



Observation of a spin-protected high-energy isomer of Al_4N^- cluster

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Abstract

Photoelectron spectroscopy experiments combined with first-principles calculations based on generalized gradient approximation to the density functional theory show that an Al_4N^- anion cluster lying 0.97 eV above its ground-state structure can exist not because it is protected by an energy barrier but because it has a different spin multiplicity. Its existence is established by comparing the calculated vertical electron detachment energies with the experimental photo-detachment spectra. The electron affinity of Al_3N , on the other hand, is anomalously low showing the characteristic of a closed-shell molecule and providing the signature of a monovalent Al. © 1999 Elsevier Science B.V. All rights reserved.

One of the unique properties of atomic clusters that distinguishes them from their crystalline state is that they can exhibit a multitude of isomeric states (i.e., the same cluster having different atomic arrangements). It is commonly believed that if these isomers are energetically nearly degenerate and are separated from each other by large energy barriers, they can be observed experimentally. In this Letter we show that a cluster isomer that lies significantly higher in energy than its ground state can exist and that too without the need of a protective energy barrier. This is possible if the spin multiplicity of the isomer is different from its ground-state spin configuration. We verify this hypothesis by calculating the total energies and equilibrium geometries of neutral

and anionic clusters of Al_4N for various spin configurations from first principles and by comparing the adiabatic and vertical detachment energies with those obtained from experimental photodetachment spectra. Similar calculations on Al_3N fail to yield any isomers. In addition, the electron affinity of Al_3N is anomalously low (0.96 eV) and is characteristic of a closed-shell molecule. This suggests that in these small clusters Al behaves like a monovalent atom.

In a typical photodetachment experiment, one starts with a mass-selected negative cluster ion and photodetaches the electron with a fixed-frequency laser beam. By analyzing the kinetic energy of the ejected electron, the binding energy of the electron in the anion is established. Since this process is rather fast, the measurement yields the difference in the energy between the ground state of the anion and that of the neutral cluster having the geometry of the anion. This is referred to as the vertical detachment

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energy (VDE). On the other hand, the difference between the ground-state energies of the anion and neutral cluster is known as the adiabatic detachment energy (ADE). Thus, the VDE is always larger than the ADE. The difference between these two energies is typically small (a few tenths of an eV) and is a measure of the energy gain due to structural relaxation. The conservation of spin angular momentum requires the spin multiplicity of the neutral cluster to differ from that of the anion by $\Delta S = \pm 1$.

The experiments discussed here were performed using a magnetic-bottle photoelectron spectroscopy apparatus with a laser vaporization cluster source. Details of this apparatus have been published elsewhere [1,2]. Briefly, we synthesized the Al_xN^- clusters by laser vaporization of a pure Al disk target with a 5% N_2/He carrier gas. The anion clusters of interest were size-selected and photoelectron spectra were taken at three photon energies, 532 (2.33 eV), 355 (3.49 eV), and 193 (6.42 eV) nm. The electron energy resolution was better than 30 meV for 1 eV electrons. We measured photodetachment spectra of Al_xN^- for $x = 2-36$. In this Letter, we focus on Al_3N^- and Al_4N^- , whose photoelectron spectra are shown in Fig. 1 at the three photon energies. Better

– resolved spectra were measured at the lower photon energies while the high photon energy probed more tightly bonded electrons.

For Al_3N^- , five distinct features were observed below 4 eV with an additional broad feature at 5 eV. The onset of the first two transitions at 0.96 and 2.72 eV represent a large energy gap and suggest that the neutral Al_3N is likely to be a closed-shell cluster. The broad nature of the 0.96 eV feature also indicates that there is a significant geometry change between the ground states of the anion and neutral. The likely ground state of Al_3N^- , which has an odd number of electrons, is a spin doublet. Thus the first two features at 0.96 and 2.72 eV presumably correspond to transitions from the doublet anion to the singlet and triplet configurations of the neutral Al_3N cluster. For Al_4N^- , two strong features at 2.32 and 3.41 eV were observed. The 2.32 eV feature is very sharp with no indication of any vibrational excitation whereas the 3.41 eV feature is broad with resolved vibrational features in the 355 nm spectrum, which yields a vibrational frequency of 330 cm^{-1} . Interestingly, there were also weak features present in the spectra. The features, occurring at 1.70 and 1.93 eV, were resolved more clearly at lower photon energies.

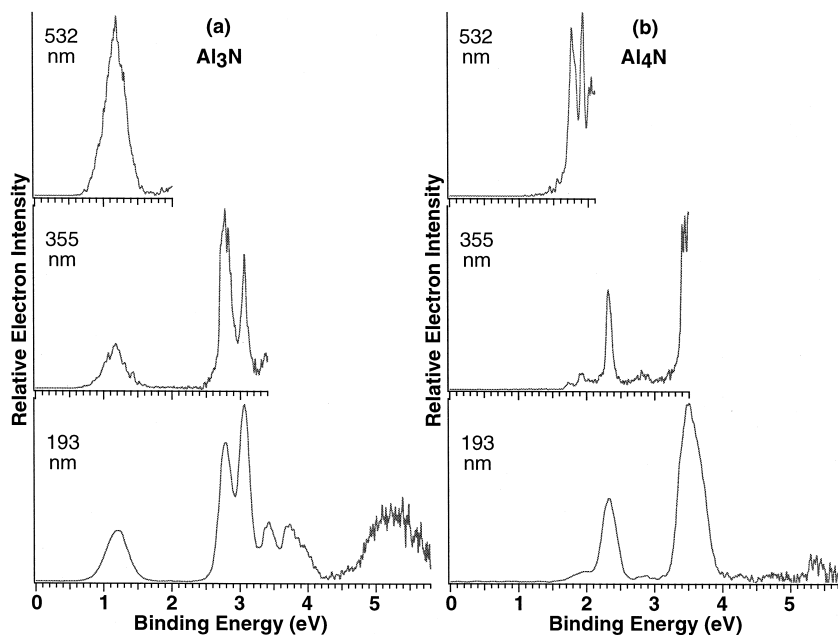


Fig. 1. Photoelectron spectra of (a) Al_3N^- and (b) Al_4N^- clusters at three photon energies.

There is also another weak feature at ~ 2.7 eV. The intensities of these features depended on the source conditions slightly, but could not be eliminated. They were most likely due to excited states or different isomers of Al_4N^- . The ground state of Al_4N^- (that has an even number of electrons) is possibly a spin singlet but could also be a triplet. If it is the former, there could only be transitions to the spin doublet configurations of neutral Al_4N , giving fairly simple photoelectron spectra. However, if the ground state of Al_4N^- is a spin triplet, one could observe two types of transitions – one to spin doublet and another to spin quartet states of the neutral. The two strong photodetachment features are likely to be due to the spin singlet ground state of Al_4N^- , on the basis of the simplicity of the spectral features. The weak features should be due to either excited states of the Al_4N^- or different isomers of Al_4N^- .

To examine these possibilities, we have undertaken a detailed investigation of the equilibrium geometries and total energies of Al_3N^- and Al_4N^- for various spin multiplicities. We then computed the total energies of their neutrals having the anion geometry for different spin configurations. Our calculations are from first principles and based on molecular orbital theory. The wave functions of the clusters were constructed by forming a linear combination of atomic orbitals centered at various atomic sites. The atomic orbitals were represented by gaussian functions. An all-electron 6-311G* basis set was used for Al and N. The total energy was calculated using the density functional theory and the generalized gradient approximation (GGA). We have used the GAUSSIAN94 software [3] and the Becke–Perdew–Wang [4,5] (BPW91) form for the GGA. The geometries were optimized for each spin multiplicity by starting from different initial configurations and relaxing the structure without *any* symmetry constraint. This optimization procedure involved calculating the forces at each atomic site and moving the atoms along the path of steepest descent until the forces vanished. The threshold for these forces were set at 10^{-5} a.u./bohr. The vibrational frequencies were analyzed to ensure that the final geometry corresponds to a stable state.

We first discuss the results on Al_3N^- . Fig. 2 shows the ground-state geometry of Al_3N^- (Fig. 2b) and that of the neutral (Fig. 2a). We note that the

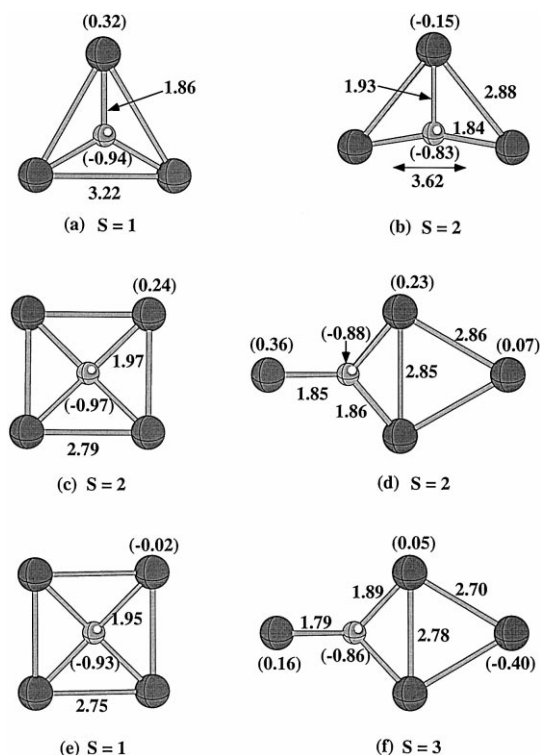


Fig. 2. Optimized ground-state geometries of neutral and anionic Al_3N and Al_4N clusters with their corresponding spin multiplicities (S). (a) Neutral Al_3N ; (b) anionic Al_3N^- ; (c) ground state of neutral Al_4N ; (d) C_{2v} isomer of Al_4N ; (e) ground state of Al_4N^- ; (f) high-spin and high-energy isomer of Al_4N^- . The smaller sphere represents N. The Mulliken charges are given in parentheses. The bond lengths are in Å.

geometries of the neutral and anion ground states, though both are planar, are rather different. In the neutral cluster which assumes a D_{3h} symmetry after optimization, the N-atom carries almost an extra electron, which is transferred from the three Al-atoms almost equally. However, the anion is distorted to a lower symmetry (C_{2v}), although the added electron is shared by the Al-atoms and the net charge on the N-atom remains essentially unchanged. This geometry change between the anion and neutral ground states is consistent with the experimental observation of a broad ground-state photodetachment feature. It was observed earlier [6] that the binding energy/atom of neutral Al_3N is larger than that of Al_2N or Al_4N , thus making Al_3N a magic cluster. This was argued to be due to the covalent character of the Al–N

bond. We could also attribute this to be due to the possibility that valence state of Al in small clusters may be different from that in the bulk. Note that the energy gap between 3s and 3p orbitals of the Al-atom is 3.6 eV [7]. Thus the hybridization of 3s² and 3p¹ that can lead to metallic bonding in trivalent Al would require large promotion energy and can only result from considerable overlap between neighboring sites. Thus in small clusters the 3s² electrons of Al would behave as core-electrons leaving the 3p¹ to be its single valence electron, as recently discussed for pure Al clusters [8]. Thus, Al₃N would have 8-valence electrons and consequently would lead to a closed electronic shell. Its electron affinity should then be low compared to other clusters, which is, indeed, the case.

We now discuss the energetics of the Al₃N⁻ cluster. As expected earlier, the preferred spin multiplicity of Al₃N⁻ is found to be 2. In Table 1, we compare the calculated ADE and VDE of Al₃N⁻ with experimental values. Excellent agreement is obtained for the ADE while the calculated VDE is slightly higher than the experimental value. We also calculated the triplet excited state of neutral Al₃N and obtained an VDE of 2.62 eV, which is in reasonable agreement with the measured VDE of the second detachment feature at 2.78 eV (Fig. 1).

The next step is the more interesting case of Al₄N. Unlike in the Al₃N case, the neutral Al₄N cluster has two nearly generate isomers. Their geometries are given in Fig. 2c,d which assume D_{4h} and C_{2v} symmetry after global optimization. Both isomers are planar. The C_{2v} isomer is built by simply attaching an Al-atom to the Al₃N cluster in Fig. 2a while in the D_{4h} isomer the N-atom is bonded to four Al-atoms symmetrically in a perfect

square. The D_{4h} isomer is in excellent agreement with previous calculations [9,10]. The binding energies/atom of the two isomers differ only by 0.04 eV with the D_{4h} isomer slightly more favored. Both the isomers have a preferred spin multiplicity of 2.

When an electron is attached to Al₄N, its ground-state spin multiplicity has a choice of being either a singlet or a triplet. An equally interesting question is whether the two neutral isomers would form stable anions with close energies. An extensive search over the entire potential energy hypersurface did *not* yield isomers of Al₄N⁻ that are energetically nearly degenerate. The ground state of Al₄N⁻ has the D_{4h} structure (Fig. 2e), nearly identical to that of the neutral. It is a closed-shell anion with a spin multiplicity of 1. Its spin triplet state lies 1.33 eV above the spin singlet configuration. The calculated ADE and VDE from this singlet D_{4h} Al₄N⁻ are in excellent agreement with the experiment, as shown in Table 1. Particularly, the sharp photodetachment feature at 2.32 eV is perfectly consistent with calculations that show the anion and neutral have nearly identical geometries. This suggests that the major isomer of Al₄N⁻, present in the cluster beam, is the D_{4h} species. The broad and intense detachment feature at 3.42 eV is then due to transition from the D_{4h} anion to a doublet excited state of the neutral.

How does one explain the weak PES features observed at 1.70, 1.93, and ~2.7 eV? Our global search yielded another structure (Fig. 2f) of Al₄N⁻ that lies 0.97 eV higher than the anion ground-state structure in Fig. 2e. This structure corresponds to the C_{2v} neutral cluster (Fig. 2d). More importantly, its spin multiplicity is 3 while that of the ground state, as noted earlier, is 1. Wave function stability analy-

Table 1
Adiabatic and vertical detachment energies of Al₃N⁻ and Al₄N⁻ clusters corresponding to different transitions

Cluster/geometry	Spin multiplicity	Adiabatic detachment energy (eV)		Vertical detachment energy (eV)		
		Theory	Experiment	Transition	Theory	Experiment
Al ₃ N ⁻ Fig. 2b (C _{2v})	2	1.00	0.96 ± 0.08	2 → 1	1.42	1.19 ± 0.04
				2 → 3	2.62	2.78 ± 0.03
Al ₄ N ⁻ Fig. 2e (D _{4h}) Fig. 2f (C _{2v})	1	2.29	2.32 ± 0.03	1 → 2	2.31	2.32 ± 0.03
	3	1.65	1.70 ± 0.03	3 → 2	1.75	1.76 ± 0.03
				3 → 4	2.61	~ 2.7

sis showed that the singlet state of this C_{2v} isomer was unstable. Let's see if this triplet isomer can explain the weak additional PES features. To do this, we calculated both the ADE and VDE of this isomer, which are compared with the experimental values in Table 1. They are again seen to be in excellent agreement with experiment. The geometries of the neutral and anions are also very similar, consistent with the sharp spectral feature at 1.70 eV. We also calculated a quartet state of the C_{2v} isomer, and obtained a VDE of 2.61 eV, which is in good agreement with the weak feature at ~ 2.7 eV. We think that the 1.93 eV feature is due to a low-lying doublet excited state of the C_{2v} isomer, but its energy is too close to the ground state for us to calculate it reliably. Thus it is clear that the existence of a high-energy isomer whose stability is guaranteed by virtue of its intrinsic spin multiplicity accounts for the weak photodetachment features in Fig. 1b.

Therefore, we found an interesting situation: while the two neutral isomers of Al_4N are nearly degenerate with the same spin multiplicity, their anions are quite different both in terms of their energetics and spin multiplicity. The question is why the triplet anion was populated at all in the experiment since it is 1 eV less stable than the D_{4h} ground-state anion. The answer lies at the different spin multiplicity. Once the triplet isomer is formed, it is protected by its high spin multiplicity and cannot be transformed to the ground state, regardless of an energy barrier. This is analogous to excited states of anions that we have observed in several transition metal-containing diatomics [11–13]. In all those cases where we observed excited states in the diatomics it is because they have different spin multiplicities from the anion ground state and thus are metastable. The observation of the spin-protected isomers in large clusters is quite interesting and they are also related to the high spin Na clusters trapped in He clusters, as observed recently [14,15].

In summary, we have provided the first evidence that an anion isomer lying significantly higher in energy (~ 1 eV) than the ground state can exist if their preferred spin multiplicities are different. It is, however, necessary that the isomers of neutral clusters that give birth to their anions be energetically nearly degenerate. This explanation of the experi-

mental photodetachment spectra of Al_4N^- in terms of isomers is somewhat different from that given earlier in the explanation [16] of the anomalous photoelectron spectrum [17] of Li_4^- . There, Li_4^- has two *nearly degenerate* isomers with *different* spin multiplicities. In the present case, the neutral cluster has *nearly degenerate* isomers with the *same* spin multiplicity, but are separated by a significant energy barrier. This finding makes the traditional interpretation of the photodetachment spectra of anion clusters in terms of excited states and vibrational progression more complicated, but certainly interesting. In a similar vein, the richness of photoelectron spectroscopy lies not only in the fact that it can probe the electronic structure of clusters, but also the existence of their isomers. We demonstrate that the synergy between experiment and theory allows us to untangle this richness of spectroscopy and obtain definitive insight into the novel physics of clusters.

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