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# Is AIOH the Astrochemical Reservoir Molecule of AIO?: Insights from Excited Electronic States

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## Abstract

Very recently, the optical bands of the  ${}^2\Sigma^+ \leftarrow X^2\Sigma^+$  system of AIO have been identified in the red supergiant star VYCMa. In an effort to explain the origin of this transition, we used state-of-the-art quantum chemical calculations with proven high accuracy to compute the lowest singlet and triplet electronic states of the AIOH and HAIO isomers as well as their equilibrium geometry and electronic properties. Our calculated potential energy surfaces implicate the three singlet electronic states  $2^1A'$ ,  $3^1A'$ , and  $1^1A''$  in the photodissociation of the [Al,O,H] system. Only AIO, H, Al, and OH products can occur through the photodissociation of [Al,O,H]; AIH and O are not allowed. For the photodissociation of AIOH, the AIO product can occur only in its excited states  $AIO(^2\Pi)$  and  $AIO(^2\Sigma^+)$ .

*Key words:* astrochemistry – supergiants – techniques: spectroscopic – ultraviolet: ISM

## 1. Introduction

Metal-containing molecules have received increased attention in the recent years as an increasing number of systems have been detected in the interstellar medium (ISM). Metal-containing species detected in the ISM include AlNC (Ziurys et al. 2001), MgCN (Ziurys et al. 1995), KCN (Pulliam et al. 2010), AIO (Tenenbaum & Ziurys 2009), and AIOH (Tenenbaum & Ziurys 2010). Among the aluminum-bearing molecules, the diatomic AIO has been detected in the circumstellar shell of red supergiant star VYCMa (Tenenbaum & Ziurys 2009), with an observed abundance of  $6 \cdot 10^{-9}$ . Its formation mechanism is associated with the gas-phase local thermodynamic equilibrium (LTE) chemistry. Recently, Kamiński et al. (2013) confirmed the existence of AIO; specifically, they observed the  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  electronic transition and suggested several mechanisms to explain its origin. Both the millimeter-wave and optical spectrum detection of AIO gas suggest its existence at  $\sim 20$  stellar radii. This result contradicts the LTE model, which predicts substantial AIO abundances to within only a few stellar radii. In 2010, aluminum monohydroxide (AIOH), the most stable isomer of HAIO, was detected in the envelope of VYCMa (Tenenbaum & Ziurys 2010), with an observed abundance of  $1 \cdot 10^{-7}$ , which is relatively higher than the abundance of AIO and closer to the abundance of aluminum ( $3 \cdot 10^{-6}$ ). Its formation has been suggested to occur by LTE chemistry. LTE calculations predict that AIOH is the most abundant aluminum-bearing molecule in the 2–8 stellar radii region (Tenenbaum & Ziurys 2009). Hydrogen is well known to be the most abundant element in the ISM, and AIO and AIOH have been detected in the envelope of VYCMa; however, the simplest diatomic aluminum molecule, AIH, has not yet been detected in the VYCMa star, which is somewhat surprising. The reasons for this non-detection are unclear.

The circumstellar envelope of red supergiant stars such as IRC+10216 and VYCMa foster gas-phase chemistry (McCabe et al. 1979; Ziurys 2006; Parsons et al. 2010). In these stars, a photochemistry process induced by UV-Vis photons can play an important role in both the formation and the destruction of molecular species. Generally, daughter molecules originate

from the photodissociation of parent molecules. For instance, OH and  $O_2$  are the most abundant oxygen-bearing daughter species triggered by the chemistry of water (Li et al. 2016). Although the electronic structures, spectral features, and isomerization processes of AIOH and HAIO isomers are well known, knowledge of their photochemistries is still lacking. Pilgrim et al. (1993) reported the electronic spectrum for AIOH formed in a laser-vaporization pulsed molecular beam source. They observed two electronic states spaced by  $1674 \text{ cm}^{-1}$ . The authors could not unambiguously assign these states to either the AIOH or the HAIO isomer. Li et al. (2003) conducted theoretical calculations to characterize the three lowest-lying singlet states of AIOH using several levels of theory.

Little is known about the electronic spectroscopy and photochemistry of the [Al, O, H] molecular system. In this work, we focus on the photochemical and photophysical processes of AIOH and HAIO isomers. The answers to some fundamental questions in photochemistry may explain the non-detection of AIH in VYCMa and reveal which products are favored after the photodissociation of AIOH and HAIO isomers. However, investigations of the lowest singlet and triplet electronic states can answer the question of whether AIO is the daughter molecule of AIOH.

## 2. Theoretical Background

All calculations were carried out with the MOLPRO2015 program (Werner 2015). The starting points of this work were the electronic structures and vertical excitation energies to the low-lying singlet and triplet electronic states. The search of the stationary points of AIOH and HAIO were performed at the explicitly coupled cluster theory RCCSD(T)-F12 (Adler et al. 2007; Werner et al. 2007; Knizia et al. 2009) in conjunction with large basis sets aug-cc-pV5Z. As shown in previous work (Hauge et al. 1980), the ground electronic state of AIOH is flat and quasilinear, and explicit treatment of the electron correlation is needed (Kalugina et al. 2014). For both isomers, optimized equilibrium geometries were carried out in the  $C_1$  symmetry group. To investigate the lowest electronic states, we used the complete active space self-consistent field (CASSCF; Knowles & Werner 1985; Werner & Knowles

**Table 1**  
Optimized Equilibrium Geometry (Distance in Å and  $\theta$  in Degrees), Harmonic Vibration Frequencies ( $\omega$  in  $\text{cm}^{-1}$ ), and Relative Energy of AIOH and HAIO Isomers in Their Ground Electronic States

| AIOH( $X^1A'$ )         |                  |                  |          |            |            |            |       |
|-------------------------|------------------|------------------|----------|------------|------------|------------|-------|
|                         | $R_{\text{AIO}}$ | $R_{\text{OH}}$  | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | Er/eV |
| CCSD(T)-F12/aug-cc-pV5Z | 1.6804           | 0.9497           | 161.0    | 4009.9     | 129.4      | 845.7      | 0.0   |
| CCSD(T)/aug-cc-pV5Z     | 1.6823           | 0.9499           | 160.9    | 4009.1     | 133.3      | 843.3      | 0.0   |
| MRCI-F12/aug-cc-pV5Z    | 1.7084           | 0.9424           | 134.2    | 4183.9     | 485.9      | 806.8      | 0.0   |
| MRCI+Q/aug-cc-pV5Z      | 1.7021           | 0.9441           | 139.0    | 4129.5     | 380.0      | 809.8      | 0.0   |
| expt <sup>a</sup>       |                  |                  |          | 3790       |            | 810.3      |       |
| expt <sup>b</sup>       |                  |                  |          |            |            | 895        |       |
| HAIO( $X^1\Sigma^+$ )   |                  |                  |          |            |            |            |       |
|                         | $R_{\text{AIO}}$ | $R_{\text{AlH}}$ | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | Er/eV |
| CCSD(T)-F12/aug-cc-pV5Z | 1.6036           | 1.5649           | 180.0    | 2014.2     | 418.0      | 1067.9     | 1.74  |
| CCSD(T)/aug-cc-pV5Z     | 1.6054           | 1.5651           | 180.0    | 2012.5     | 418.5      | 1064.9     | 1.74  |
| MRCI-F12/aug-cc-pV5Z    | 1.6001           | 1.5551           | 180.0    | 2101.9     | 461.3      | 1077.6     | 1.49  |
| MRCI+Q/aug-cc-pV5Z      | 1.6051           | 1.5563           | 180.0    | 2097.5     | 456.4      | 1076.7     | 1.54  |

#### Notes.

<sup>a</sup> Reference: Pilgrim et al. (1993).

<sup>b</sup> Reference: Hauge et al. (1980).

1985) followed by the internally contracted multireference configuration interaction (MRCI; Knowles & Werner 1988; Werner & Knowles 1988) methods, as implemented in the MOLPRO package. In MRCI/CASSCF calculations, all the valence orbitals were employed without any restriction. In these calculations, the atoms were described by the aug-cc-pV5Z basis sets. Our interest was in the dissociation of AIOH and HAIO isomers along the Al–O, O–H, and H–Al stretches. Evolution of the lowest electronic state along the bending angle were also mapped. To consider all the states involved in the photodissociation process, all singlet and triplet electronic states that correlated to the first three dissociation limits of AIO+H, the first two dissociation limits of AlH+O and one dissociation limit of Al+OH, were calculated. Because of the non-size consistency of the MRCI method, the Davidson correction (Langhoff & Davidson 1974) was used to obtain an accurate value of the dissociation limits and the equilibrium geometries of the lowest electronic states. From the CASSCF wavefunction, the transition dipole moment was evaluated to calculate the lifetime ( $\tau$ , in s), which is related to the square of the transition dipole moment ( $|R_{e,i}|^2$ , in Debye) via the equation

$$\tau_n(s) = 6.07706 \times 10^{-6} \sum_i^n \frac{1}{|R_{e,i}|^2 \delta E_i^3}, \quad (1)$$

where  $\delta E_i$  is the energy transition in eV and  $n$  is the number of electronic states.

### 3. Results and Discussion

#### 3.1. Electronic Ground States of AIOH and HAIO

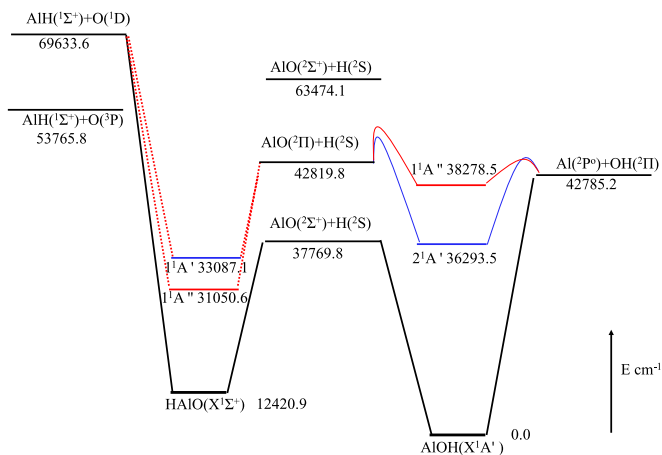
The optimized equilibrium geometries of AIOH and HAIO isomers in their ground electronic states are listed in Table 1. All levels of theory suggested that AIOH is the most stable isomer, with Al–O and O–H bond lengths of 1.702 and 0.944 Å, respectively, at the MRCI+Q level of theory. Table 1 shows no coherence between the equilibrium geometries of AIOH calculated at the MRCI and the CCSD(T) levels of theory. Multireference and explicitly multireference treatment of the electron correlation at the MRCI+Q and MRCI-F12 levels, respectively, in conjunction with the large basis sets aug-cc-pV5Z showed that the global minimum was located at

$\theta \approx 134^\circ$ , whereas an explicit treatment of the electron correlation at the CCSD(T)-F12 level showed that the global minimum was located at  $\theta = 161^\circ$ . All levels of theory showed a real minimum on the potential energy surface because all their harmonic vibrational frequencies were positives.

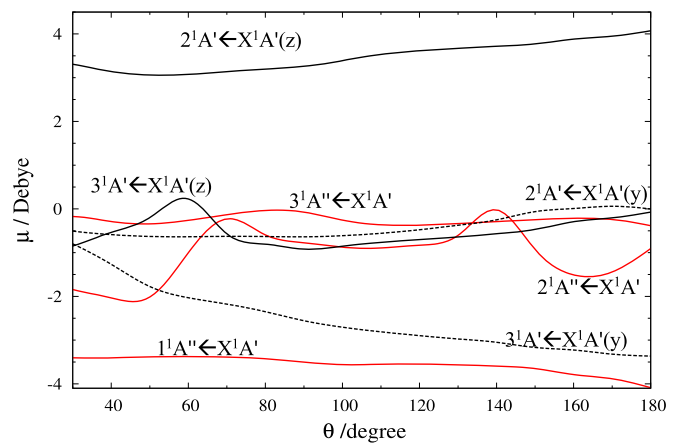
The AIOH molecule is quasilinear in its ground electronic state, meaning that, along the bending angle, the potential energy surface will be too flat with small harmonic vibrational frequencies. For the bending mode, we calculated the harmonic vibrational frequency at the MRCI+Q level to be  $\omega_2 = 380 \text{ cm}^{-1}$  and that at the MRCI-F12 level to be  $\omega_2 = 485 \text{ cm}^{-1}$ . These values are relatively large and cannot describe a flat potential. At the CCSD(T)-F12 level, the barrier to linearity was calculated at  $5.3 \text{ cm}^{-1}$ , confirming that AIOH is quasilinear, with small bending frequencies calculated at  $129.4 \text{ cm}^{-1}$ . The results obtained with both methods, CCSD(T) and CCSD(T)-F12, are in good agreement with previous work (Li et al. 2003) which showed that the bending angle of AIOH in its ground electronic state is  $160^\circ$ .

The predicted harmonic vibrational frequency  $\omega_1$  for AIOH is in good agreement with previous theoretical work (Li et al. 2003) and relatively far compared to the experimental work of Pilgrim et al. (1993). In fact, in the diatomic OH, the experimental values of the harmonic vibrational frequencies and the OH bond length (Mizushima 1972) are  $\omega(\text{OH}) = 3737 \text{ cm}^{-1}$  and  $r_{\text{OH}} = 0.969 \text{ Å}$ , respectively. Optimized equilibrium geometry at CCSD(T) and CCSD(T)-F12 levels show that the equilibrium distance of OH decreased by 0.02 Å, meaning that the harmonic stretch (OH) should increase.

For the HAIO( $X^1\Sigma^+$ ) isomer, which is 1.74 eV higher in energy than AIOH, CCSD(T) and MRCI were in good agreement. At the MRCI-F12 level of theory, the AIO bond length was predicted to be  $R_{\text{AIO}} = 1.6036 \text{ Å}$  and  $R_{\text{AlO}} = 1.6804 \text{ Å}$  in the AIOH isomer. The equilibrium bond length for the diatomic AIO( $X^2\Sigma^+$ ) was determined to be  $R_{\text{AIO}} = 1.620 \text{ Å}$  at the same level. Therefore, the AIO distance of AIOH was predicted to be longer than in AIO( $X^2\Sigma^+$ ) and HAIO, which is in agreement with the AIO stretch ( $\omega_3$ ) that is decreased relative to its value in AIO ( $994.1 \text{ cm}^{-1}$ ; Sghaier et al. 2016) and HAIO ( $1077.6 \text{ cm}^{-1}$ ). Here, we were interested in the electronic spectroscopy and the stability



**Figure 1.** MRCI+Q/aug-cc-pV5Z adiabatic energetic diagram of the lowest dissociation limits of the AIOH and HAIO systems. The reference energy is the energy of AIOH( $X^1A'$ ) including zero-point vibrational correction.



**Figure 2.** One-dimensional cut of the evolution of the transition dipole moment from the ground state of AIOH( $X^1A'$ ) to  $2^1A'$ ,  $3^1A'$ ,  $1^1A''$ ,  $2^1A''$ , and  $3^1A''$  electronic states along the bending angle. The  $y$  and  $z$  components of the transition moments are plotted separately.

**Table 2**  
MRCI+Q/aug-cc-pV5Z Optimized Equilibrium Geometry (Distance in Å and  $\theta$  in Degrees), Harmonic Vibration Frequencies ( $\omega_i$  in  $\text{cm}^{-1}$ ), and Vertical ( $T_e$  in eV) and Adiabatic ( $T_0$  in eV) Excitation Energy of the Lowest Electronic States of AIOH and HAIO

| AIOH          |         |                  |                   |          |            |            |            |       |       |               |             |
|---------------|---------|------------------|-------------------|----------|------------|------------|------------|-------|-------|---------------|-------------|
| States        |         | $R_{\text{AIO}}$ | $R_{\text{OH}}$   | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $T_e$ | $T_0$ | $ \mu _{A-X}$ | $\tau$ (ns) |
| $X^1A'$       |         | 1.702            | 0.944             | 139.0    | 4129.5     | 380.0      | 809.8      | 0.00  | 0.00  |               |             |
| $1^3A'$       |         | 1.717            | 0.961             | 117.1    | 3841.9     | 674.7      | 824.2      | 3.37  | 2.67  |               |             |
| $1^3A''$      |         | 1.702            | 0.952             | 130.7    | 3969.4     | 448.2      | 839.4      | 3.46  | 2.80  |               |             |
| $2^1A'$       |         | 1.755            | 0.963             | 110.1    | 3834.2     | 657.8      | 843.5      | 5.54  | 4.50  | 4.25          | 1.97        |
| $1^1A''$      |         | 1.741            | 0.960             | 116.7    | 3854.6     | 575.7      | 780.3      | 5.59  | 4.73  | 4.26          | 1.91        |
| HAIO          |         |                  |                   |          |            |            |            |       |       |               |             |
| States        |         | $R_{\text{AIO}}$ | $R_{\text{HAIO}}$ | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $T_e$ | $T_0$ | $ \mu _{A-X}$ | $\tau$ (ns) |
| $X^1\Sigma^+$ | $X^1A'$ | 1.601            | 1.556             | 180.0    | 2086.0     | 452.0      | 1069.1     | 0.0   | 0.00  |               |             |
| $^3\Pi$       | $^3A'$  | 1.726            | 1.610             | 94.7     | 1827.9     | 808.5      | 948.3      | 3.79  | 2.19  |               |             |
|               | $^3A''$ | 1.780            | 1.602             | 116.9    | 1827.8     | 582.6      | 735.5      |       | 2.22  |               |             |
| $^1\Pi$       | $^1A''$ | 1.772            | 1.599             | 116.5    | 1835.9     | 596.0      | 748.4      | 4.07  | 2.29  |               |             |
|               | $^1A'$  | 1.743            | 1.609             | 119.4    | 1792.6     | 568.4      | 809.1      |       | 2.54  | 1.87          | 25.7        |
| $^3\Sigma^+$  | $^3A'$  |                  |                   |          |            |            |            | 4.08  |       |               |             |

**Note.** Also given are the transition dipole moment ( $|\mu|_{A-X}$  in debye) and the lifetime ( $\tau$  in ns) of the lowest singlet states.

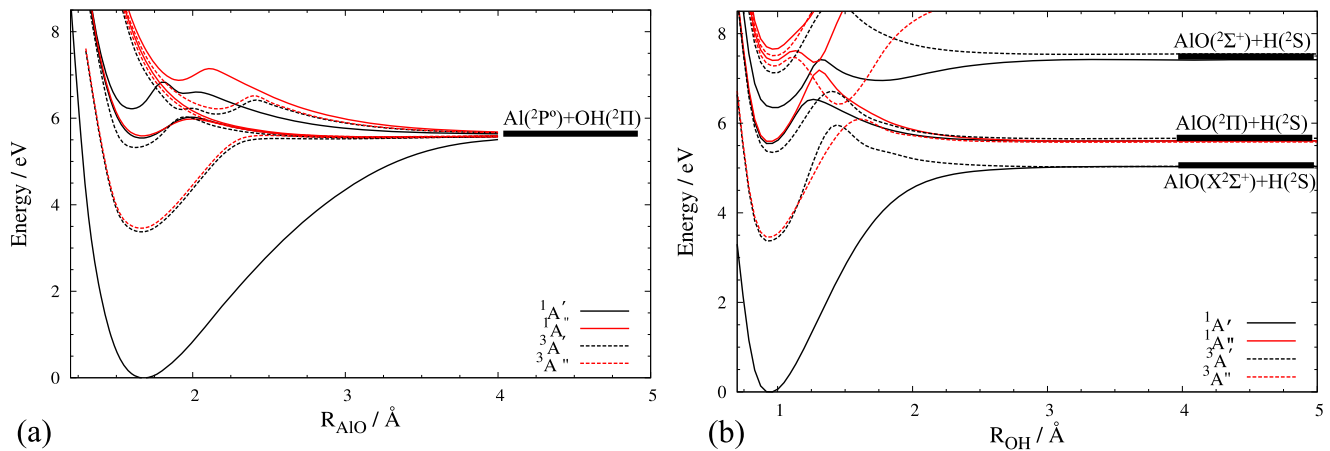
of the lowest electronic state of both the AIOH and the HAIO isomer. In the following section, we use the CCSD(T)-F12/aug-cc-pV5Z optimized equilibrium geometries to describe the behavior of the lowest electronic states.

### 3.2. Potential Energy Surfaces

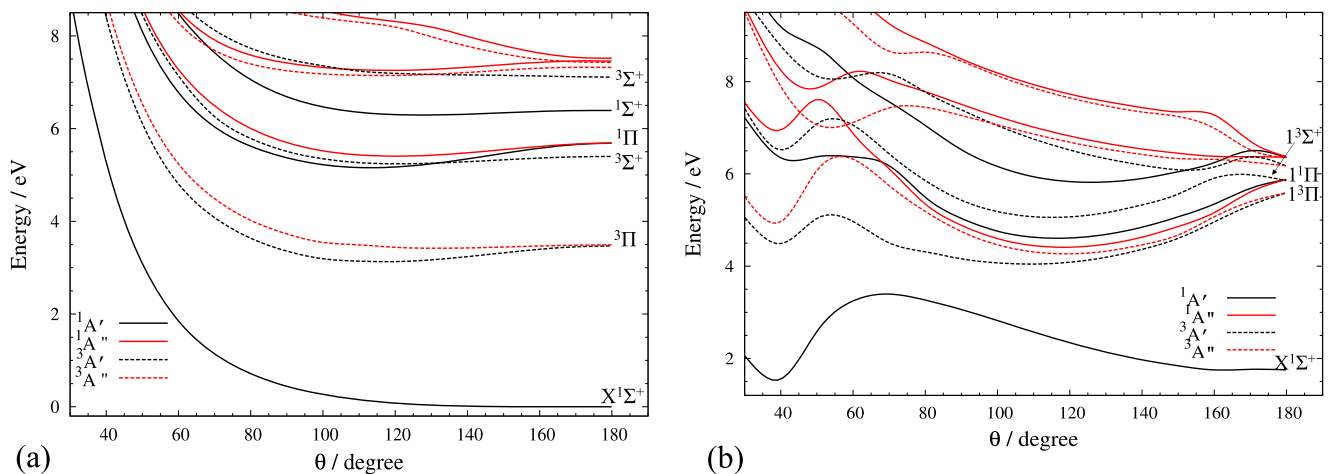
We started our investigations by exploring the topology of the potential energy surfaces (PESs) of the low-lying singlet and triplet electronic states for linear AIOH (i.e.,  $C_{\infty v}$  point group) and bent HAIO isomer (i.e.,  $C_s$  point group). Figure 1 displays the energetic diagram of AIOH and HAIO calculated at the MRCI+Q/aug-cc-pV5Z level of theory. The adiabatic electronic excitation energies of AIO were taken from Michels (1972) and Rosenwaks et al. (1975). This diagram was corrected at the zero-point energy (ZPE), and the origin of energy is the energy of AIOH in its ground electronic state ( $X^1A'$ ). The optimized equilibrium geometry of the lowest singlet and triplet states, as well as the vertical and adiabatic excitation energies and transition dipole moment, are listed in Table 2.

Figure 2 shows the evolution of the transition dipole moment along the bending angle. Figure 3 displays one-dimensional cuts of the lowest electronic states of the bent AIOH isomer along the AIO (Figure 3(a)) and OH (Figure 3(b)) bond lengths to approximately 8 eV above the ground-state minimum. The other coordinates were fixed to their equilibrium values.

Figure 4 shows the evolution of the PESs along the bending angle. Their correlations at linearity were made explicit by the corresponding spectroscopic term placed at the right-hand side of the figure. Figure 3 shows that the first two triplet states,  $1^3A'$  and  $1^3A''$ , are stable with respect to dissociation, their minimum is located below the first dissociation limit, and they have a potential well. These two states were located at 2.67 eV for  $1^3A'$  and at 2.80 eV for  $1^3A''$ , respectively, above the global minimum of AIOH. Along the bending angle, several excited states showed a flat potential and were coupled by Renner-Teller coupling (Figure 4(a)). For instance, the  $1^3A'$  and  $1^3A''$  states correlated to the  $^3\Pi$  state at linearity. The optimized geometries of these two triplet states predicted a larger OH bond length than the OH bond length of the ground state (Table 2). The first lowest singlet states  $2^1A'$  and  $1^1A''$  showed a shallow potential along the AIO and OH coordinates.



**Figure 3.** MRCI/aug-cc-pV5Z one-dimensional cut of the lowest singlet and triplet electronic states of AIOH along the  $R_{\text{AIO}}$  (a) and  $R_{\text{OH}}$  (b) distances. The remaining coordinates were kept fixed at their equilibrium values.



**Figure 4.** MRCI/aug-cc-pV5Z one-dimensional cut of the lowest singlet and triplet electronic states of AIOH (a) and HAIO (b) along the bending angle. The remaining coordinates were kept fixed at their equilibrium values. The origin of energy was the energy of AIOH in its ground electronic state.

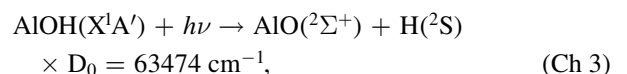
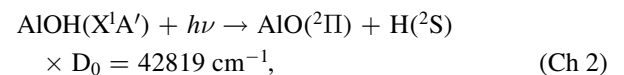
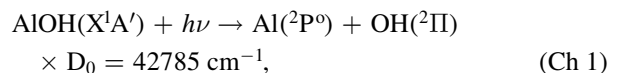
These two electronic states,  $2^1A'$  and  $1^1A''$ , correlate to a  $^1\Pi$  state at linearity and are coupled by Renner–Teller coupling.

Both the  $2^1A'$  and the  $1^1A''$  potential energies exhibited several avoided crossings. Because of the limited number of states calculated, some avoiding crossing at energies above 7.5 eV were not fully resolved. The relatively flat potential around  $R_{\text{OH}} = 1.75 \text{ \AA}$  in Figure 3(b) is the result of avoidance with the next-higher  $4^1A'$  state. These avoided crossings between the electronic state with the same spin symmetry should favor mixing of their wavefunctions and complicate their electronic and rovibrational spectra. Furthermore, they play an important role in the photodissociation process. At the MRCI+Q/aug-cc-pV5Z level of theory, we calculated the adiabatic excitation energy from the ground state to the  $2^1A'$  and  $1^1A''$  electronic states to be 4.58 and 4.83 eV, respectively. This result suggests that numerous rovibrational levels were located above the  $\text{AIO}(^2\Pi) + \text{H}(^2\text{S})$  and  $\text{Al}(^2\text{P}^\circ) + \text{OH}(^2\Pi)$  dissociation limits.

Inspection of Figures 3 and 4(a) and Table 2 reveals that the  $2^1A'$  and  $1^1A''$  electronic states absorb strongly in the deep UV. The transition dipole moments from the ground state to these two states, which were evaluated at the CASSCF/aug-cc-pV5Z level to be 4.25 Debye, was relatively large. However, the oscillator strength that expresses the probability of absorption to these two electronic states was calculated to be 0.38 at the

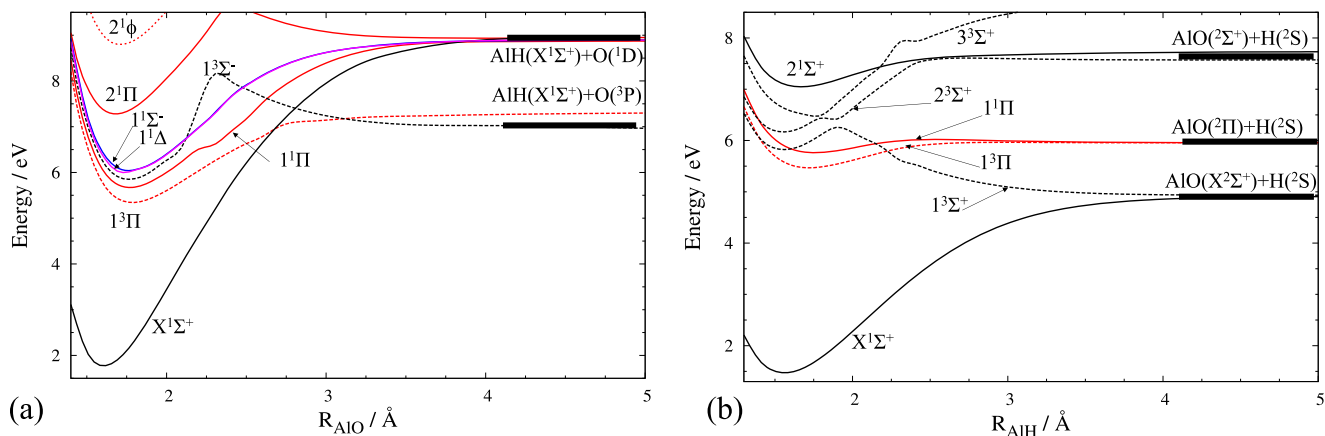
EOMCCSD/aug-cc-pV5Z level; the probability of this transition occurring is therefore relatively high.

Furthermore, the vertical excitation energies from the ground state to the  $2^1A'$  and the  $1^1A''$  states were calculated to be 5.54 and 5.59 eV, respectively. Therefore, the absorption of a photon at 5.5 eV ( $\sim 220\text{--}225 \text{ nm}$ ) to these two states could lead to dissociation of the AIOH through three primary channels:



Ch 1: after UV absorption, the wave packet will explore the  $2^1A'$  and  $1^1A''$  PESs and the molecule will undergo a large amplitude of motion. If it has sufficient energy, it can cross the barrier located at  $R_{\text{AIO}} = 2 \text{ \AA}$  and foster Al and OH in their ground electronic states (Figure 3(a)). As evident in Figure 1, the dissociation energy of the  $1^1A''$  electronic state was less than  $5000 \text{ cm}^{-1}$  relative to the  $\text{Al}(^2\text{P}^\circ) + \text{OH}(^2\Pi)$  dissociation limit. This mechanism is in good agreement with the optimized geometry





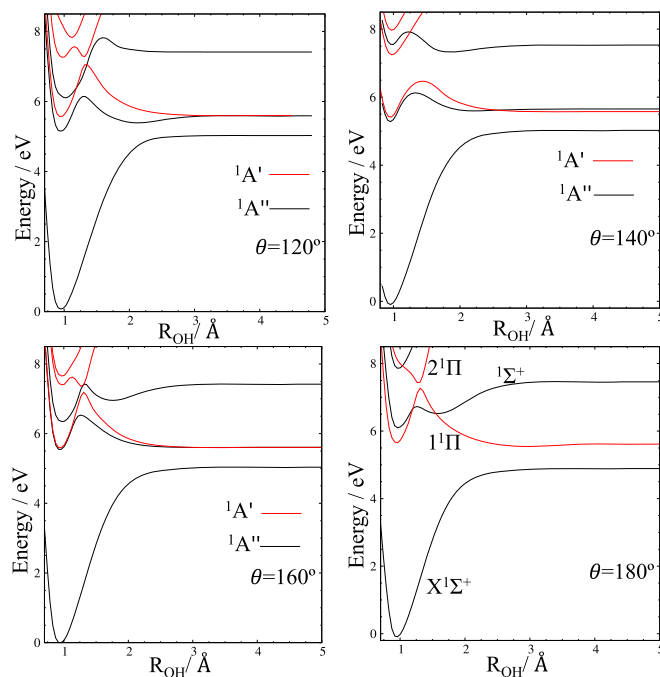
**Figure 5.** MRCI/aug-cc-pV5Z one-dimensional cut of the lowest singlet and triplet electronic states of HAIO along the  $R_{\text{AIO}}$  (a) and  $R_{\text{AIH}}$  (b) distances. The remaining coordinates were kept fixed at their equilibrium values. The origin of energy is the energy of AIOH in its ground electronic state.

of the  $2^1A'$  and  $1^1A''$  electronic states. In fact, the AIO bond length in the  $2^1A'$  and  $1^1A''$  states was increased by 0.053 and 0.039 Å, respectively, relative to the values in the ground electronic state. The lifetimes of these singlet states were, however, calculated to be 1.97 ns for  $2^1A'$  and 1.91 ns for  $1^1A''$ .

The  $3^1A'$  electronic state can be implicated in the photodissociation of AIOH because all its rovibrational levels are above the first dissociation limit  $\text{Al} + \text{OH}$ . Furthermore, the transition dipole moment  $3^1A' \leftarrow X^1A'$ , which was calculated to be 3.45 Debye at the CASSCF/aug-cc-pV5Z level of theory, and the oscillator strength, which was calculated at 0.30, were both relatively large. Figure 3(a) shows that the  $3^1A'$  electronic state was crossed by four dissociative states,  $2^1A''$ ,  $2^3A''$ ,  $3^3A''$ , and  $3^3A'$ . The crossing of the  $3^1A'$  state with the triplet states could, in principle, shorten the lifetime of the singlet  $3^1A'$  state by spin-orbit coupling. Therefore, after UV absorption (6.36 eV at  $\sim 194$  nm), the Al and OH products can occur through vibronic coupling with the  $2^1A''$  electronic state or through spin-orbit coupling with the  $2^3A''$ ,  $3^3A''$ , and  $3^3A'$  states.

Ch 2: the other path of photodissociation is to produce AIO and H (Figure 3(b)). After UV absorption (5.5 eV at  $\sim 220$ – $225$  nm), the AIOH molecule would be excited to the  $2^1A'$  or  $1^1A''$  vibrational level, where it is considered to dissociate by H-atom tunneling through the barrier located at 1.21 Å and foster AIO ( $^2\Pi$ ) +  $\text{H}(^2\text{S})$  products. The optimized equilibrium geometries of these two singlets states showed that the OH bond length increased by 0.019 Å for the  $2^1A'$  and by 0.016 Å for the  $1^1A''$  state compared with the bond lengths in its ground electronic states. This result is in good agreement with the asymmetric stretch ( $\omega_1$ ), which was decreased by more than  $250 \text{ cm}^{-1}$ .

As shown in Figure 4(a), the PES of the ground electronic state along the bending angle was flat; therefore, a large variation of the bending angle corresponds to a small variation of the electronic energy. A small temperature change or infrared excitation of the vibrational mode ( $\nu_2$ ) could easily induce an important change in the equilibrium angle. A series of such one-dimensional cuts of the lowest singlet electronic states along the OH coordinate and at different bending angles is shown in Figure 6. These cuts give an overview of the behavior of the lowest singlet state when the bending angle changed from  $120^\circ$  to  $180^\circ$ . The evolution along the bending angle of the transition dipole moment from the ground electronic state to the lowest singlet state is shown in Figure 2. This figure shows that the transition dipole moment of  $2^1A'$ ,  $3^1A'$ , and  $1^1A''$  was relatively large ( $>3$  Debye). Inspection



**Figure 6.** One-dimensional cuts of the lowest singlet state of AIOH along the  $R_{\text{OH}}$  distance and different bending angles.

of these cuts and Figure 2 shows that the  $3^1A'$  electronic state can be populated after UV absorption and that the  $\text{AIO}(^2\Sigma^+) + \text{H}(^2\text{S})$  products can form (Ch 3).

For  $\theta = 140^\circ$ , the  $3^1A'$  state shows a low barrier at  $R_{\text{OH}} = 1.3$  Å. If the molecule has sufficient energy, the wave packet will cross this low barrier and foster  $\text{AIO}(^2\Sigma^+)$  and  $\text{H}(^2\text{S})$ . At linearity ( $\theta = 180^\circ$ ), the  $3^1A'$  state correlates to the  $1^1\Sigma^+$  state and both  $2^1A'$  and  $1^1A''$  form a Renner-Teller pair and correlate to the  $1^1\Pi$  state. These two states,  $1^1\Sigma^+$  and  $1^1\Pi$ , are crossed at  $R_{\text{OH}} = 1.24$  Å and  $R_{\text{OH}} = 1.57$  Å. After UV absorption, the vibrational levels of the  $1^1\Pi$  state can dissociate to give AIO ( $^2\Pi$ ) through tunneling of an H atom or through vibronic coupling with the  $1^1\Sigma^+$  state and foster  $\text{AIO}(^2\Sigma^+)$ .

Figure 5 shows the evolution of the lowest state of HAIO along the AIH distance (Figure 5(a)) and along the AIO distance (Figure 5(b)). In these figures, the origin of energy is the energy of AIOH in its ground electronic state. Unlike the

AIOH isomer, the ground state of HAIO is linear and rigid because the bending mode  $\omega_2$  is relatively large (calculated to be  $452\text{ cm}^{-1}$  at the MRCI+Q level). These figures show that the lowest singlet and triple electronic state are unstable with respect the first dissociation limit AIO+H (Figure 5(a)). This figure shows that several excited electronic states are stable with respect the AIH+O dissociation limit, that their minimum is located below the dissociation limit, and that they have a potential well. The evolution of the lowest singlet and triplet state along the bending angle (see Figure 4(b)) shows that several excited states are coupled by Renner–Teller coupling at linearity. When the bending angle decreases, these states split into two components,  $A'$  and  $A''$ , in  $C_s$  symmetry. The optimized equilibrium geometry of the  $^1\Pi$  ( $^1A'$  and  $^1A''$ ) and  $^3\Pi$  ( $^1A'$  and  $^1A''$ ) electronic states showed them to have a bent structure (Table 2) and showed that their global minimum is located below the first dissociation limit AIO( $^2\Sigma^+$ )+H( $^2S$ ).

We now focus on the electronic spectroscopy of the HAIO isomer. We examined all allowed electronic transitions, transition dipole moments, and adiabatic and vertical excitation energies of HAIO at the MRCI+Q level. The electronic state  $^1\Pi$ , which is split into two components,  $^1A'$  and  $^1A''$ , absorbed strongly in the near-UV. The transition dipole moment, which was calculated to be 1.87 Debye, was relatively large. The absorption of a photon to this state can easily lead to the AIO( $^2\Pi$ ) and H( $^2S$ ) products. As evident in Figure 3(a), the PES of the  $^1\Pi$  state was flat and the HAIO could dissociate directly to AIO( $^2\Pi$ ) and H( $^2S$ ). The  $^1\Pi$  electronic state was crossed by the  $^3\Sigma^+$  state at  $R_{\text{AIH}} = 2.19\text{ \AA}$ .

At this crossing, the AIO( $^2\Sigma^+$ ) and H( $^2S$ ) products can also occur through spin–orbit coupling with the  $^3\Sigma^+$  state. Figure 3(b) shows a high density of electronic states in the near-UV region, which favors mixing between their wavefunctions and complicates their electronic and rovibrational spectra. In this figure, all electronic states are stable with respect to the AIH+O dissociation limit and they are not crossed by any dissociative state, meaning that the photodissociation of HAIO to give AIH and O cannot occur.

#### 4. Discussion

Close inspection of the PESs along the AIO, OH, and AIH stretching coordinates, together with the data in Table 2 and Figure 1, suggest that only Al, H, AIO, and OH products are possible through the photodissociation of AIOH and HAIO. In the case of the photodissociation of AIOH, the AIO diatomic molecule can occur only in its excited state AIO( $^2\Pi$ ) or AIO( $^2\Sigma^+$ ). Its production in its ground electronic state from the photodissociation of the AIOH isomer is not allowed. After the photodissociation, the diatomic AIO should return to its ground electronic state, accompanied by photon emission in the near-infrared ( $\sim 2.5\text{ }\mu\text{m}$ ) in the case of AIO( $^2\Pi$ )+H( $^2S$ ) (Ch 2) products and visible (blue-green) in the case of AIO( $^2\Sigma^+$ )+H( $^2S$ ) (Ch 3).

Based on our results and previous astrophysical observations, we propose that the AIO originates from the photodissociation of AIOH. The UV and visual echelle spectrograph at the large telescope does not reach the  $A^2\Pi \leftarrow X^2\Sigma^+$  transition of AIO, which is located above  $1.05\text{ }\mu\text{m}$ . Only the  $^2\Sigma^+ \leftarrow X^2\Sigma^+$  transition was detected (Kamiński et al. 2013). Despite the high abundance of hydrogen and aluminum in VYCMa, the detection of AIH failed and the reasons for its non-detection are unclear. It has, however, been suggested to be present in VYCMa. Inspection of our PES showed that the AIH and O products cannot occur from the

photodissociation of the [H, Al, O] system, which may explain why the detection of AIH has failed. At low-energy collisions, the potential energy surface suggests that AIOH formation by direct radiative association of AIO and H can occur. In fact, Figures 3(a) and (b) show that the electronic ground state and the first triplet state correlate adiabatically to the first dissociation limit AIO+H. At the CCSD(T)-F12/aug-cc-pVTZ level of theory, the optimized equilibrium geometry of the AIO–H( $^3A'$ ) complex show the existence of two minima corresponding to the weakly bound structure of AIOH. These two minima are bent with  $R_{\text{OH}} = 3.0181\text{ \AA}$ ,  $R_{\text{AIO}} = 1.6332\text{ \AA}$ , and  $\theta = 118.7^\circ$  for the AIO–H( $^3A'$ ) complex and  $R_{\text{AIH}} = 4.6561\text{ \AA}$ ,  $R_{\text{AIO}} = 1.6251\text{ \AA}$ , and  $\theta = 151.0^\circ$  for the H–AIO( $^3A'$ ) complex. These two equilibrium structures showed a real minimum on the triplet PES because all their harmonic vibrational frequencies were positive. At low temperatures, the union of AIO and H may occur through the  $^3\Pi$  state and form a H–AIO( $^3A'$ ) van der Waals complex (Figure 5(b)). The HAIO isomer can then occur in its triplet or singlet state, followed by radiative decay to the ground electronic state.

#### 5. Conclusion

We have reported an accurate calculation of the potential energy surfaces for the lowest singlet and triplet electronic states of AIOH and HAIO isomers. The ground electronic state of the AIOH isomer is flat, and the barrier to linearity was calculated to be  $5.3\text{ cm}^{-1}$ . Our PES suggests that the production of AIO from AIOH is a plausible mechanism and can occur through two channels, whereas AIH and O are not allowed. Further progress can be made by combining these data with dynamics on the global PES of the first excited singlet states  $^1A'$  and  $^1A''$ .

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