

Electronic structure and photoelectron spectroscopy of AlSi mixed dimer

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The electronic structure of the heterodimer AlSi is experimentally studied using anion photoelectron spectroscopy. Four low-lying electronic excited states are observed for AlSi. The electron affinity of AlSi is measured to be 1.32 (5) eV, which is lower than that of both Al₂ and Si₂. The electronic structure of AlSi is understood by comparing to that of the known Al₂ and Al₂⁻ molecules. The ground state of AlSi is determined to be X ⁴Σ⁻ with a vibrational frequency of 400 (50) cm⁻¹. The four excited states are A ²Σ⁻, B ²Δ, C ²Π, and D ²Σ⁺ with excitation energies of 0.23, 0.67, 0.82, and 1.13 eV, respectively. The photoelectron spectra of Al₂⁻ are also presented and excited states of the Al₂⁻ anion are definitively observed. The electronic structure of AlSi is discussed and compared to that of the homonuclear dimers, Al₂ and Si₂. © 1997 American Institute of Physics.
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I. INTRODUCTION

Understanding the chemical bonding between Al and Si is of both fundamental and technological importance. Although Al and Si are neighbors in the periodic table, they exhibit rather different characteristics of bonding. Bulk aluminum is an excellent metal while bulk silicon is a covalently bonded semiconductor. The bonding between Al and Si is expected to show both ionic and covalent characters. Technologically, aluminum thin films are widely used in Si-based microelectronic devices as electrical contacts and conductors. The interactions between Al and Si play important roles in determining the nature and quality of the Al/Si interface. Extensive work has been conducted on the deposition and growth of Al thin films on Si and SiO₂ surfaces.¹⁻³ Studying Al_xSi_y mixed clusters can provide knowledge about the nature of the Al/Si chemical bonding, as well as insight into the properties of the Al/Si interfaces important to the current electronic devices. Surprisingly, there has been no work on the Al_xSi_y mixed clusters, although there have been numerous studies on pure Al⁴⁻⁹ and Si clusters.¹⁰⁻¹⁴ Part of the difficulty in studying the Al_xSi_y clusters is their production and mass analyses. Al and Si have very close atomic masses and good mass resolution will be required to analyze the Al_xSi_y clusters, which may show complicated mass patterns.

We are interested in studying the electronic structure of the Al_xSi_y clusters by using anion photoelectron spectroscopy (PES). In the present paper, we first report the results on the simplest of the Al/Si mixed clusters, the AlSi mixed dimer. We obtained vibrationally resolved PES spectra for AlSi⁻ at 2.33 and 3.49 eV photon energies. We observed four electronic excited states for AlSi within about 1.1 eV above the ground state. For comparison, we also studied the PES spectra of Al₂⁻ at 2.33, 3.49, and 4.66 eV photon energies. Beside the neutral states, we observed two electronically excited states for the Al₂⁻ anion. Interestingly we found that the electron affinity (EA) of AlSi (1.32 eV) is smaller

than that of both Al₂ (1.46 eV) and Si₂ (2.20 eV, Ref. 14). The results of the Al₂⁻ are compared with previous theoretical calculations.⁵ We discuss the bonding and electronic structures of AlSi by comparison with Al₂ and Si₂ since there has been no theoretical calculation on the AlSi dimer.

II. EXPERIMENT

The details of our experimental apparatus have been published before.^{15,16} Briefly, it involves a pulsed laser vaporization cluster source and magnetic-bottle time-of-flight photoelectron analyzer. A Si/Al alloy disk target (4:1 atomic ratio) is vaporized by a Q-switched Nd:YAG laser to produce the Al_xSi_y clusters. The clusters are entrained into a helium carrier gas and expanded through a 2 mm diameter nozzle to form a supersonic cluster beam. The anions in the beam are extracted perpendicularly into a time-of-flight (TOF) mass spectrometer for size analysis. In the dimer region, all the dimers, including Al₂⁻, AlSi⁻, and Si₂⁻, are produced in about equal abundance and they are separated by one atomic mass unit. Since Al has only one natural isotope (100% ²⁷Al), the main AlSi⁻ mass peak (²⁷Al²⁸Si) contains no other species while the main Si₂⁻ peak contains about 5% AlSi⁻ (²⁷Al²⁹Si) due to the natural isotope distributions of Si (92.23% ²⁸Si, 4.67% ²⁹Si, 3.10% ³⁰Si). During the PES experiments, a cluster of interest is mass selected and decelerated before detached in the interaction zone of the magnetic bottle by a laser beam from a second Nd:YAG laser. The photoelectrons are collected by the magnetic bottle at near 100% efficiency and energy analyzed in a 3.5 m long field-free TOF tube at a resolution of better than 30 meV for 1 eV electrons. The photoelectron TOF spectra are calibrated by the known spectrum of Cu⁻ to obtain the binding energy spectra usually presented.¹⁶

III. RESULTS

Figure 1 shows the 355 nm (3.49 eV) spectrum of AlSi⁻ compared to that of Al₂⁻. Five features are observed for AlSi,

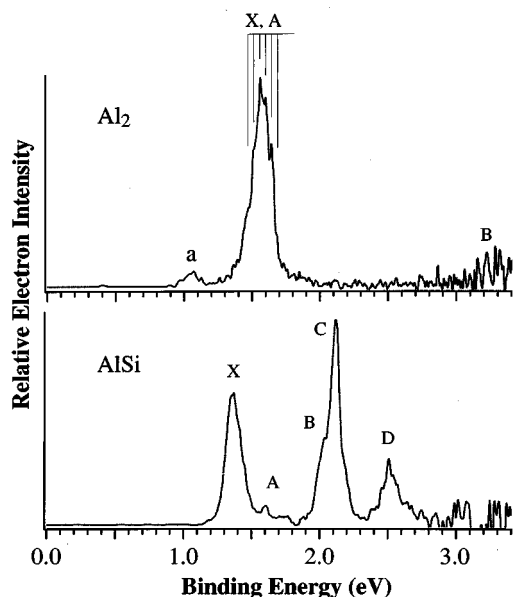


FIG. 1. Photoelectron spectra of Al_2^- and AlSi^- at 355 nm (3.49 eV).

labeled as X, A, B, C, and D. The feature A is very weak and the feature B is shown as a shoulder on the feature C. The 355 nm spectrum of Al_2^- shows a strong and partially vibrationally resolved feature near 1.6 eV, which actually contains transitions to two electronic states of Al_2 (X and A, see below). There are also two weak features in the Al_2^- spectrum, labeled as a and B, although the count rate and statistics for the feature B are poor.

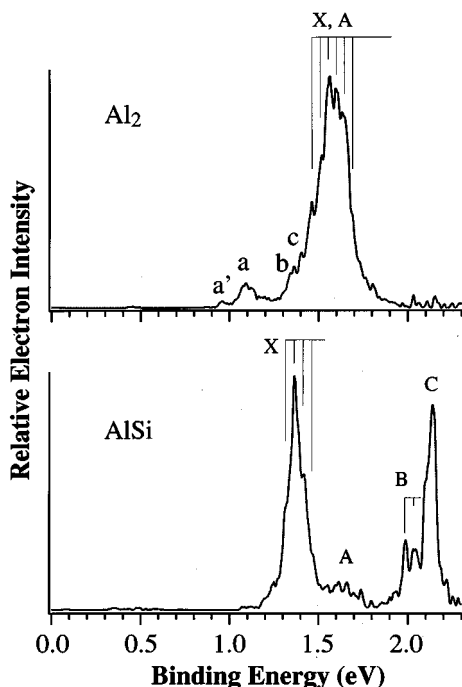


FIG. 2. Photoelectron spectra of Al_2^- and AlSi^- at 532 nm (2.33 eV).

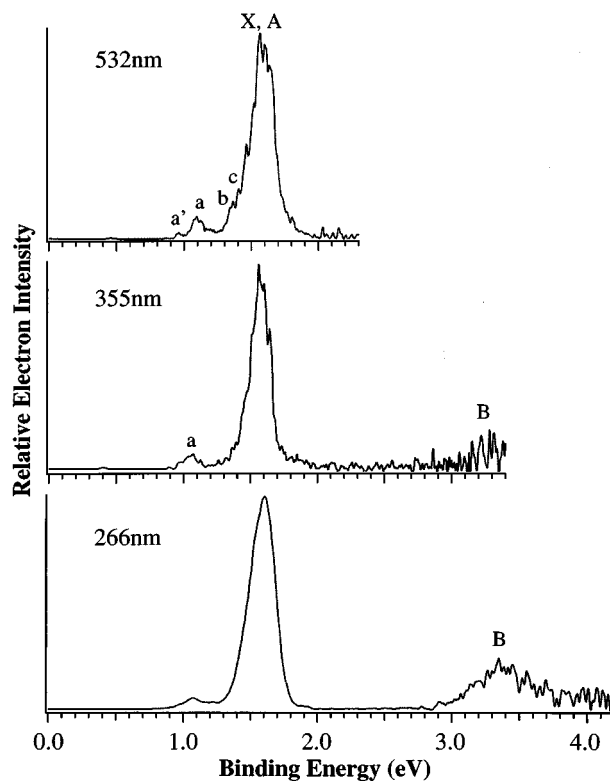


FIG. 3. Photoelectron spectra of Al_2^- at 532 nm (2.33 eV), 355 nm (3.49 eV), and 266 nm (4.66 eV).

The 532 nm (2.33 eV) spectra of Al_2^- and AlSi^- are shown in Fig. 2. The spectra are better resolved at the lower photon energy. The X, A, and B features for AlSi^- are clearly vibrationally resolved. The 532 nm spectrum of Al_2^- is only slightly better resolved, but several weak features, labeled as a', b, and c, are clearly observed. We also obtained PES spectra for Al_2^- and AlSi^- at 266 nm (4.66 eV). Figure 3 shows the 266 nm spectrum of Al_2^- , compared with the two spectra at lower photon energies. It is seen that the feature B is observed much more clearly in the 266 nm spectrum. However, we did not observe any new features for the 266 nm spectrum of AlSi^- . All the observed binding energies and spectroscopic constants for Al_2^- and Al_2 , and AlSi^- are listed in the Tables I and II, respectively. The detailed assignments and discussion will be given in the following.

IV. DISCUSSION

A. Al_2 and Al_2^-

Before discussing AlSi , we first discuss Al_2 and Al_2^- which are better understood. The spectroscopy and electronic structure of Al_2 have been extensively investigated.⁴⁻⁷ Its electronic structure can be understood from the simple molecular orbital (MO) picture depicted in Fig. 4. The Al atom has a $3s^2 3p^1$ (2P) ground state configuration. In the Al_2 dimer, the $3s$ orbitals combine to form the $1\sigma_g$ and $1\sigma_u$ MOs which are fully occupied. The $3p$ orbitals combine to form the $2\sigma_g$ and $1\pi_u$ bonding MOs and the $1\pi_g$ and $2\sigma_u$ antibonding MOs. Depending on the spacing between the

TABLE I. Observed binding energies (BE) and spectroscopic constants for Al_2^- and Al_2 , compared to literature values.

		BE (eV)		Term value (eV)		Vib. freq. (cm^{-1})	
		Current	Ref. 5	Current	Ref. 5	Current	Ref. 7
Al_2^-	$X^4\Sigma_g^-(\sigma_g^1\pi_u^2)$			0	0		
	$a^2\Pi_u(\pi_u^3)$	1.05(70)	0.93	0.41(70)	0.57		
	$a'^2\Pi_u(\sigma_g^2\pi_u^1)$	0.95(70)	0.86	0.51(70)	0.64		
Al_2	$X^3\Pi_u(\sigma_g^1\pi_u^1)$	1.46(60) ^a	1.50	0		320(50)	285.8
	$A^3\Sigma_g^-(\pi_u^2)$ ^b				<0.025		350.0
	$B^5\Sigma_u^-(\sigma_u^1\sigma_g^1\pi_u^2)$	3.1(1)		1.6(1)			

^aThe measured adiabatic electron affinity for Al_2 .

^bWithin the current resolution, the $X^3\Pi_u-A^3\Sigma_g^-$ separation is too small to be resolved.

$2\sigma_g$ and $1\pi_u$ MOs, there are three ways to fill the two electrons; $2\sigma_g^2(1\Sigma_g^+)$, $1\pi_u^2(3\Sigma_g^-)$, and $2\sigma_g^11\pi_u^1(3\Pi_u)$. Theoretical calculations predicted that the ground state of Al_2 is the $3\Pi_u$ state with a nearly degenerate $3\Sigma_g^-$ state. Although there has been no direct experimental measurement on the $3\Pi_u-3\Sigma_g^-$ splitting, Sunil and Jordan predicted this splitting to be within 200 cm^{-1} and Bauschlicher *et al.*'s best estimate is 174 cm^{-1} .^{5,6} The $1\Sigma_g^+$ state is calculated to lie at least 2000 cm^{-1} higher in energy. Sunil and Jordan also calculated the various anion states of Al_2^- . In the anion ground state, the extra electron enters the $1\pi_u$ MO to give a $4\Sigma_g^-(2\sigma_g^11\pi_u^2)$ state.⁵

The PES spectra of Al_2^- can be assigned easily using the known information about Al_2 and Al_2^- . Detachment of a $1\pi_u$ electron from Al_2^- yields the $X^3\Pi_u(2\sigma_g^11\pi_u^1)$ ground state while removal of the $2\sigma_g$ electron gives the $A^3\Sigma_g^-(1\pi_u^2)$ excited state. We assign the main features of the PES spectra of Al_2^- near 1.6 eV to these two transitions, as shown in Figs. 1 and 2. Unfortunately, these two states cannot be clearly resolved in the current experiment due to the small spacing between the two states. The partially resolved vibrational structure gives an average spacing of about 320 cm^{-1} , which is between the vibrational frequencies of the $X^3\Pi_u(285.8\text{ cm}^{-1})$ and $A^3\Sigma_g^-(350.0\text{ cm}^{-1})$ states (see Table I).⁷ At 532 nm, the spectrum of Al_2^- (Fig. 2) is only slightly better resolved than the 355 nm spectrum (Fig. 1), even though the spectral resolution was better at the low photon energy. This is consistent with the fact of two overlapping states. The 532 nm spectrum also shows an unusual Franck-Condon envelope. This suggests that probably the relative cross sections of the two states are photon-energy

dependent. The hot band transitions (features b and c) also seem to be more significant in the 532 nm spectrum.

Besides the $X^3\Pi_u$ and $A^3\Sigma_g^-$ states, detachment from the $1\pi_u$ and $2\sigma_g$ MOs of Al_2^- can also produce singlet states; $1\Pi_u(2\sigma_g^11\pi_u^1)$, $1\Delta_g(1\pi_u^2)$, and $1\Sigma_g^+(1\pi_u^2)$. These excited states of Al_2 neutral were predicted to be all within 1 eV of the ground state.⁶ However, none of these states is observed in the PES spectra within about 1.5 eV above the ground state, as shown in Fig. 3, where the spectra at three photon energies are compared. A broad band, labeled as B, is observed near about 3.1 eV (1.6 eV above the ground state). This feature was assigned to be from detachment of a $1\sigma_u$ electron ($5\Sigma_u^-,1\sigma_u^21\sigma_u^12\sigma_g^11\pi_u^2$, Fig. 4) by Cha *et al.* in a previous PES study of Al_n^- clusters, on the basis of their resolved vibrational frequency ($\sim 450\text{ cm}^{-1}$).⁹ We did not vibrationally resolve this band due to the low count rate in the 355 nm and the poor deceleration of the Al_2^- anion in the 266 nm spectrum. Since the excitation energy ($\sim 1.6\text{ eV}$) of the B feature is significantly higher than any of the calculated singlet states, its assignment to the $5\Sigma_u^-$ state seems reasonable. However, we cannot explain why none of the singlet states is observed for the Al_2 dimer since we have shown that such low spin states are easily observed in PES

TABLE II. Observed binding energies (BE) and spectroscopic constants for AlSi dimer.

	BE (eV)	Term value (eV)	Vib. freq. (cm^{-1})
$X^4\Sigma^-(\sigma^1\pi^2)$	1.32(4) ^a	0	400(50)
$A^2\Sigma^-(\sigma^1\pi^2)$	1.55(4)	0.23(4)	400(80)
$B^2\Delta(\sigma^1\pi^2)$	1.99(4)	0.67(4)	400(60)
$C^2\Pi(\sigma^2\pi^1)$	2.14(4)	0.82(4)	
$D^2\Sigma^+(\sigma^1\pi^2)$	2.45(5)	1.13(4)	400(80)

^aThe measured adiabatic electron affinity of AlSi.

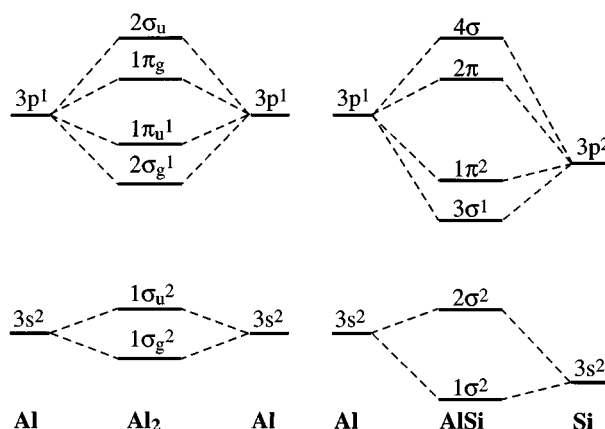


FIG. 4. Schematic molecular orbital diagrams of Al_2 and AlSi . For simplicity, the nonvalent inner orbitals ($1s, 2s, 2p$) of Al and Si are ignored.

experiments of many open shell dimer systems,¹⁷ including AlSi (see below) and Si₂.¹⁴

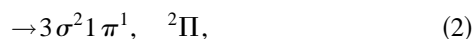
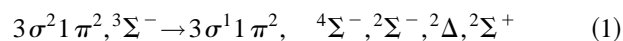
The low binding energy features (a', a, b, and c, Fig. 2) that are more prominent in the 532 nm spectrum seem to depend on source conditions and are likely due to hot bands or excited states of the Al₂⁻ anions. The a' and a features are present in all the spectra in Fig. 3 while the b and c features are more prominent in the 532 nm spectrum. We assign the b and c features to be hot band transitions. The a' and a features should be due to electronically excited states of the Al₂⁻ anion.

Sunil and Jordan have extensively calculated the anion excited states and found five such states.⁵ The Al₂⁻ ground-state configuration, 2σ_g¹1π_u², can result in four electronic states; ⁴Σ_g⁻, ²Σ_g⁻, ²Δ_g, and ²Σ_g⁺, where the ⁴Σ_g⁻ is the ground state. There are also two ²Π_u states resulting from the following configurations: 1π_u³ and 2σ_g²1π_u¹. All of these five excited states were calculated by Sunil and Jordan and were found to be bound in their configuration-interaction (CI) calculations. They also calculated the adiabatic detachment energy for the ⁴Σ_g⁻ ground state (EA of Al₂) and the two ²Π_u states using the coupled-cluster doubles+single and triple excitations (CCD+ST) methods, which gave more accurate energies. The latter results are listed in Table I and compared with the current measured values. The agreement is excellent, particularly for the EA, for which the calculated value is well within the experimental uncertainty. Therefore, it seems reasonable to assign the two observed excited states of Al₂⁻ (a and a') to the two ²Π_u states, respectively.

B. AlSi

The electronic structure of the AlSi dimer may be understood by comparing with that of Al₂⁻ to which it is isoelectronic. The AlSi⁻ is isoelectronic to Si₂, which is also well understood.¹¹⁻¹⁴ Due to the difference of the ionization potentials of Al (5.98 eV) and Si (8.15 eV),¹⁸ the Al-Si chemical bonding is expected to exhibit both ionic and covalent characters with some degree of charge transfer from Al to Si.

Figure 4 shows a schematic MO diagram of AlSi, compared to that of Al₂⁻. The 3σ and 1π orbitals are the bonding MOs between the 3p orbitals of Al and Si. AlSi has one more electron than Al₂⁻, and again there are three ways to fill the three 3p-type electrons depending on the 3σ and 1π orbital separation; 3σ¹1π², 3σ²1π¹, 3σ⁰1π³. Since Al₂⁻ has a 2σ_g¹1π_u² ground-state configuration, we think that AlSi most likely has a similar configuration, giving a ⁴Σ_g⁻(3σ¹1π²) ground state for AlSi. Analogously, it would be reasonable to assume that the AlSi⁻ anion should have a similar configuration as the isoelectronic Si₂ dimer, i.e., a ³Σ_g⁻(3σ²1π²) ground state. Based on this ground-state configuration of AlSi⁻, the following detachment channels can be expected by removing electrons from the 3σ and 1π orbitals:



where the ⁴Σ_g⁻ state represents the ground state of AlSi, and all the other states are the excited states of AlSi. The detachment from the 3s-type 2σ orbital is expected to have much higher energy and is probably not accessible at the photon energies used presently.

According to Eqs. (1) and (2) above, we expect to observe five detachment channels. These are indeed born out from our observation of the five features in the photoelectron spectrum, as shown in Fig. 1. The ground state feature (X) corresponds to the ⁴Σ_g⁻ state. The C feature is quite strong and its intensity seems to increase at the higher photon energy, as seen from Figs. 1 and 2. Since detachment cross section is expected to increase with photon energies for electrons with higher angular momenta, we assign the feature C to the ²Π state, as a result of removing a 1π electron. The A, B, and D features are relatively weak and they are likely to be due to the doublet states derived from the 3σ¹1π² configuration, as shown above.

AlSi is isoelectronic to Al₂⁻ whose electronic states have been calculated by Sunil and Jordan, as mentioned above. The ordering of the doublet states derived from the 2σ_g¹1π_u² configuration of Al₂⁻ at the CI level of calculations is ²Σ_g⁻, ²Δ_g, ²Σ_g⁺. Therefore, we assign the A, B, and D features to the ²Σ_g⁻, ²Δ, ²Σ_g⁺ states, respectively, as shown in Table II. All the three doublet states show a vibrational progression, similar to the ground state, consistent with the fact that they all derive from the same electron configuration. The ²Π(3σ²1π¹) state (feature C) shows one single peak with little vibrational excitation, suggesting that the 1π orbital is rather nonbonding in AlSi. Our assignment and the observed spectroscopic constants for all the states for AlSi are summarized in Table II. Figure 5 shows pictorially the energy levels of the AlSi dimer and the detachment transitions from the AlSi⁻. It is interesting to point out that the ²Π_u(2σ_g²1π_u¹) state in Al₂⁻ is between the ²Δ_g and ²Σ_g⁺ states in Sunil and Jordan's calculations. This is also consistent with our spectral assignment for AlSi. Nevertheless, our assignments should be considered tentative, largely based on the known information about Al₂⁻ and Si₂. Accurate *ab initio* theoretical calculations on this simple heterodimer are indeed called for in light of the current spectroscopic and electronic energy level information.

C. Comparison of the electronic structures of Al₂⁻, AlSi, and Si₂

The Al₂, AlSi, and Si₂ dimers form an interesting series of electronic systems, each with an additional electron. AlSi is expected to show properties between Al₂⁻ and Si₂, as well as different properties due to the heterobonding. All three dimers are open shell electronic systems and all possess rich low-lying electronic states. These low-lying electronic states are easily observed for the AlSi and Si₂ dimers in their anion photoelectron spectra. However, these states are not observed in the Al₂⁻ photoelectron spectra, even though such states have been calculated to exist within the energy range accessible at our photon energies. The vibrational frequency for the ground state of AlSi is 400 cm⁻¹, which is almost

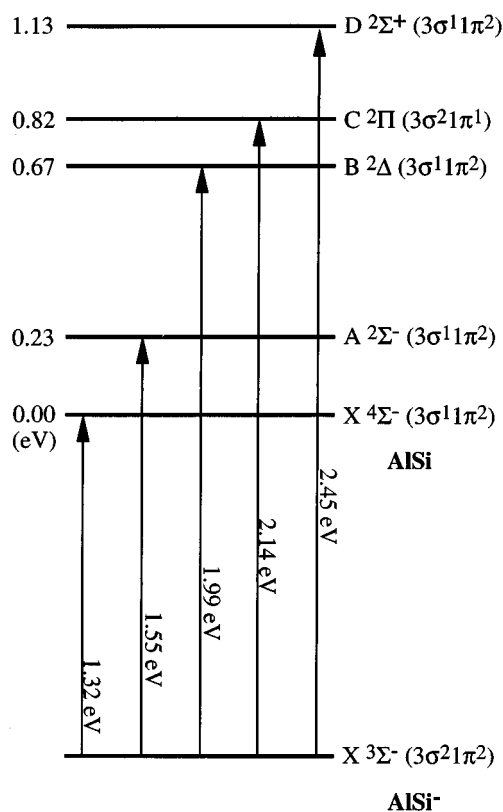


FIG. 5. Observed energy levels for AlSi and the photodetachment transitions with electron binding energies.

exactly the average of the ground-state vibrational frequencies of Al_2 (285.8 cm^{-1})⁷ and Si_2 (509 cm^{-1}).¹⁴ This suggests that the bonding energy of AlSi is probably also between that of Al_2 and Si_2 . The Si_2 has a much higher EA than Al_2 . We expected that the EA of AlSi would be between the values of Al_2 (1.46 eV) and Si_2 (2.20 eV).¹⁴ Surprisingly, our observed EA for AlSi (1.32 eV) is smaller than that of both Al_2 and Si_2 .

It is interesting to compare the energy separation between the σ_{3p} and π_{3p} orbitals among the three molecules. As shown in Fig. 6 (upper) schematically, both Al_2 and Si_2 have an excited state very close to the ground state, involving the transfer of an electron from the $\sigma_g(3p)$ to the $\pi_u(3p)$ orbitals. This suggests that the $\sigma_g(3p)$ and the $\pi_u(3p)$ orbitals are nearly degenerate in these two homonuclear molecules. The AlSi heterodimer is different from Al_2 and Si_2 in two respects. First, the electron transfer in AlSi is from the $\pi(3p)$ to $\sigma(3p)$; and second, the energy separation is much larger in AlSi (Fig. 6, upper). This implies that the π orbital is more stable in AlSi than that in Al_2 and Si_2 . Schematic MO diagrams depicting the $3p-3p$ interactions for the three molecules are compared in Fig. 6 (lower). The heteronature of bonding between Al and Si is shown clearly. The stabilization of the 1π orbital in AlSi indicates that it probably has more Si character. Similarly, the 3σ orbital is probably of more Al $3p_z$ character, naturally explaining the lower EA of the AlSi heterodimer, because the Al atom itself has a very small EA (0.441 eV, Ref. 19).

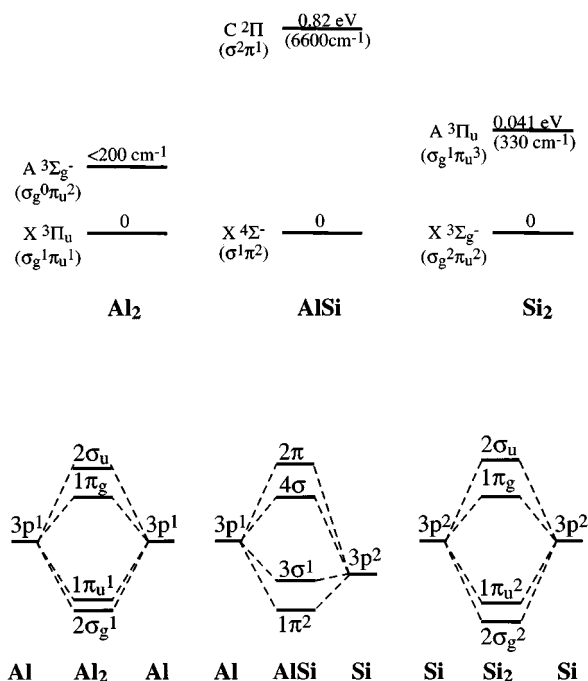


FIG. 6. Comparison of the low-lying excited states involving $\sigma-\pi$ electron transfers (upper) and the molecular orbital diagrams involving $3p-3p$ interactions for Al_2 , AlSi, and Si_2 .

The near degeneracy of the $2\sigma_g$ and $1\pi_u$ orbitals causes the existence of low-lying excited states for the Al_2^- and Si_2^- anions. Such low-lying excited states for the AlSi^- anion are not observed, consistent with the simple MO picture presented here.

V. CONCLUSIONS

We report the first study of the AlSi heterodimer using anion photoelectron spectroscopy. Four low-lying excited states are observed for AlSi. The electronic structure of AlSi is understood by comparing with that of the well-studied Al_2 and Si_2 dimers. We find that the electron affinity of AlSi, is surprisingly lower than that of both Al_2 and Si_2 although the ground-state vibrational frequency of AlSi is found to be nearly the average of that of Al_2 and Si_2 . This is explained based on the heteronature of the molecular interactions between the Al $2p$ and Si $3p$ orbitals. We also present the photoelectron spectra of Al_2^- and the definitive observation of low-lying excited states for the Al_2^- anions, which are compared to existing *ab initio* calculations. Theoretical studies on the simple AlSi heterodimer would be interesting to confirm the current assignments and interpretation.

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