Table XV. Importance of Crystal Lattice Forces in Biphenyl Crystal

A. Energy of Conformations in the Isolated System

model	description	rel internal energy
1	X-ray (dihedral 0.0°)	1.98
2	hypo (dihedral 20.0°)	0.71
3	gas (dihedral 40.2°)	0.00

B. Energy of Conformations in the Crystal Lattice

model	internal energy[a]	lattice energy[b]	total energy[c]	heat of sublimation[d]
1	1.98	−20.28	−18.26	18.26
2	0.71	−17.65	−16.94	16.94
3	0.00	−15.64	−15.64	15.64

C. Comparison of Crystal Unit Cell Parameters of Conformations

parameters	model 1	model 2	model 3	exptl[28]
a	7.79	8.21	8.51	7.82 ± 0.02
b	5.60	5.78	6.03	5.58 ± 0.01
c	9.34	9.29	9.36	9.44 ± 0.02
α	89.3	87.8	84.1	90.0 ± 0.0
β	93.1	98.0	102.4	94.62 ± 0.10
γ	88.9	88.7	88.2	90.0 ± 0.0
vol	406.7	436.1	466.4	410.6
E_{sub}	18.26	16.94	15.64	19.5 ± 0.5[40]

[a] The internal energy is the difference in steric energy between the indicated conformation and the most stable conformation (model 3). [b] The lattice energy is the energy required to pull central molecule from the crystal lattice to an infinite distance. [c] The total energy of the crystal is taken to be the sum of internal energy and lattice energy. [d] The heat of sublimation (E_{sub}) is the difference between the internal energy of most stable isolated conformation (model 3) and the total energy of the appropriate crystal lattice.

angle of 40°, similar to that which was found with MM2. But it also has been long known that the biphenyl molecule is planar in the crystal.[28] The explanation ordinarily given is that crystal packing forces favor the planar over the nonplanar structure and hence force the molecule into a planar conformation. To understand this fact, we separately packed two rigid molecules, the planar one, and the one which has the benzene rings rotated 40°, into crystal lattices made up of 27 unit cells and 54 molecules. We then optimized the lattice parameters, keeping the molecules rigid in each case. The internal molecular energy of an isolated biphenyl molecule increases about 1.98 kcal/mol in going from the twisted conformation to the planar one, but there was a stabilization of the planar crystal relative to the nonplanar one from the lattice forces by 4.64 kcal/mol, which easily outweighed the energy required to flatten the molecule. This information is summarized in Table XV.

Conclusions

van der Waals' parameters were derived to describe carbon and hydrogen in the MM3 force field that are significantly improved over those used in MM2. These new parameters adequately describe the crystals of the normal alkanes, both with respect to their structure and their heats of sublimation; they also describe a few simple aromatics, including graphite, benzene, and hexamethylbenzene. The long-standing problem of the conformation of biphenyl is resolved, with the demonstration that the lattice forces are sufficient to planarize the otherwise twisted molecule.

The van der Waals' function for hydrogen bound to carbon arrived at is in fairly good agreement with that postulated earlier by Bartell,[49] based on theoretical studies by Kochanski.[50] Since this work was completed, Wiberg has also published[51] van der Waals' functions for hydrogen–hydrogen interactions, based on ab initio calculations, and they are also quite similar to the MM3 function. The MM3 functions also work very well for intramolecular interactions (see papers 1[7] and 2[8]) at distances much shorter than the intermolecular distances found in crystals.

Acknowledgment. The authors are grateful to the National Institutes of Health, Grant R24 RR02165, for partial support of this work.

Registry No. *n*-Hexane, 110-54-3; *n*-octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-heptane, 142-82-5; *n*-nonane, 111-84-2; benzene, 71-43-2; biphenyl, 92-52-4; hexamethylbenzene, 87-85-4.

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Structural Investigations of Aluminum Cluster Ions, Al_n^- (n = 3–50)

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Abstract: Laser ablation of a flat aluminum metal target (without using the bath gas/supersonic expansion technique) was used to generate aluminum cluster anions containing from 3 to 50 atoms. The structures and reactivities of Al_n^- for n = 3–23 were then probed with the use of Fourier transform mass spectrometry. Charge exchange reactions were used to bracket the electron affinities of these clusters, which were in good agreement with other theoretical and experimental values. Collisional dissociation of Al_n^- for n = 3–13 indicated elimination of neutral aluminum atoms for all cluster ions, except Al_7^-, Al_6^-, and Al_3^-, which fragmented primarily by electron detachment. Aluminum cluster ions are unreactive with CH_4 and N_2O, but the small cluster ions will react with O_2 to generate AlO_2^- and AlO^-. For clusters containing more than eight aluminum atoms, the even-numbered clusters react much more rapidly than the odd-numbered clusters with oxygen to form AlO_2^- and AlO^-.

The investigation of neutral and ionic metal clusters is of considerable interest since these compounds may serve as models for studying the nature of catalysis and related processes.[1] The generation and reactions of positively charged clusters, such as

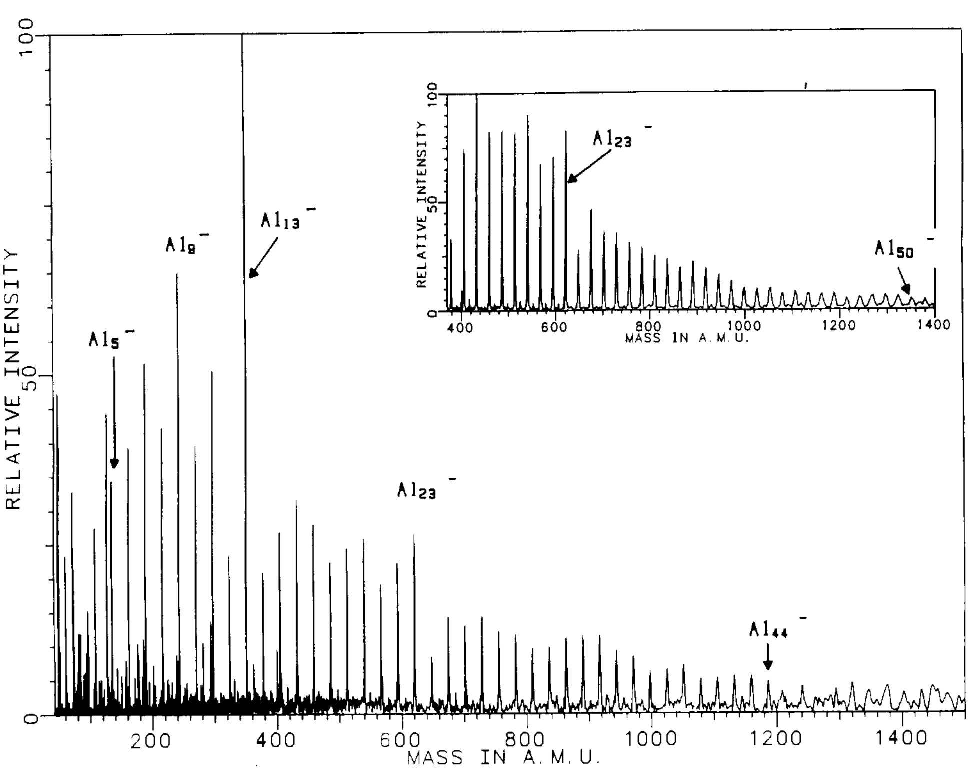

Figure 1. The negative ion spectrum obtained by laser ablation of an aluminum disk (no argon present). Aluminum clusters anions containing from 3 to 50 atoms (see insert) are observed.

aluminum, have been described.[2-5] Fewer reports of negatively charged clusters exist, although the generation and photodetachment spectroscopy of aluminum cluster anions have recently been reported.[6,7] Aluminum cluster anions containing from 3 to 50 atoms have recently been generated in our laboratory by laser ablation (without using the bath gas/supersonic expansion technique) and studied with Fourier transform mass spectrometry (FTMS). The ease of aluminum cluster anion formation combined with the capabilities of FTMS for accurate mass measurements and ion trapping provide a powerful method for examining the structures and reactivities of these ions. This report examines the structures and reactivities of aluminum cluster anions (specifically Al_n^- for $n = 3$–23). Charge exchange reactions were used to bracket electron affinities. Collision-induced dissociation provided information about fragmentation pathways for these ions. The reactivity of these cluster ions was probed using ion–molecule reactions, specifically reactions with O_2. Comparison of the properties of these aluminum cluster anions with those of neutral and positively charged aluminum clusters should provide insight into how electronic configuration influences reactivity and geometry.

Experimental Section

The 1064-nm line of a Quanta Ray Nd:YAG pulsed laser was focused (10^7 W/cm^2) onto a flat aluminum target to generate the cluster ions,[8] which were detected approximately 10 ms later with a Nicolet FTMS-2000 Fourier transform mass spectrometer (FTMS). The presence (up to 5×10^{-6} Torr) or absence of a static pressure of argon did not affect cluster ion formation or reactions. The relative intensities of the ions were unaffected by trapping times of up to 4 s with or without argon present, implying that the cluster ions did not have sufficient internal energy to induce further fragmentation and change the relative ion intensities. This result suggests that the cluster ions have cooled prior to detection, although the presence of some internally excited cluster ions cannot be absolutely ruled out.

Ion–molecule reactions (including charge exchange) were examined by trapping selected ions of interest in the presence of approximately 1×10^{-6} Torr of the reagent gas. Charge exchange reactions were determined by monitoring both the disappearance of specific aluminum clusters anions as well as the appearance of the reagent anions as a function of time.

Collision-induced dissociation (CID) was accomplished by isolating an ion of interest and then accelerating that ion into argon as a collision gas. Translational CID energies on the order of 50–200 eV were used for these experiments.

Results and Discussion

I. Generation of Al_n^-. Laser ablation of an aluminum disk generated an abundance of negatively charged aluminum cluster ions, ranging continuously from Al_3^- (m/z 81) to Al_{50}^- (m/z 1349), shown in Figure 1. A small amount of Al_2^- (m/z 54) was also observed. High resolution and accurate mass measurements revealed that these cluster ions do not contain hydrogen or other ligands but are present as the bare clusters. These clusters ions were trapped for times up to 4 s with or without argon present (5×10^{-6} Torr) and indicated no change in the relative intensities of the cluster ions. The lack of additional fragmentation of the cluster ions observed with either increased trapping times or increased argon pressure implies that these ions had relatively low internal energies. The major aluminum cluster ion observed in Figure 1 is Al_{13}^-, implying that this structure is quite stable. For comparison, aluminum metal has a face-centered cubic packing (D_{3d} symmetry), in which each atom in the bulk is surrounded by 12 nearest neighbors.[9] Inspection of Figure 1 reveals differences in cluster ion intensities; for example, Al_n^- for $n = 7, 9,$

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(1) Many research groups have been active in the examination of metal clusters. For recent reviews concerning the status of some of the current research, see: (a) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049. (b) Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589. (c) Phillips, J. C. *Chem. Rev.* **1986**, *86*, 619.

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(8) The aluminum target was placed on the tip of a solids probe, which was located approximately 3 mm from the source cell of the FTMS (i.e., the aluminum cluster anions were not externally injected into the cell).

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Table I. Electron Affinity Measurements

cluster	electron affinity, eV CE[a]	PD[b]	calcd[c]
Al_2	N.D.[d]	N.D.	0.09
Al_3	<1.89	1.4, 1.53	1.43
Al_4	1.89 < x < 2.30	2.0, 1.74	1.50
Al_5	1.89 < x < 2.30	2.1, 1.82	1.91
Al_6	1.89 < x < 2.30	2.3, 2.09	2.16
Al_7	1.89 < x < 2.30	2.2, 1.96	
Al_8	1.89 < x < 2.30	2.2, 2.22	
Al_9	1.89 < x < 2.30	2.5, 2.47	
Al_{10}	1.89 < x < 2.30	2.4, 2.47	
Al_{11}	1.89 < x < 2.30	2.5, 2.53	
Al_{12}	1.89 < x < 2.30	2.6, 2.53	
Al_{13}	1.89 < x < 2.30	2.6, 2.86	
Al_{23}	1.89 < x < 2.30	2.86	

[a] Charge exchange results obtained from this study. [b] These vertical electron affinities were measured using photodetachment thresholds from ref 6 and 7, respectively. [c] Calculated values from ref 12. [d] Not determined.

11, and 13 are more intense than the even-numbered clusters in the same region ($n = 6$, 8, 10, and 12), implying an increased stability (or reduced reactivity) for these odd-numbered clusters. An abrupt decrease in cluster ion intensity is observed for ions above Al_{13}^-. Clusters in the range of $n = 14$–44 decrease almost uniformly, although certain ions such as Al_{24}^- appear to be particularly unstable and are observed in low intensity. For comparison, generation of aluminum cluster anions by laser vaporization–supersonic expansion did not reveal these abrupt changes in ion intensities,[6] which may be due to the fact that the supersonic experiment generates "cold" cluster ions or that this time-of flight experiment was short enough (hundreds of microseconds) that dissociation was not observed.

In general, the most abundant aluminum cluster anions (Al_9^- and Al_{13}^-) are not the same as the most abundant aluminum cluster cations, which were observed to be Al_7^+ and Al_{14}^+ [10,11] However, Al_{23}^+ and Al_{23}^- are major peaks in both the positive[2a] and negative ion spectra. Theoretical examinations of aluminum clusters predict stable structures based on valence electron shell closings for Al_n where $n = 6$, 13, 19, and 23.[12,13] Smalley and co-workers have reported the excellent agreement between the experimental vertical electron affinities for aluminum clusters (determined by photodetachment measurements) and the theoretical electron affinities predicted by the ellipsoidally distorted shell model.[7] The electronic effect on structural stability can be quite pronounced, as is evident from the fact that Al_{14}^+ is a predominant ion in the positive ion spectrum whereas Al_{14}^- is very small in the negative ion spectrum.

II. **Electron Affinities.** The electron affinities (EA) of Al_n for $n = 3$–13, 23, were bracketed using charge exchange reactions. Specifically, each aluminum cluster anion was isolated and allowed to react with either nitrogen dioxide (EA = 2.30 ± 0.10 eV[14]) or *p*-benzoquinone (EA = 1.89 ± 0.10 eV[14]). The results of these reactions are summarized in Table I. All clusters for $n = 3$–13, 23 indicated charge exchange with nitrogen dioxide, suggesting that these clusters have electron affinities below 2.30 eV. Al_2^- could not even be observed in the presence of either nitrogen dioxide or *p*-benzoquinone, which might be expected based on its estimated low electron binding energy of 0.1 eV.[12] Al_3^- was found to charge exchange with *p*-benzoquinone, suggesting $EA(Al_3) <$ 1.89 eV, in good agreement with a upper limits of 1.4[6] and 1.53[7] eV reported for the electron affinity of Al_3. All clusters in the range of $n = 4$–13, 23 did not charge exchange with *p*-benzoquinone, suggesting 1.89 eV < $EA(Al_n$ for $n = 4$–13, 23) < 2.30 eV. A comparison of these bracketed electron affinities with other experimental (photodetachment experiments) and theoretical values is given in Table I. The good agreement between the bracketing and photodetachment methods further supports the assumption that the internal energies of the aluminum cluster ions created in this FTMS experiment were relatively low.

Table II. Collision-Induced Dissociation of Al_n^-

parent ion	fragment ions obsd
Al_{13}^-	Al_{12}^-, Al_{11}^-, Al_{10}^-, Al_9^-, Al_8^-, Al_7^-
Al_{12}^-	Al_{11}^-, Al_{10}^-, Al_9^-, Al_8^-, Al_7^-
Al_{11}^-	Al_{10}^-, Al_9^-, Al_8^-, Al_7^-
Al_{10}^-	Al_9^-, Al_8^-, Al_7^-
Al_9^-	Al_8^-, Al_7^-
Al_8^-	Al_7^-
Al_7^-	electron detachment obsd (slight amount of Al_6^-)
Al_6^-	electron detachment obsd (slight amount of Al_5^-)
Al_5^-	Al_4^-
Al_4^-	Al_3^-
Al_3^-	electron detachment obsd (no ionic products)

From the results given above, a bracketed electron affinity of 2.1 ± 0.3 eV is obtained for Al_{13}. Photoelectron spectroscopy of Al_{13}^- has established 2.6[6] and 2.8 eV[7] as upper limits for the adiabatic electron affinity of Al_{13}. Al_{13}^- has been predicted to be a closed-shell cluster with a relatively high electron binding energy.[6] Two possible geometries have been predicted for Al_{13}: a hexagonally close-packed (hcp) structure (D_{3h} symmetry with an electron affinity of 2.09 eV) and a face-centered cubic (fcc) structure (D_{3d} symmetry and an electron affinity of 1.87 eV).[15] The lowest energy structure for Al_{13} was predicted to be the hexagonally close-packed (D_{3h}). The experimental electron affinity of 2.1 ± 0.3 eV for Al_{13} determined above supports the D_{3h} structure (EA = 2.09 eV) more closely than the D_{3d} structure, although the large uncertainty in experimentally determined value (and presumably in the calculated values as well) makes the exact assignment difficult.

III. **Collisional Dissociation.** The collisional dissociation of Al_n^- cluster ions for $n = 3$–13 was investigated in order to probe the structures and fragmentation of each of these species. A summary of these results is given in Table II. The fragmentation of these cluster ions is usually characterized by loss of one or more aluminum atoms. For comparison, small aluminum cluster cations fragment to generate predominately Al^+, whereas larger aluminum cluster cations indicate Al_{n-1}^+ as the primary fragment product.[3b,11] Isolation and collisional dissociation of Al_{13}^- at 130-eV translational energy indicated several fragment ions, shown in Figure 2. The most abundant daughter ions observed at this energy were Al_9^- and Al_7^-. No fragment ions below Al_7^- were observed in the collisional dissociation spectrum of Al_{13}^- at any energy. In general, cluster ions for $n > 7$ fragment to generate a greater abundance of the odd-numbered cluster ions than even-numbered cluster ions. Interestingly, Al_7^- is the smallest daughter ion observed in the fragmentation of any of clusters containing eight or more atoms (see Table II). Collisional dissociation spectra of Al_7^- and Al_6^- indicate formation of a slight amount of Al_{n-1}^-; however, electron detachment appears to compete quite readily with aluminum atom elimination for these two ions. Al_5^- and Al_4^- each fragment by loss of one aluminum atom, whereas Al_3^- does not yield any daughter ions upon collisional activation.

The fragmentation of these cluster ions upon collisional dissociation is competition between electron detachment and aluminum atom elimination, as shown in eq 1 and 2. For clusters

$$Al_n^- \longrightarrow Al_n + e^- \quad \text{electron affinity (EA)} \qquad (1)$$

$$Al_n^- \longrightarrow Al_{n-1}^- + Al \quad \text{bond energy, } D^\circ(Al_{n-1}^- \text{–} Al) \qquad (2)$$

of $n = 4$, 5, 8–13, elimination of an aluminum atom dominates over electron detachment, which may imply that the bond energies

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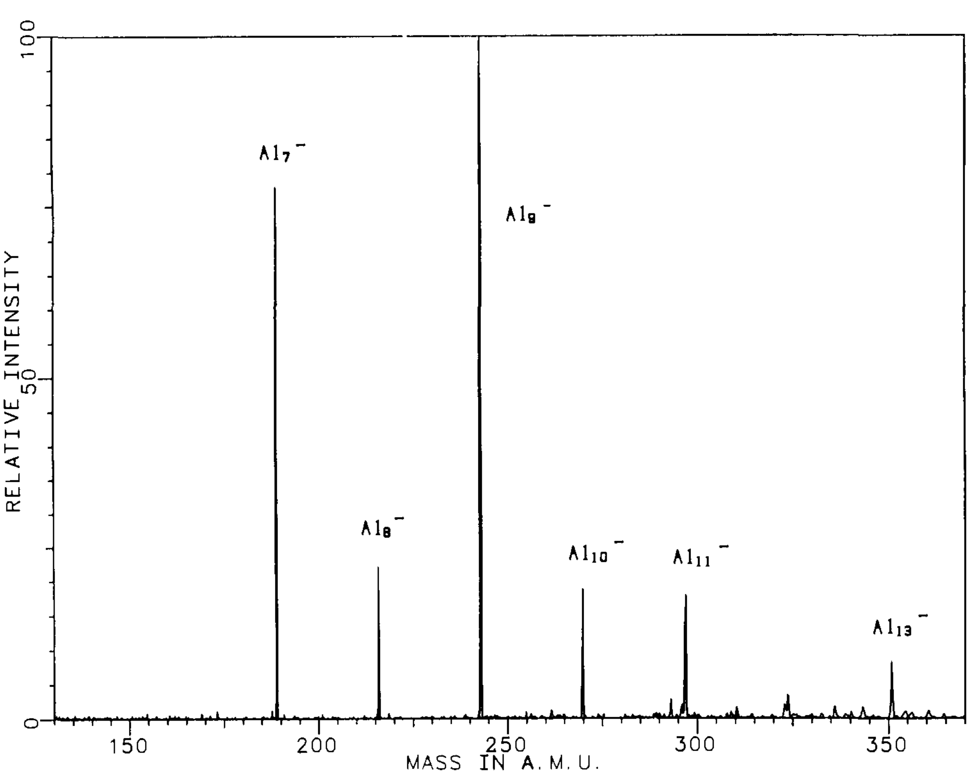


Figure 2. The collision-induced dissociation spectrum of Al_{13}^- at 130-eV translational energy with argon as the collision gas.

for these clusters ($D°(Al_{n-1}^- - Al)$) are lower than the respective electron affinities, which were determined to be between 1.89 and 2.30 eV. This comparison of bond energies to electron affinities based on collisional dissociation must be made with caution, since other factors may influence the fragmentation process. For Al_6^- and Al_7^-, electron detachment is the main fragmentation observed, implying that these two clusters may be bound more strongly (higher bond energies) than the other cluster ions.

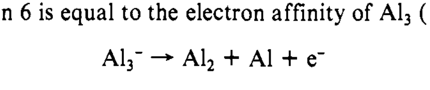
The low electron affinity of Al_3 allows electron detachment to dominate over aluminum atom elimination in the collisional dissociation of Al_3^-. Equation 3 can be used to calculate the bond

$$D°(Al_2^- - Al) = D°(Al_2 - Al) + EA(Al_3) - EA(Al_2) \quad (3)$$

energy for the Al_3^- cluster. Given that $D°(Al_2-Al) = 1.37 \pm 0.60$ eV,[16] $EA(Al_3) = 1.43$ eV,[12] and $EA(Al_2) = 0.09$ eV,[12] a bond energy $D°(Al_2^- - Al) = 2.7$ eV is calculated. Clearly, this value is larger than the electron binding energy of Al_3^- (1.5 eV), verifying that electron detachment is a lower energy process than aluminum atom elimination for this ion.

For aluminum clusters where $n > 4$, the electron affinities of Al_n are approximately equal to the electron affinities of Al_{n-1} (see Table I). This implies that the bond energies of the neutral aluminum clusters are roughly equal to the bond energies for the aluminum cluster anions (i.e., $D°(Al_n^- - Al) = D°(Al_n - Al)$). Upton has calculated bond energies for Al_2–Al_6 ranging from 0.77 to 1.22 eV.[12] The calculated bond energies reported for Al_4 (1.12 eV) and Al_5 (1.06 eV) should be roughly equal to the bond energies for Al_4^- and Al_5^-, respectively. Clearly, these values are significantly below the electron binding energies of the anions (see Table I), implying that aluminum atom elimination should dominate over electron detachment for the two ions. The CID results indicate that the bond energy for Al_6^- (and presumably Al_6 as well) may be larger than the electron affinity of Al_6.

IV. Reactions with Oxygen. Apart from charge exchange reactions, these aluminum cluster ions are unreactive with most small molecules, including N_2O and CH_4. For comparison, neutral aluminum clusters are also unreactive with methane.[17] However, some of these cluster anions react quite specifically with O_2. For example, Al_n^- for n = 3–8 will react with O_2 to generate both AlO_2^- and AlO^-. The reaction of Al_3^- with O_2 is shown in Figure 3 and summarized below. Continuous ejection of AlO^- indicated



$$Al_3^- + O_2 \rightarrow AlO_2^- + (Al_2) \quad (4)$$

$$Al_3^- + O_2 \rightarrow AlO^- + (Al_2O) \quad (5)$$

that AlO_2^- was a product of reaction 4 rather than resulting from subsequent reaction of AlO^- with O_2.

In order to examine the energetics of reactions 4 and 5, it is necessary to calculate heats of formation for Al_2 and Al_3^-. A heat of formation for $Al_2 = 125 \pm 5$ kcal/mol can be calculated from the bond energy of Al_2 ($D°(Al-Al) = 1.35 \pm 0.20$ eV)[18] and the heat of formation of Al (78 kcal/mol).[14] The reaction enthalpy for reaction 6 is equal to the electron affinity of Al_3 (1.43 eV)[12]

$$Al_3^- \rightarrow Al_2 + Al + e^- \quad (6)$$

plus the bond energy of Al_3 (1.37 eV),[16] and is calculated to be 2.8 eV. Using the heat of formation of Al_2 determined above (125 kcal/mol) along with the heat of formation of Al yields a calculated heat of formation for Al_3^-, $\Delta H_f°(Al_3^-) = 138$ kcal/mol from reaction 6.

The heats of formation for Al_2 and Al_3^- along with $\Delta H_f°(AlO_2^-) = -139.3$ kcal/mol[19] imply that reaction 4 is exothermic by 152 kcal/mol (6.6 eV), assuming that Al_2 is the neutral product. Examination of the energetics for reaction 5 lends insight into the neutral product which is lost. Using the heat of formation of Al_3^- (138 kcal/mol) and $\Delta H_f°(AlO^-) = -64.6$ kcal/mol[19] reveals that reaction 5 would be exothermic by 19 kcal/mol if $Al_2 + O$ are the neutral products. However, the most likely neutral product of reaction 5 would be Al_2O, a stable molecule with a heat of formation of 1.35 eV.[20] Assuming Al_2O as the neutral product,

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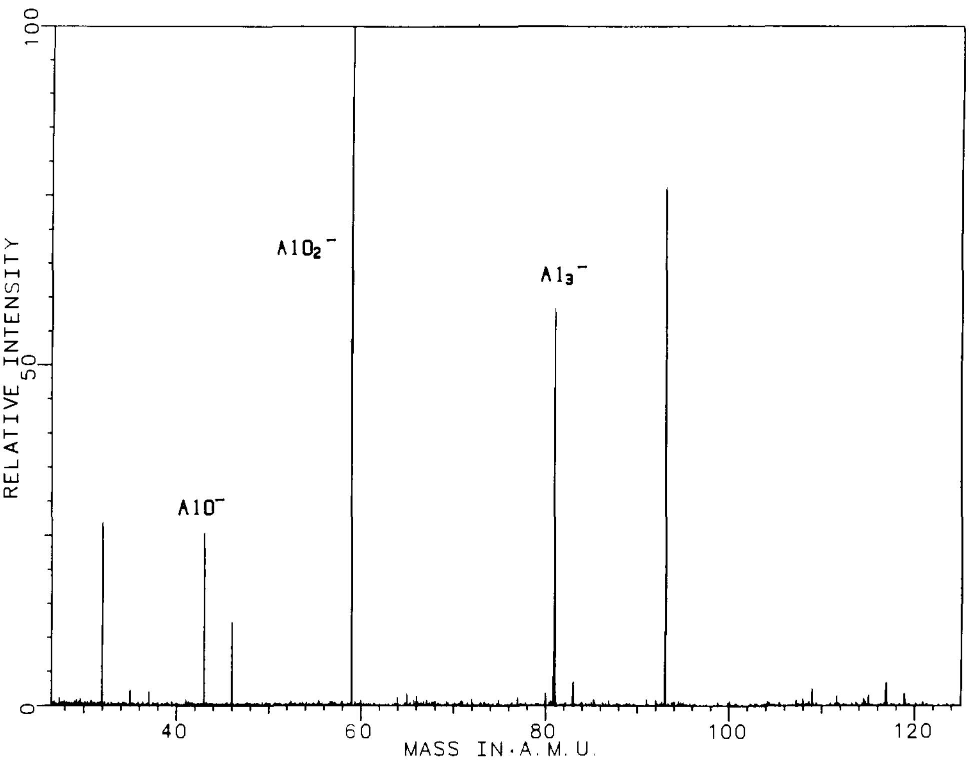

Figure 3. Reaction of Al_3^- with O_2. Ions at m/z 93, 46, and 32 are present in the background and do not originate from Al_3^-.

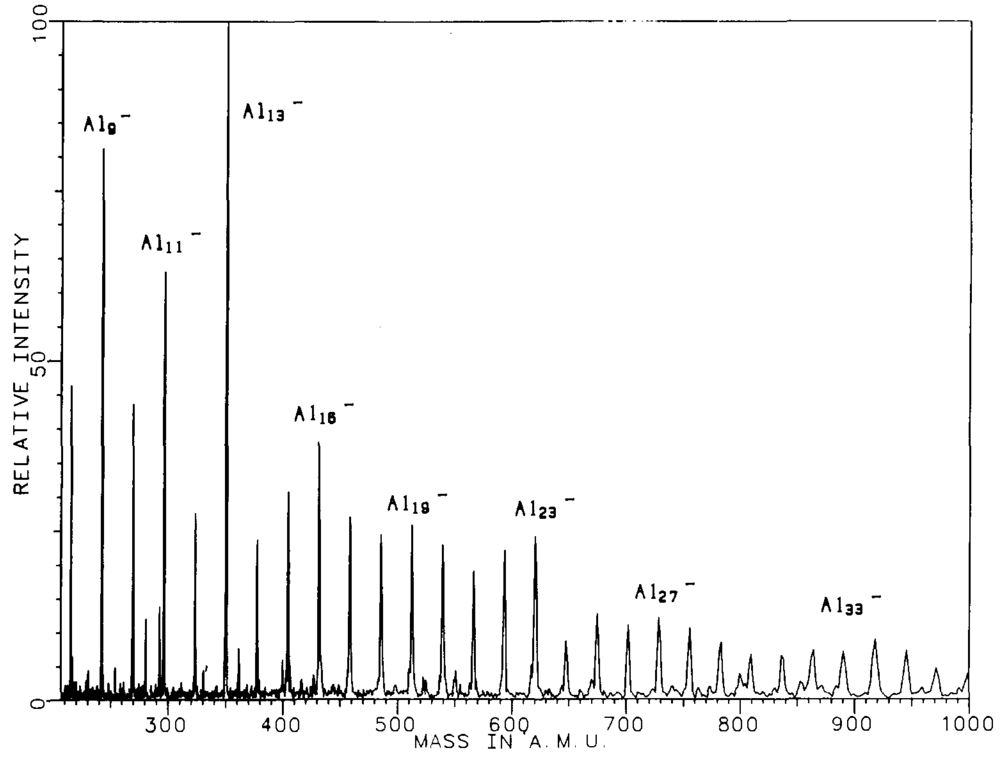

Figure 4. Generation of Al_n^- by laser ablation.

reaction 5 is calculated to be exothermic by 172 kcal/mol (7.5 eV).

Large aluminum clusters (n = 8–32) also exhibit interesting oxygen reactions. Figure 4 shows the negative ion spectrum obtained by laser ionization of the aluminum target. Al_n^- clusters for n = 8–30 are observed, with the odd-numbered clusters more abundant than the even-numbered clusters, as observed in Figure 1. Trapping these cluster ions in a static pressure of argon at 4 × 10^{-6} Torr does not dramatically change the relative distributions of the cluster ions, as shown in Figure 5. Figure 6 shows the negative ion spectrum under the same conditions as in Figure 4, except these ions have now been trapped in the presence of oxygen (O_2 at 1 × 10^{-6} Torr). The odd-numbered clusters for n = 9–29 are unchanged (their intensities are the same as in Figure 4), but the intensities of the even-numbered clusters for n = 8–32 have been greatly reduced. These even-numbered clusters react more rapidly than the odd-numbered clusters with O_2 to generate AlO_2^- and AlO^- as the ionic products and presumably Al_{n-1} and $Al_{n-1}O$ as the neutral products. The observation of this size-dependent

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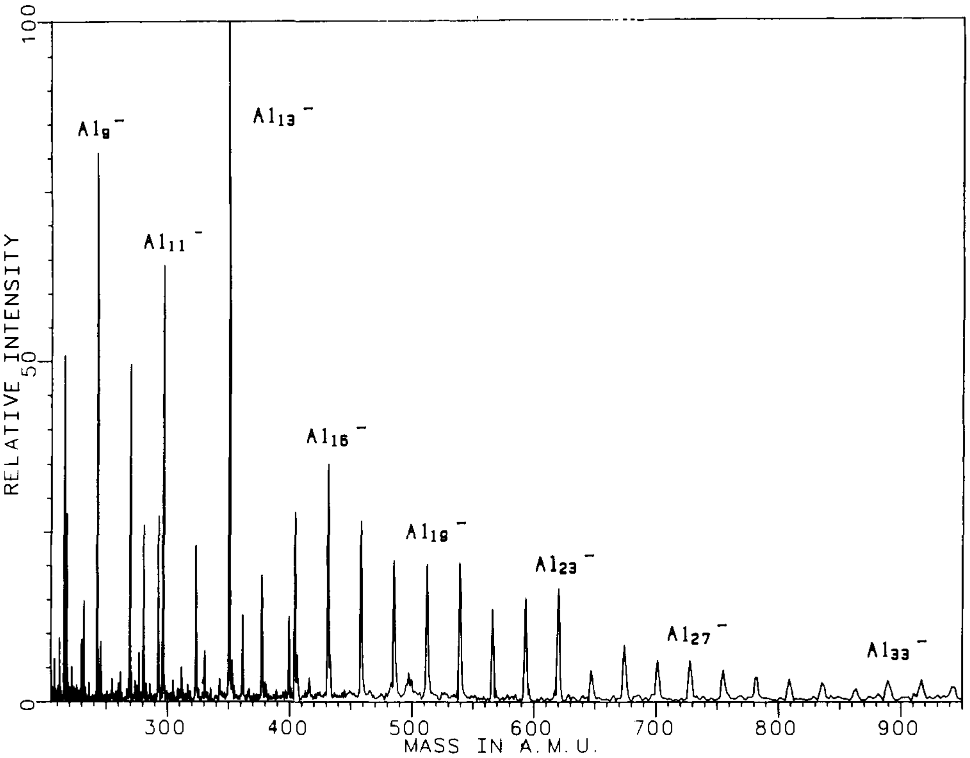

Figure 5. Trapping Al_n^- in argon for 2 s.

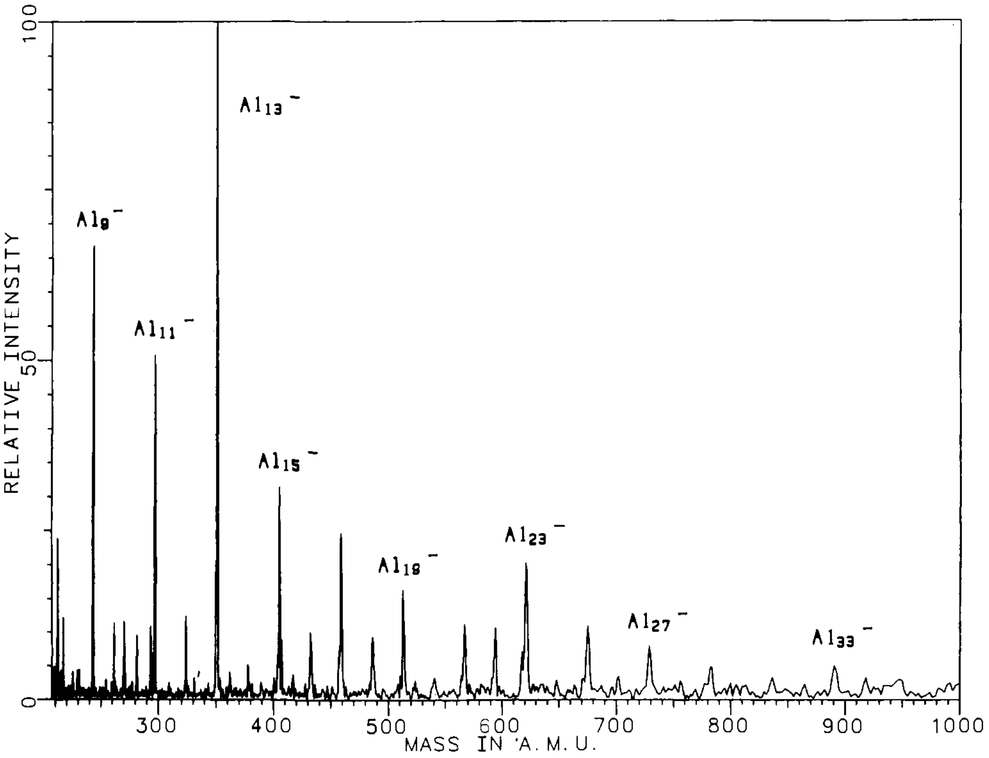

Figure 6. Trapping Al_n^- in O_2 for 4 s.

reactivity may be related to the stability of the neutral products, implying that the odd-numbered neutral aluminum clusters are more stable than the even-numbered neutral aluminum clusters. For comparison, aluminum cluster cations also react with O_2 resulting in cluster fragmentation and formation of Al_2O^+ and Al_{n-1}^+,[2a,3a] whereas small neutral aluminum clusters react with O_2 to generate products such as Al_5O_3, Al_7O_4, and Al_9O_7.[21] The reactivity of oxygen with both neutral aluminum clusters and aluminum cluster cations is sharply dependent on the size of the aluminum cluster.

Conclusions

Laser ablation is very useful for the generation of large negatively charged aluminum clusters (containing from 3 to 50 atoms in each ion). These clusters do not require a bath gas such as argon or helium for formation. Selective ion trapping and manipulation with FTMS can be used to obtain structural information for the cluster ions. The odd-numbered cluster ions were more intense than the even-numbered cluster ions, with Al_{13}^- observed

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as the most abundant ion. Charge exchange reactions were used to bracket the electron affinities of these clusters, producing values which were in good agreement with photodetachment results. Collision-induced dissociation was used to investigate the fragmentation pathways. In general, the collisional activation of these cluster ions resulted in aluminum atom elimination for all clusters, except Al_7^-, Al_6^-, and Al_3^-, which fragmented primarily by electron detachment. Similar results have recently been reported for the photofragmentation of aluminum cluster negative ions.[22]

These clusters ions are quite unreactive with small molecules, such as CH_4 and N_2O. Some of these clusters will react with O_2 to generate AlO_2^- and AlO^-, along with the appropriate neutral aluminum cluster or aluminum cluster oxide. For Al_n^- where $n > 8$, the even-numbered clusters were observed to react more rapidly than the odd-numbered clusters with oxygen, yielding AlO^- and AlO_2^- as the ionic products.

We are currently studying the extension of laser ionization FTMS for the examination of other metal cluster anions. This instrumental technique, with its high resolution measurement and ion trapping capabilities, offers great promise for examining the reactivities and structures of metal cluster ions.

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Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase: Reactions of $ScFe^+$ with Hydrocarbons

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Abstract: Fourier transform mass spectrometry was used to study the chemistry of the heteronuclear diatomic metal cluster $ScFe^+$. As has been observed for a variety of other metal dimer ions involving first-row transition metals, this cluster was found to be reactive with various alkenes but unreactive with alkanes. In the reactions with alkenes, C–H bond-activation processes predominate over C–C bond activations. In a number of the observed reactions, cleavage of the cluster occurs, implying a weak Sc^+–Fe bond. Also, collision-induced dissociation was performed on a variety of $ScFe^+$–ligand species, resulting almost exclusively in cleavage of the cluster yielding neutral losses of either Fe, FeH, or FeH_2. These observations provide further support for a weak Sc^+–Fe bond relative to the corresponding Sc^+–ligand bond strengths as well as to other M^+–Fe dimer bonds.

The interest in both ionic and neutral metal clusters has increased dramatically in the past decade. The ability to generate and study clusters of varying sizes and compositions has shed new light on the physical and chemical properties of these species. Understanding the chemistry of these metal clusters is important because it can provide insights into processes occurring in a wide variety of areas such as astronomy, surface science, and catalysis.

As the subject has developed, a growing variety of techniques have become available for these studies. In some of the earlier work on neutral clusters, matrix isolation techniques have been used in conjunction with optical,[1] ESR,[2] and Mossbauer[3] spectroscopy. Knudsen cell mass spectrometry has also proven to be a useful technique for obtaining bond energies for various neutral metal dimers.[4] Smalley and co-workers have developed a supersonic expansion source with a fast-flow reaction tube and have studied hydrogen chemisorption on niobium and cobalt clusters.[5] Kaldor and co-workers have also used a fast-flow chemical reactor with photoionization/time-of-flight detection to determine ionization potentials of various transition-metal clusters.[6] More recently, Smalley and co-workers have interfaced a supersonic expansion source to a Fourier transform mass spectrometer to study ionic metal clusters,[7] while Anderson and co-workers have studied ionic metal clusters generated in a sputter source.[8] Multiphoton dissociation/ionization of metal cluster carbonyl complexes has also been used successfully for generating ionic clusters.[9]

In our laboratory, we have developed a method for synthesizing, in situ, small mixed-metal cluster ions. This method, which involves the reaction of laser-generated metal ions with volatile metal carbonyl complexes such as $Fe(CO)_5$, has been used to generate and study a variety of MFe^+ species including M = V,[10] Fe,[11] Co,[12] Cu,[13] Rh,[14] La,[15] and Nb.[16] In this paper, we extend

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