

Magic numbers in $\text{Al}_n^+(\text{H}_2\text{O})_1$ cluster cations

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Abstract

We report the observation of magic numbers in the mass spectrum of $\text{Al}_n^+(\text{H}_2\text{O})_1$. These cluster cations were produced in a laser vaporization source in the presence of trace amounts of water. The most prominent magic number species observed was $\text{Al}_{13}^+(\text{H}_2\text{O})_1$. We attribute its pronounced intensity to its enhanced stability resulting from the formation of a coordinate bond between the Al_{13}^+ moiety and the oxygen atom of water. The sharing of an oxygen lone electron pair with Al_{13}^+ lends to it some of the character of the 40-valence electron, closed shell Al_{13}^- magic cluster. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The term, magic number, refers to a reproducible discontinuity in the intensity pattern of a mass spectrum of clusters. The appearance of magic numbers in such spectra can be caused by both kinetic and energetic factors. Sometimes, it is the electronic structure of a given cluster that is the basis for its observation as a magic number. For example, abundance patterns in the mass spectra of alkali metal clusters were successfully explained on the basis of jellium-like electronic shell closings [1,2]. For spherical clusters of free-electron metals, the shell model predicts enhanced stability of clusters containing 2, 8, 18, 20, 34, 40, 58, 68, 70, ... valence electrons. In other cases, geometric structure or kinetic factors govern the appearance of magic numbers.

Magic numbers in the mass spectra of homogeneous aluminum cluster ions tend to reflect their

relative stability due to both electronic and geometric structure. In the case of negatively charged aluminum clusters Al_{13}^- , the magic number $n = 13$ corresponds to a closed electronic shell with 40 valence electrons [3–7]. Moreover, the cluster itself has a highly symmetrical icosahedral geometry [8–11] that lends extra stability to Al_{13}^- . Likewise, for the positively charged aluminum clusters Al_n^+ , the magic number $n = 7$ is explained by the filling of an electronic shell with 20 valence electrons [12–15]. In addition, Al_7^+ has a more compact geometrical structure compared to its neighboring-size cluster cations [16].

Interactions of aluminum atoms and ions with water have attracted much attention because of an unexpected reaction that takes place in argon and neon matrices at low temperatures [17–19]. There, it was found that an aluminum atom inserts itself into a water molecule to form a divalent molecular species of the type, HAIOH . Under slightly different conditions, the divalent radical AlHOH was produced [20]. Interestingly, the man-made visible night glow caused

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by the release of aluminum vapor and gaseous aluminum compounds in the upper atmosphere has been attributed to electronically excited HAlOH .

Adduct formation is yet another way in which aluminum can bind water molecules. An adduct is a type of coordination compound, i.e. it has one or more coordinate bond(s) in which both of the electrons are donated by the lone electron pair of the ligand (a Lewis base) to fill an available empty orbital of a Lewis acid. Interestingly, another source of the observed night glow was reported to be excited AlO^* , which is a product resulting from the reaction of oxygen atoms with weakly bound aluminum adducts $\text{Al}\cdot\text{OH}_2$ [21,22]. In coordination chemistry, metal cations often act as Lewis acids. Aluminum cations bind water molecules mainly by forming coordination complexes [23–25]. Al^+ also forms coordination complexes with small organic ligands such as H_2 , CH_4 , C_2H_2 , C_2H_6 [26], C_6H_6 and HCN [27,28]. The formation of multiple adducts was implicated in the reaction between Al_{25}^+ and ethylene molecules C_2H_4 [29]. In its neutral form, aluminum and its compounds are usually electron-deficient, since aluminum has only three valence electrons of its own. In order to have a complete octet around Al, aluminum compounds (as well as those of boron) often form adducts with electron-donating ligands. Other group IIIA metals (M), namely indium and gallium, form water adducts, $\text{M}\cdot\text{OH}_2$ and $\text{M}_2\cdot\text{OH}_2$, in argon matrices at low temperatures [17].

In this Letter, we report magic number behavior in the aluminum/water cation cluster series, $\text{Al}_n^+(\text{H}_2\text{O})_1$. The heightened stability of $\text{Al}_{13}^+(\text{H}_2\text{O})_1$ may be understood in terms of a coordinate bond between Al_{13}^+ and H_2O , i.e. $\text{Al}_{13}^+ \leftarrow \text{:OH}_2$, resulting in the presence of Al_{13}^+ like character in this species.

2. Experimental

The cluster cations, Al_n^+ and $\text{Al}_n^+(\text{H}_2\text{O})_1$, were generated in a laser vaporization source. The second harmonic of a YAG laser (532 nm) was employed to laser ablate a rotating and translating aluminum rod. A pulsed valve was used to admit bursts of helium gas into the ion-rich region created by the laser. In the experiments reported here, traces of water were always present in the source due to residual hygro-

scopic substances left over from earlier runs. The length of the ‘waiting room’ where clustering occurred was varied by using expansion nozzles $\frac{1}{4}$ – $1\frac{1}{2}$ in. long. The ion clusters produced in the ablation/expansion region were skimmed, extracted with a high negative potential, sent through a system of lens elements, and mass analyzed in a quadrupole mass spectrometer.

3. Results

A typical mass spectrum recorded during these experiments is presented in Fig. 1. The pattern seen in this mass spectrum was very persistent and was observed when we extracted cations from the laser-ablated aluminum in the presence of trace amounts of water. The intensities of Al_n^+ cluster cations follow the general pattern established by previous investigators [12–15]. Accompanying each homogeneous aluminum cluster cation peak, however, there is a satellite feature with a mass 18 amu greater than that of the pure aluminum cluster cations. We interpret these satellite peaks to be $\text{Al}_n^+(\text{H}_2\text{O})_1$ cation clusters. The satellite series starts at $n \approx 4$ –6. At $\text{Al}_7^+(\text{H}_2\text{O})_1$, there is always a local maximum in intensity. For $n = 9$, there is always a local minimum. For $n = 9$ –13, there is a ramp of increasing intensity peaking at $\text{Al}_{13}^+(\text{H}_2\text{O})_1$. The $\text{Al}_{13}^+(\text{H}_2\text{O})_1$ species is always the strongest intensity peak in the $\text{Al}_n^+(\text{H}_2\text{O})_1$ homologous series. After $\text{Al}_{13}^+(\text{H}_2\text{O})_1$, $\text{Al}_{14}^+(\text{H}_2\text{O})_1$ is markedly diminished in intensity, even though the intensities of their precursors, Al_{13}^+ and Al_{14}^+ , are comparable. Thus, encounters between Al_{14}^+ and H_2O presumably must occur as frequently as those between Al_{13}^+ and H_2O . This is an important piece of information because it implies that the intensities of these peaks are determined not only by the availability of reactants (kinetics), but also (and substantially) by energetic stability factors. Among $\text{Al}_n^+(\text{H}_2\text{O})_1$ species larger than $\text{Al}_{14}^+(\text{H}_2\text{O})_1$, the $\text{Al}_{15}^+(\text{H}_2\text{O})_1$ peak is barely noticeable in many of our mass spectra, while $\text{Al}_{16}^+(\text{H}_2\text{O})_1$, $\text{Al}_{17}^+(\text{H}_2\text{O})_1$ and $\text{Al}_{18}^+(\text{H}_2\text{O})_1$ are always present and more abundant. While the reasons for this are not completely clear, we note that Al_{15}^+ has an enhanced cross-section for collision-induced fragmentation [15,30]. Overall, our mass spectra are dominated by $\text{Al}_{13}^+(\text{H}_2\text{O})_1$ and $\text{Al}_7^+(\text{H}_2\text{O})_1$ clusters. The intensities of these two

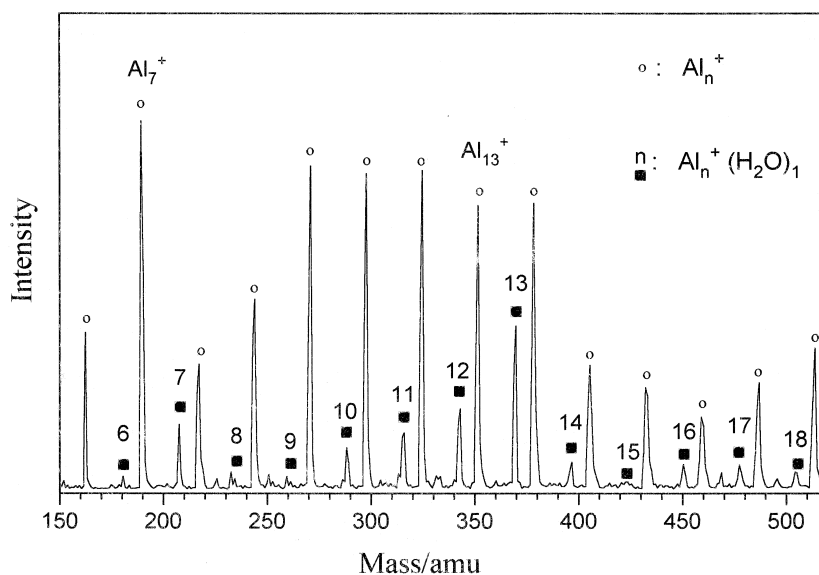


Fig. 1. A typical mass spectrum showing Al_n^+ (open circles) and $\text{Al}_n^+(\text{H}_2\text{O})_1$ (solid squares) cluster cations produced in a laser vaporization source during these studies.

peaks were always observed to be strong, i.e., they are magic number species.

4. Analysis and discussion

In the experiments reported here, the series $\text{Al}_n^+(\text{H}_2\text{O})_1$ was very persistent, it being seen when aluminum cation clusters were formed in the presence of trace water. The smallest $\text{Al}_n^+(\text{H}_2\text{O})_1$ magic number occurs at $n = 7$. Its intensity may be due in part to the fact that Al_7^+ is present in substantial abundance. In order to distinguish between energetic stability and kinetic effects as factors affecting its intensity, we computed the ratios of intensities $I[\text{Al}_n^+(\text{H}_2\text{O})_1]/I[\text{Al}_n^+]$. For $n = 7$, this ratio is always higher than that for $n = 5, 6, 8, 9$, suggesting that energetic factors are at least partially responsible for its persistent prominence. Electronically, Al_7^+ is a 20-electron closed-shell species. In addition to its electronic stability, Al_7^+ has a very compact geometrical structure and the smallest volume among its neighbors [16]. All of these factors may contribute to the enhanced intensity of $\text{Al}_7^+(\text{H}_2\text{O})_1$ compared to neighboring-size Al_n^+ clusters.

The species, $\text{Al}_{13}^+(\text{H}_2\text{O})_1$, displays the highest abundance in the $\text{Al}_n^+(\text{H}_2\text{O})_1$ series, both in terms of

its absolute intensity and the ratio $I[\text{Al}_{13}^+(\text{H}_2\text{O})_1]/I[\text{Al}_{13}^+]$. From the standpoint of electronic structure, this at first seems puzzling, because the Al_{13}^+ cation has 38 valence electrons and hence is 2 electrons shy of the closed shell at 40. Recall, however, that electron-deficient compounds of aluminum are well known for their ability to form strong coordinate bonds in order to complete their electronic shells. Thus, the unusually high intensity of $\text{Al}_{13}^+(\text{H}_2\text{O})_1$ may be attributable to the formation of such a bond between Al_{13}^+ and H_2O through a lone electron pair on the oxygen atom. In other words, the water molecule may be supplying, via its oxygen atom, a lone electron pair to the Al_{13}^+ moiety to complete its jellium-like electronic shell at 40 electrons. In this case, the magic number properties of $\text{Al}_{13}^+(\text{H}_2\text{O})_1$ may arise from it having some Al_{13}^- like character, with water acting as a Lewis base, and Al_{13}^+ functioning as a Lewis acid. Note that when an H_2O molecule adsorbs on an aluminum metal surface, the adsorption is accomplished through one of the oxygen lone pair orbitals with the water molecular axis tilted away from the surface normal [31,32].

There are precedents in other cluster experiments for ligand coordination affecting stabilities and the appearance of magic numbers. For example, in the $\text{Co}_n^+(\text{CO})_m$ system, it was the coordination of Co_n^+

cations by CO molecules that accounted for the magic numbers observed in the mass spectra [33]. The opposite effect is produced by an electron-withdrawing group, as was observed in $Al_n^+O_m$, where $Al_{15}^+O_2$ became magic when its two oxygen atoms withdrew four negative charges from the Al_{15}^+ moiety (44 valence electrons), effectively leaving it with 40 valence electrons and thus a closed shell [30].

Lastly, we should also mention two related experiments which did not give results analogous to ours. When isoelectronic B_n^+ clusters were allowed to react with D_2O , $B_n^+(D_2O)_1$ species were not observed among the products [34]. In that experiment, B_n^+ ions were formed first, and then the ion beam was passed through a collision chamber containing water vapor. In another related study, neutral Al_n clusters were passed through the reactor tube containing D_2O vapor and then photoionized for mass-detection [35]. There, the product distribution was different from the one observed here too. Apparently, and not surprisingly, specific source conditions and the order in which ion and neutral components come together are important.

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