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 2.0873 | 1.5108 | 180.0 | 2661 | 2661 | 0 | -716.74495265 | 1.10 |
| | | | lir | <i>iear-</i> SAlO ⁺ (X | °11) | | | | |
| Method | Basis | R _{AlO} | R _{AIS} | θ | Α | В | С | E_{T} | $E_{\rm r}$ |
| MRCI MRCI-F12 | aug-cc-pwCVTZ-DK aug-cc-pVQZ | 1.6886 1.6865 | 2.1242 2.1171 | 180.0 180.0 | 3012 3027 | 3012 3027 | 0 0 | -715.99901313 -714.46456316 | 3.56 3.59 |
| | | | lir | near-SAlO $^+$ (A | ¹ Π) | | | | |
| Method | Basis | R _{AlO} | R _{AIS} | θ | Α | В | С | E_{T} | $E_{ m r}$ |
| MRCI MRCI | aug-cc-pVQZ aug-cc-pwCVTZ-DK | 1.6912 1.6874 | 2.1226 2.1251 | 180.0 180.0 | 3011 3011 | 3011 3011 | 0 0 | -714.35980809 -715.98783300 | 5.05 3.86 |

linear-AlOS⁺ and the rest of the cation isomers. Inclusion of core relativistic effects markedly increases the stability of triplet *linear*-AlOS⁺, as it is 1.06 and 1.15 eV lower in energy than the triplet and singlet *cyc*-AlOS⁺ isomers at the MRCI/aug-cc-pwCVTZ-DK level of theory. As mentioned before, taking the Davidson correction into account changes the predicted stability, with triplet *cyc*-AlOS⁺ becoming 0.11 eV lower than triplet *linear*-AlOS⁺ at MRCI+Q/aug-cc-pV(T+d)Z. Increasing the basis set size to aug-cc-pV(Q+d)Z causes the stability to switch back and agree with the other levels of theory. Finally, explicit treatment of the electron correlation at the MRCI-F12/aug-cc-pVQZ level of theory predicts similar stability as the inclusion of relativistic effects, with triplet *linear*-AlOS⁺ 0.99 eV and 1.07 eV lower in energy than the triplet and singlet *cyc*-AlOS⁺ isomers.

Single reference CCSD(T) methods showed a large discrepancy in results when considering different corrections and basis set sizes, including the switching of stability for the higher energy isomers. The T1 diagnostic is calculated to be 0.031, 0.026, 0.021, and 0.023 for triplet *linear*-AlOS⁺, triplet *cyc*-AlOS⁺, singlet *linear*-AlOS⁺ ($A^{1}\Pi$), and singlet *cyc*-AlOS⁺ at the CCSD(T)/ aug-cc-pV(5+d)Z level of theory, respectively, showing the multireference character of this cation system. Nevertheless, at the CCSD(T)/CBS level, triplet *linear*-AlOS⁺ is the lowest energy isomer, followed by triplet *cyc*-AlOS⁺, singlet *linear*-AlOS⁺, and then singlet *cyc*-AlOS⁺.

The *linear*-SAIO⁺ isomers are the two highest energy structures found. The two levels of theory that were able to achieve optimization convergence agree on the stability of triplet *linear*-SAIO⁺ ($X^{3}\Pi$), with MRCI/aug-cc-pwCVTZ-DK predicting an energy of 3.56 eV and MRCI-F12/aug-cc-pVQZ predicting an energy of 3.59 eV above triplet *linear*-AIOS⁺. For singlet *linear*-SAIO⁺ ($A^{1}\Pi$), MRCI/aug-cc-pVQZ and MRCI/aug-cc-pwCVTZ-DK predicted a stability of 4.05 eV and 3.86 eV, respectively, compared to triplet *linear*-AIOS⁺. The remaining levels of theory were plagued by large and imaginary frequencies at the stationary points.

The equilibrium geometries of the cations showed some very interesting patterns when compared to each other and the neutral species. Triplet *linear*-AlOS⁺ is predicted to have an AlO bond length of 2.2042 Å and an SO bond length of 1.4923 Å at the MRCI/aug-cc-pV(Q+d)Z level of theory, while triplet cyc-AlOS⁺, singlet cyc-AlOS⁺, and triplet *linear*-AlOS⁺ are predicted to have AlO bond lengths of 1.7727 Å, 1.7756 Å, and 1.6141 Å, and SO bond lengths of 1.6497 Å, 1.6556 Å, and 1.6497 Å, respectively. When the Davidson correction is incorporated, all bond lengths were shown to increase in all cation isomers. Explicit treatment of the electron correlation does not show the same pattern. For triplet *linear*-AlOS⁺, the AlO bond length increases to its largest predicted value, while the SO bond decreases to its shortest predicted value. For the cyclic isomers, explicit treatment of electron correlation predicted similar bond lengths for both. For the singlet *linear*-AlOS⁺, no change is seen in the AlO bond length with a slight increase in the SO bond. With increasing basis set size, a shortening of the SO bond is observed for all cation isomers. No such pattern is seen for the AlO bond. Single reference treatment utilizing CCSD(T) methods proved erratic with major changes in bond lengths for some isomers, while others saw no change in the predicted geometric parameters.

The AlO bond length in the ground state triplet *linear*-AlOS⁺ is predicted to be 2.2042 Å at the MRCI/aug-cc-pV(Q+d)Z

level of theory, compared to 1.6141 Å in singlet *linear*-AlOS⁺. The SO bond length in each isomer at the same level of theory is 1.4923 Å and 1.6497 Å, respectively. Comparing both to the AlO and SO bond lengths of 1.7728 and 1.5883 Å in the neutral *linear*-AlOS species, upon photoionization to the triplet state electron density is shifted from the AlO bond to the SO bond, elongating the former and shortening the latter. The opposite effect is seen in photoionization to the singlet state, where the AlO bond becomes stronger and the SO bond lengthens. This trend holds at all MRCI levels of theory and is accentuated when relativistic effects are taken into account.

3.2. Spectroscopy

Rotational constants were calculated using the average atomic mass as implemented in MOLPRO and are reported in Tables 1 and 2. At the MRCI+Q/aug-cc-pV(Q+d)Z level of theory, the rotational constants for *linear*-AlOS and *linear*-SAlO were calculated to be A = B = 3159 MHz and 3026 MHz, respectively. For the linear isomers, the rotational constants do not show a large dependence on the level of theory used, with all predicted values within 30 MHz of each other. For *cyc*-AlOS, there is slightly more variability in the rotational constants based on level of theory, with convergence seen using the largest basis sets.

A better picture of the bonding nature can be obtained by analysis of the natural population and dipole moments of these molecules. A natural bond order analysis for linear-AlOS predicts positive charges on the Al (+0.84e) and S (+0.35e) and a negative charge on the O (-1.19e). For *linear*-SAIO, a large positive charge is seen on the Al (+1.59e), while O (-1.18e) and S (-0.41e) carry negative charges. Large ionic bond character is seen between the Al and O atoms in linear-SAIO, as would be expected for such a large charge separation. Additionally, the large charge separation between the Al and O, combined with the larger (and less rigid nature) of the AlS bond ($R_{AlS} = 2.1505 \text{ \AA}$) compared to the free diatomic ($R_{AIS} = 2.0129$ Å; Huber & Herzberg 1979), indicates that linear-SAIO may be formed in the CSE around a star via the reaction OAI + S. Although still present, less ionic bonding character is seen in linear-AlOS, because of lower charge differences (Al (+0.845e), O (-1.19e), S (0.351e)). Based on the charge separation and the geometric analysis in Section 3.1.1, linear-AlOS isomer may be formed via the reaction Al + OS.

The harmonic vibrational frequencies and zero-point vibrational energy calculated for the neutral species are reported in Table 3. Linear-AlOS is predicted to have a large asymmetric stretching frequency (ω_1). The magnitude of the frequency increases with basis set size, which is consistent with shortening of the bond lengths, especially the AlO bond. The bending mode (ω_2) has very low amplitude ($<200 \text{ cm}^{-1}$), with a few levels of theory predicting an imaginary frequency. This trouble characterizing the PES in this region can be attributed to the flatness of the potential along the bending angle. As can be seen in Figure 1, the potential is extremely flat for bond angles near $\theta = 180^{\circ}$. For this reason, the harmonic oscillator model does not describe the potential in this region well; inclusion of anharmonicity is needed for better characterization of this mode. The symmetric stretch (ω_3) shows good agreement throughout the various levels of theory, with the largest basis sets converging to the same frequency value.

Cyc-AlOS is well characterized with these methods, showing good agreement for all vibrational modes at all levels of theory.

 Table 3

 Harmonic Vibrational Frequencies and Zero-point Vibrational Energy of Neutral [Al, S, O] Species

| | | <i>linear</i> -AlOS ($X^2\Pi$) | | | |
|-------------|------------------|---------------------------------------|----------------------------|----------------------------|-----------------------------|
| Method | Basis | $(\mathrm{cm}^{\omega_{\mathrm{I}}})$ | (cm^{ω_2}) | (cm^{ω_3}) | ZPVE (cm ⁻¹) |
| MRCI | aug-cc-pV(T+d)Z | 1074 | 75 | 502 | 826 |
| | aug-cc-pV(Q+d)Z | 1121 | 102 <i>i</i> | 503 | 812 |
| | aug-cc-pwCVTZ-DK | 1177 | 15 | 518 | 843 |
| MRCI+Q | aug-cc-pV(Q+d)Z | 1126 | 51 <i>i</i> | 508 | 817 |
| MRCI-F12 | aug-cc-pVQZ | 1160 | 73 <i>i</i> | 508 | 851 |
| CCSD(T) | aug-cc-pwCVTZ-DK | 1040 | 77 | 498 | 808 |
| CCSD(T)-F12 | aug-cc-pVQZ | 1118 | 513 | 814 | 1223 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 1045 | 86 | 501 | 816 |
| | | cyc -AlOS (A^2A'') | | | |
| Method | Basis | ω_1 | ω_2 | ω_3 | ZPVE |
| MRCI | aug-cc-pV(T+d)Z | 823 | 493 | 509 | 913 |
| | aug-cc-pV(Q+d)Z | 832 | 504 | 515 | 926 |
| | aug-cc-pwCVTZ-DK | 825 | 492 | 509 | 913 |
| MRCI+Q | aug-cc-pV(T+d)Z | 812 | 478 | 500 | 895 |
| | aug-cc-pV(Q+d)Z | 821 | 489 | 507 | 909 |
| MRCI-F12 | aug-cc-pVQZ | 822 | 500 | 513 | 928 |
| CCSD(T) | aug-cc-pwCVTZ-DK | 809 | 456 | 496 | 881 |
| CCSD(T)-F12 | aug-cc-pVQZ | 822 | 480 | 508 | 905 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 814 | 455 | 498 | 884 |
| | | <i>linear</i> -SAlO ($X^2\Pi$) | | | |
| Method | Basis | ω_1 | ω_2 | ω_3 | ZPVE |
| MRCI | aug-cc-pV(Q+d)Z | 1091 | 161 | 456 | 935 |
| | aug-cc-pwCVTZ-DK | 1107 | 140 | 460 | 854 |
| MRCI+Q | aug-cc-pV(T+d)Z | 1084 | 133 | 459 | 838 |
| | aug-cc-pV(Q+d)Z | 1077 | 163 | 448 | 844 |
| CCSD(T) | aug-cc-pwCVTZ-DK | 1053 | 167 | 441 | 831 |
| CCSD(T)-F12 | aug-cc-pVQZ | 1060 | 165 | 447 | 836 |
| CCSD(T)-AE | aug-cc-pwCVTZ-DK | 1074 | 153 | 445 | 837 |

All large basis sets predicted the AlO stretching (ω_1) frequency with a spread of only 25 cm⁻¹ between the highest and lowest value. The MRCI-F12/aug-cc-pVQZ level of theory predicts ω_1 to be 822 cm⁻¹ compared to the experimental diatomic AlO $(X^2\Sigma^+)$ frequency of 979.2 cm⁻¹ (Huber & Herzberg 1979). This level of theory calculates a lower magnitude for this vibrational mode due to the lengthening of the AlO bond by 0.1036 Å compared to the free diatomic. The lowest amplitude normal mode (ω_2) is assigned to the SAIO scissor motion. This mode is less well characterized than the AlO stretch, as the predicted frequencies vary by as much as 50 cm^{-1} . From the vibrational analysis, the final vibrational mode (ω_3) can be described as mixing of the AIS stretching mode and the bending mode. This is predicted to be 513 cm^{-1} at the MRCI-F12/aug-cc-pVQZ level of theory, quite far from the experimentally determined diatomic AlS $(X^2\Sigma^+)$ frequency of 617 cm^{-1} (Huber & Herzberg 1979). This agrees with the assertion that this is not purely an AIS stretch and that there is mixing between the two normal modes.

The asymmetric stretching mode (ω_1) frequencies of *linear*-SAIO follow a similar trend to those of the other linear neutral isomer, increasing in magnitude with increase in basis set size. This is again consistent with shortening of the bond lengths. The bending mode (ω_2) in this isomer is better characterized

than that in *linear*-AlOS, with frequencies above 130 cm^{-1} at all levels of theory. This indicates that there is a deeper well in the PES, along the bending angle, compared to *linear*-AlOS. The symmetric stretch (ω_3) is very consistent at the MRCI levels of theory, differing by only a few wavenumbers. This is also true of the CCSD(T) predicted frequencies, with the MRCI symmetric frequencies generally larger than those predicted at with CCSD(T) methods.

A set of accurate spectroscopic constants were calculated from the 3D-PESs obtained in the ground state of *linear*-AlOS (X^2A'') , *linear*-SAIO (X^2A''), and *linear*-SAIO⁺ (X^3A'') isomers to help in their detection. These parameters include equilibrium bond distances $(r_{\rm e})$, rotational constants at the equilibrium geometry $(B_{\rm e})$, vibrationally corrected rotational constants $(B_{\rm o})$, secondorder centrifugal distortion constants (D_i) , Coriolis coupling constants (ζ), rotation-vibration constants (α), vibrational anharmonicity constants (χ_{ii}), and anharmonic vibrational frequencies (ν_i) , and they are reported in Table 4. The rovibrational levels were not studied here because of the small difference between cyclic and linear-AlOS isomers. This small difference favors the mixing of the rovibrational levels causing both isomers to exhibit complicated spectra. The anharmonic vibrational frequency for the asymmetric stretching mode (ν_1) is predicted to be 1155 cm⁻¹ for linear-AlOS, while the same mode in linear-SAlO is predicted to

Table 4

MRCI-F12+Q/aug-cc-pVQZ Equilibrium Geometries and a Set of Spectroscopic Constants for the *linear*-AlOS (X^2A''), *linear*-SAlO (X^2A'') and *linear*-SAlO⁺ (X^3A'') Isomers

| Parameter | <i>linear</i> -AlOS (X^2A'') | <i>linear</i> -SAIO (X^2A'') | <i>linear</i> -SAlO ⁺ ($X^{3}A''$) |
|--------------------------------|--------------------------------|--------------------------------|---|
| r _e (Al–O), Å | 1.7264 | 1.6051 | 1.7140 |
| $r_{\rm e}$ (Al–S), Å | | 2.1534 | 2.1222 |
| <i>r</i> _e (S–O), Å | 1.5745 | | |
| Theta, deg | 180.0 | 180.0 | 180.0 |
| B _e , MHz | 3168.7 | 3070.4 | 2987.6 |
| B _o , MHz | 3186.9 | 3049.0 | 2965.8 |
| $\mu_{\rm tot},{\rm D}$ | 1.555 | 4.288 | |
| D _i , MHz | 0.00053 | 0.00055 | 0.00050 |
| ζ ₂₃ | -0.1751 | 0.2944 | 0.2228 |
| ζ_{13} | 0.9845 | -0.9556 | -0.9748 |
| α_1^B , MHz | -0.1982 | 10.8663 | 13.8172 |
| α_2^B , MHz | 8.4599 | 9.8872 | 9.3830 |
| α_3^B , MHz | -20.4469 | -6.5347 | -8.7061 |
| α_1^C , MHz | -0.1982 | 10.8863 | 13.8172 |
| α_2^C , MHz | 8.4599 | 9.8872 | 9.3830 |
| α_3^C , MHz | -20.4469 | -6.5347 | -8.7061 |
| $\chi_{11}, {\rm cm}^{-1}$ | 36.9330 | -5.6479 | -3.2368 |
| $\chi_{12}, {\rm cm}^{-1}$ | 32.7600 | -0.4519 | -5.4329 |
| $\chi_{13}, {\rm cm}^{-1}$ | -78.8377 | -1.8186 | -1.4805 |
| $\chi_{22}, {\rm cm}^{-1}$ | -4.3191 | -1.6283 | -0.6927 |
| $\chi_{23}, {\rm cm}^{-1}$ | -31.0579 | 1.4281 | 1.5783 |
| $\chi_{33}, \mathrm{cm}^{-1}$ | -23.6987 | -0.5272 | -0.1811 |
| $\nu_1, {\rm cm}^{-1}$ | 1155 | 1090 | 910 |
| $\nu_2, {\rm cm}^{-1}$ | 58 | 174 | 135 |
| ν_3 , cm ⁻¹ | 508 | 464 | 476 |

Table 5

Vertical Excitation Energies and Corresponding Oscillator Strengths (f) Calculated at the MRCI+Q/aug-cc-pV(Q+d)Z Level of Theory for the Doublet Electronic Excited States of *linear*-AIOS and *linear*-SAIO

| | linear-AlOS | | linear-SAlO | | | |
|----------------|----------------|-------|------------------|----------------|-------|--|
| State Symmetry | VEE eV (nm) | f | State Symmetry | VEE eV (nm) | f | |
| $1^2\Sigma^+$ | 2.619 (473) | 0.001 | 2 ² Π | 1.091 (1138) | 0.015 | |
| $1^2\Delta$ | 3.431 (361) | 0.000 | $1^2\Sigma^+$ | 1.349 (919) | 0.001 | |
| $1^2\Sigma^-$ | 3.458 (358) | 0.000 | $2^2\Sigma^+$ | 3.048 (406) | 0.001 | |
| $2^{2}\Pi$ | 4.342 (285) | 0.041 | $1^2\Sigma^-$ | 3.492 (355) | 0.005 | |
| $2^2\Sigma^+$ | 4.814 (257) | 0.070 | $1^2\Delta$ | 3.497 (354) | 0.002 | |
| $1^2\Phi$ | 5.013 (247) | | $2^2\Sigma^-$ | 3.715 (333) | 0.007 | |
| | | | $3^2\Pi$ | 4.581 (270) | 0.003 | |

Note. Transitions with high oscillator strengths are in bold.

be 1090 cm^{-1} . This mode is expected to have the highest IR intensity of all three vibrational modes. The bending mode of all linear isomers is less than 200 cm^{-1} , especially for *linear*-AlOS where $\nu_2 = 58 \text{ cm}^{-1}$, which indicates that the molecules examined are floppy and undergo a large amplitude of motion along the bending mode. It should be noted that the perturbative methods used here improve the accuracy of the vibrational frequencies; however, further refinement of the low-frequency bending mode (ν_2) can be accomplished using the more computationally expensive variational method.

Vertical excitation energies and corresponding oscillator strengths (f) to the lowest doublet electronic excited states were calculated at the MRCI+Q/aug-cc-pV(Q+d)Z level of theory for the *linear*-AlOS and *linear*-SAlO isomers and are listed in Table 5. Both isomers are characterized by a high density of electronic states in the UV–visible region (270–500 nm), complicating the electronic spectra, as many states are degenerate and will have multiple crossings. The vertical excitations of *linear*-SAIO are characterized by low oscillator strengths, decreasing the possibility that they will be observed. For *linear*-AIOS, excitation to the $2^{2}\Pi$ (4.342 eV) and $2^{2}\Sigma^{+}$ (4.814 eV) states show large oscillator strengths and have a greater chance to occur.

3.3. Detectability and Observation

The triatomic [Al, S, O] isomers may exist in the CSEs of the oxygen-rich stars VY CMa, IK Tau, and R Dor, and may be detectable through observational studies. To assist in this detection, frequencies for various rotational transitions calculated around the most populated rotational levels are provided. It is anticipated that [Al, S, O] triatomic isomers will exist in a region of the CSEs that exhibits a temperature of approximately 200 K. This temperature region was chosen based on the observation of AlO with $T_{\rm rot} \sim 230$ K in the CSE of VY CMa

Table 6

Relevant Data for Use in Experimental and Observational Studies, Including Frequencies^a for Rotational Transitions in the Ground Vibrational State Surrounding J_{max} and up to States with 75% of the Relative Population of J_{max} , Vibrationally Corrected Rotational Constants $(B_o)^a$, and Anharmonic Vibrational Frequencies $(\nu_t)^a$

| Isomer | J | J' | Frequency (GHz) | J | J' | Frequency (GHz) | B _o (MHz) | (cm^{ν_1}) | (cm^{ν_2}) | (cm^{ν_3}) |
|---------------|----|----|----------------------|----|----|--------------------|-------------------------|-----------------------|----------------|----------------|
| linear-AlOS | 21 | 20 | 133.833 | 31 | 30 | 197.529 | 3186.9 | 1155 | 58 | 508 |
| | 22 | 21 | 140.204 | 32 | 31 | 202.897 | | | | |
| | 23 | 22 | 146.575 | 33 | 32 | 210.264 | | | | |
| | 24 | 23 | 152.946 | 34 | 33 | 216.621 | | | | |
| | 25 | 24 | 159.315 ^b | 35 | 34 | 222.997 | | | | |
| | 26 | 25 | 165.685 | 36 | 35 | 229.363 | | | | |
| | 27 | 26 | 172.055 | 37 | 36 | 235.728 | | | | |
| | 28 | 27 | 178.424 | 38 | 37 | 242.093 | | | | |
| | 29 | 28 | 184.793 | 39 | 38 | 248.458 | | | | |
| | 30 | 29 | 191.161 | 40 | 39 | 254.822 | | | | |
| linear-SAlO | 21 | 20 | 128.041 | 31 | 30 | 188.976 | 3049.0 | 1090 | 174 | 464 |
| | 22 | 21 | 134.136 | 32 | 31 | 195.068 | | | | |
| | 23 | 22 | 140.231 | 33 | 32 | 201.159 | | | | |
| | 24 | 23 | 146.325 | 34 | 33 | 207.250 | | | | |
| | 25 | 24 | 152.419 | 35 | 34 | 213.340 | | | | |
| | 26 | 25 | 158.514 | 36 | 35 | 219.430 | | | | |
| | 27 | 26 | 164.608 | 37 | 36 | 225.519 | | | | |
| | 28 | 27 | 170.700 | 38 | 37 | 231.608 | | | | |
| | 29 | 28 | 176.793 | 39 | 38 | 237.697 | | | | |
| | 30 | 29 | 182.885 | 40 | 39 | 243.784 | | | | |
| linear-SAlO + | 21 | 20 | 124.548 | 31 | 30 | 183.823 | 2965.8 | 910 | 135 | 476 |
| | 22 | 21 | 130.476 | 32 | 31 | 189.749 | | | | |
| | 23 | 22 | 136.405 | 33 | 32 | 195.674 | | | | |
| | 24 | 23 | 142.334 | 34 | 33 | 201.599 | | | | |
| | 25 | 24 | 148.262 | 35 | 34 | 207.524 | | | | |
| | 26 | 25 | 154.190 | 36 | 35 | 213.448 | | | | |
| | 27 | 26 | 160.117 | 37 | 36 | 219.372 | | | | |
| | 28 | 27 | 166.044 | 38 | 37 | 225.295 | | | | |
| | 29 | 28 | 171.971 | 39 | 38 | 231.218 | | | | |
| | 30 | 29 | 177.898 | 40 | 39 | 237.140 | | | | |

Note.

^a All calculated at MRCI-F12+Q/aug-cc-pVQZ.

^b Rotational transitions originating from J_{max} are shown in bold.

by Tenenbaum & Ziurys (2009). At 200 K, the most highly populated rotational energy level for *linear*-AlOS, *linear*-SAIO, and *linear*-SAIO⁺ are predicted to be $J_{\text{max}} = 25$, 26, and 26, respectively, according to a Boltzmann distribution. These rotational levels have energies of 99.3, 102.7, and 99.8 K, respectively.

Frequencies in the ground vibrational state, including the second-order centrifugal distortion correction, for many transitions around J_{max} , where the population is predicted to be large, are included in Table 6. Also reported are frequencies for transitions originating from states predicted to have a relative population greater than 75% of J_{max} . These transitions will have a lower but nonnegligible intensity, and, more importantly, occur in the frequency range accessible from groundbased telescopes. Additionally, the vibrationally corrected rotational constants (B_{0}) and anharmonic vibrational frequencies are included in the table. The $J = 25 \rightarrow 24$ transition in linear-AlOS is predicted to be 159.315 GHz, while the $J = 26 \rightarrow 25$ transition in *linear*-SAIO is predicted to occur at 158.154 GHz. The larger dipole moment in linear-SAIO (4.288 D) will likely make it easier to detect via observational studies compared to linear-AlOS (1.555 D) because the intensity of a rotational transition depends on the interaction of the incoming light with the dipole moment of the molecule.

The SURFIT code that is used to calculate the spectroscopic parameters does not provide intensities of vibrational or rotational transitions; however, similar triatomic molecules exhibiting low abundance ($\sim 10^{-10}$ relative to H₂) have previously been detected via observational studies, such as AINC in IRC+10216 (Ziurys et al. 2002). Although the stars referred to in this paper are either farther away (IK Tau and VY CMa) or have a lower number density in their CSE based on a smaller mass-loss rate (R Dor) than IRC+10216, making the detection of [Al, S, O] molecules potentially more difficult, the larger dipole moment of *linear*-SAIO (4.288 D) compared to that of molecules such as AINC (3.14 D; Ma et al. 1995) may help compensate for these difficulties, and improve its detectability.

Recent spectral scans of R Dor (De Beck & Olofsson 2018) and IK Tau (Velilla Prieto et al. 2017) each include several unidentified lines over the frequency range covered in Table 6. A reexamination of the scans, or even additional observational studies in the region predicted in this work, might be helpful in the identification of new [Al, S, O] triatomic species, using the results from this work as a useful spectroscopic guide.

The vibrational frequencies corresponding to the bending motion (ν_2 , ~100 cm⁻¹) and symmetric stretch (ν_3 , ~500 cm⁻¹) are quite low, and as such, in experiments and in astronomical

 Table 7

 Adiabatic Ionization Energy of *linear*-AlOS, *cyc*-AlOS, and *linear*-SAlO Calculated for the Transition to Both the Triplet and Singlet States

| Isomer | Method | Basis Set | AIE $(X^3\Pi)$ (eV) | АІЕ (A ¹ П) (eV) |
|----------------------------------|-------------|------------------|------------------------|--------------------------------|
| <i>linear</i> -AlOS ($X^2\Pi$) | MRCI | aug-cc-pV(Q+d)Z | 7.55 | 8.77 |
| | | aug-cc-pwCVTZ-DK | 7.39 | 9.87 |
| | MRCI+Q | aug-cc-pV(Q+d)Z | 7.70 | 10.44 |
| | MRCI-F12 | aug-cc-pVQZ | 7.50 | 9.90 |
| | CCSD(T) | CBS | 7.90 | 8.97 |
| | CCSD(T)-F12 | aug-cc-pVQZ | 7.89 | 8.98 |
| | | CBS | 7.92 | 8.98 |
| | CCSD(T)-AE | aug-cc-pwCVTZ-DK | 7.81 | 8.91 |
| cyc -AlOS (A^2A'') | MRCI | aug-cc-pV(Q+d)Z | 7.92 | 8.05 |
| | | aug-cc-pwCVTZ-DK | 7.87 | 7.96 |
| | MRCI+Q | aug-cc-pV(Q+d)Z | 8.11 | 8.19 |
| | MRCI-F12 | aug-cc-pVQZ | 7.95 | 8.03 |
| | CCSD(T) | CBS | 8.21 | 9.58 |
| | CCSD(T)-F12 | aug-cc-pVQZ | 8.21 | 9.59 |
| | | CBS | 8.23 | 9.59 |
| | CCSD(T)-AE | aug-cc-pwCVTZ-DK | 8.17 | 9.56 |
| <i>linear</i> -SAlO ($X^2\Pi$) | MRCI | aug-cc-pVQZ | | 12.13 |
| | | aug-cc-pwCVTZ-DK | 10.41 | 10.72 |

observations, could be vibrationally excited beyond the ground state. In this case, one would expect to see rotational transitions in the vibrationally excited ν_2 state, or even excited ν_3 state. The set of frequencies for rotational transitions in the ground vibrational state from this study should aid the experiments and/or experimental analysis in determining the role of these excited vibrational states. Using this study as a foundational guide, future experimental work is needed to address these important questions.

3.4. Ionization Energy

Adiabatic ionization energies were calculated for the ionization of the neutral species to both the triplet and singlet cation states, and these values are reported in Table 7. Calculated energies are consistent within each method, converging at the largest basis sets. For all isomers, ionization to the triplet state is a lower energy transition than to the singlet state. Focusing in on ionization to the triplet state, MRCI methods consistently predict lower ionization energies for both linear-AlOS and cyc-AlOS isomers than CCSD(T) methods. This effect may arise from the treatment of electron correlation in the MRCI methods that CCSD(T) misses with its single-determinant calculation. The ionization energies for the transition from linear-AlOS to triplet and singlet *linear*-AlOS⁺ are 7.50 and 9.90 eV, respectively, at the MRCI-F12/aug-cc-pVQZ level of theory, corresponding to 165 and 125 nm light in the vacuum ultraviolet regime. This is light that is readily available in the outer envelope of a star like VY CMa, meaning if linear-AlOS is formed, both spin states of *linear*-AlOS⁺ may be produced via photoionization and would be detectable. If triplet *linear*-AlOS⁺ is formed, the singlet state of linear-AlOS⁺ will not be easily accessed from this state because excitation would require a spin flip. Any excitation from triplet linear-AlOS⁺ would be expected to access the spinsymmetric triplet cyclical isomer.

3.5. Bond Dissociation Energies

Because of the nonsize consistency of the MRCI method, bond dissociation energies (BDE) of *linear*-AlOS and *linear*-SAlO

were calculated using the CCSD(T)-AE/aug-cc-pwCVTZ-DK level of theory. Even though the CCSD(T) method loses some information due to its single reference determinant, the all-electron approximation coupled with the scalar relativistic corrections implemented in the Douglas–Kroll basis set help remedy this. The *linear*-AlOS BDE for AlO–S and Al–OS are 3.18 and 3.48 eV, respectively. For *linear*-SAlO, the BDE for S–AlO and SAl–O are 3.46 and 4.61 eV, respectively. These results, coupled with the low frequency of the bending mode, suggest that for both linear isomers elimination of the sulfur atom is the most likely pathway of dissociation through the excited-state cyclic isomer.

4. Conclusion

New triatomic isomers arising from the [Al, S, O] group of molecules have been characterized for the first time using highlevel ab initio methods. *linear*-SAIO ($X^2\Pi$) is predicted to be a potential candidate for detection via radio astronomy, in the 150–250 GHz frequency range, because of its relative stability and large permanent dipole moment. Accurate spectroscopic parameters are also reported for use in potential laboratory explorations of this system. Two important follow-up studies arise from this work: (1) the need to decipher the most likely formation mechanism of this group of molecules, and (2) exploration of the rotational transitions in the excited vibrational states.

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