Formation of aluminium clusters in helium nanodroplets

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Abstract

The addition of aluminium atoms to helium nanodroplets has been explored using electron impact mass spectrometry. A series of aluminium cluster ions, Al_n^+, were observed as the major products, which contrasts with a recent study where such cluster ions were not detected in any significant quantities (S. A. Krasnokutski, F. Huisken, *J. Phys. Chem. A* **115**, 7120 (2011)). The earlier finding was interpreted as evidence that Al atoms are separated by one or more layers of helium and therefore form a 3-dimensional 'foam' inside helium droplets. The current observations are not consistent with this suggestion and instead indicate that when multiple Al atoms are added to helium droplets they aggregate to form Al_n clusters inside the helium droplets.

Introduction

The study of metal atoms picked up by helium nanodroplets has provided many intriguing observations. It is now well established that alkali metal atoms reside in a dimple on the surface of helium nanodroplets rather than settling inside.[1-3] The driving force for adopting a surface location stems from the diffuse valence electron distribution in the alkalis, which generates an exceptionally weak attractive interaction with helium. Consequently, the displacement of sufficient helium to create a cavity which can host the alkali atom is energetically unfavourable relative to the creation of a dimple on the droplet surface. Small alkali clusters also reside on the surface of helium droplets and have been found to exist in high spin electronic states, since the low spin states release sufficient energy as the atoms coalesce to expel the cluster from the droplet surface.[4-6]

The situation for the alkaline earth metals is a little more complicated. All of the available evidence points towards a surface location for Ca, Sr and Ba atoms.[7-12] However Mg has, until very recently, proved a more challenging case to decipher. Evidence has been presented both in favour and against an interior location,[11,13,14] but this now looks to be resolved by recent calculations which suggest that Mg atoms do solvate inside helium droplets but are highly delocalized within the droplet because of the weak Mg-He interaction.[15] Another consequence of the weak Mg-He interaction is the formation of a foam-like structure for multiple Mg atoms in helium droplets. Here the Mg-He interaction is so weak that it becomes energetically unfavourable for two Mg atoms to come into direct contact. Instead, one or more solvation layers of helium form around each Mg atom and as two Mg atoms approach the energy required to displace the helium to allow the two Mg atoms to come into contact creates a barrier which cannot be overcome at the temperature of a helium droplet, 0.38 K. Consequently, the Mg_n system is thought to form a metastable threedimensional foam-like structure and recent experimental and theoretical studies seem to confirm this behaviour.[14,16,17]

Given the foam-like behaviour for magnesium, it is interesting to consider whether other metals might show similar behaviour. Recently, Krashnokutski and Huisken have suggested aluminium as a possible candidate.[18] Evidence for this was collected from mass spectrometry. Several arguments were presented in favour of a foam-like structure for when multiple Al atoms are present in the liquid helium droplet, including the absence of any significant quantities of Al_n^+ cluster ions. Here we report a similar mass spectrometric study of Al in helium droplets, but we obtain very different findings. In particular, we see an abundant array of aluminium cluster ions, which suggests that Al atoms aggregate to form Al_n clusters in helium nanodroplets rather than foam-like structures.

Experimental

The apparatus used is described in detail elsewhere.[19] Briefly, helium nanodroplets were formed by expansion of highly pure gaseous helium into a vacuum through a small aperture. The stagnation pressure of the helium and the temperature of the nozzle can be adjusted to control the mean size of the droplets. A collimated beam of droplets is formed by passage through a skimmer and the droplets then entered a pickup region, where Al atoms were added. This was achieved using a resistively heated oven comprised of a cylindrical alumina cell with tantalum heating wire on the outside, in which solid aluminium was placed. As the helium droplets passed through this pickup zone Al atoms were able to collide with and be captured by the droplets. The kinetic energy of each added atom is removed by evaporative loss of helium atoms, which quickly cools the ensemble back to 0.38 K. The doped droplets then passed through a second skimmer and entered the ionization zone of a quadrupole mass spectrometer, where they were subjected to electron ionization at an energy of 60 eV.

Results and Discussion

Figure 1 shows a mass spectrum obtained at a nozzle temperature of 12 K and a helium pressure of 15 bar, which is expected to give helium droplets with an average of 12000 helium atoms.[20] The oven temperature for this particular experiment was estimated to be 1100 K, as measured by a thermocouple in contact with the oven. The spectrum shows an array of cluster ions, including a strong series of peaks from He_n^+ cluster ions in the lower mass part of the spectrum. At higher masses the most prominent series of ions comes from Al_n^+, which can be seen with n up to 15 in this particular spectrum. The observation of Al_n^+ cluster ions is in marked contrast to the absence of these species in the work reported by Krashnokutski and Huisken.[18] The Al_n^+ ions show a general decline in abundance with n but there are exceptions, the most notable of which corresponds to $n = 7$. This peak is significantly more intense than its neighbours, Al_6^+ and Al_8^+, which suggests that Al_7^+ has enhanced stability, *i.e.* it is a ‘magic’ number cluster. The stability of this particular cluster has been reported in previous studies and can be explained by the jellium model, since Al_7^+ has 20 valence electrons which form a closed-shell in the jellium model.[21]

The next most prominent peaks seen in Figures 1 and 2 arise from ions of aluminium oxides. Specifically, we observed Al_2O^+ and also the series $[(Al_2O)Al_n]^+$. The aluminium oxides are not the target of the current study and so we shall not dwell on them here but we suspect that the preponderance of the reduced oxide, Al_2O, rather than AlO_2, derives from the use of an alumina (solid Al_2O_3) crucible, which in combination with heated aluminium produces aluminium oxide vapours under reducing conditions.

Also seen in the current work are the helium-solvated ions $AlHe_n^+$ and $Al_2He_n^+$, as shown in the expanded view in Figure 2. The $AlHe_n^+$ ions form the more prominent series and can be seen up to at least $n = 17$. The observation of $AlHe_n^+$ ‘snowball’ ions was reported previously by Krashnokutski and Huisken[18] and is evidence in favour of an interior location for Al atoms in the droplets (other evidence comes from spectroscopy[22]), since a surface-location is likely to expel a bare rather than a heavily solvated ion. However, Krashnokutski and Huisken were unable to observe snowball ions associated with Al_2^+ and larger Al_n^+ ions, which contrasts with the findings reported here.

In an attempt to resolve the differences between our observations and those reported by Krashnokutski and Huisken, we present in Figure 3 the response of three ions, He_2^+, Al^+ and Al_2^+, to changes in the oven temperature. In their study Krashnokutski and Huisken found a weak and essentially linear decline of He_2^+ signal with the Al vapour pressure, with a gradient which is far lower than would be expected if the Al atoms combined to form Al_n clusters. This is because the Al-Al bond energies are relatively strong and should produce a major change in droplet size as each atom is added, which would evaporate many He atoms and thus produce a large change in the He_2^+ signal (since the He_2^+ signal should be proportional to the geometric cross section of the helium droplet, which in turn is expected to be proportional to the electron impact cross section). On the other hand, addition of each Al atom in the limit of no clustering should add only about 140 meV of energy, which will result in the evaporation of *ca*. 230 helium atoms.[23]

The data shown in Figure 3 are dramatically different from the findings reported by Krashnokutski and Huisken. Even though we use smaller helium droplets than in the study by Krashnokutski and Huisken (whose mean droplet size was 2×10^4 helium atoms[18]), we nevertheless see abundant Al pickup at far lower vapour pressures than those implied by Krashnokutski and Huisken. For example, for the data shown in Figure 3 we use helium droplets with an estimated mean size of 10^4 helium atoms and see a maximum in the Al^+ signal at an oven temperature of 1100 K, which corresponds to an Al vapour pressure of about 6.5×10^{-6} mbar. Invoking Poisson statistics for the pickup process means a pickup probability for a single dopant atom given by $P = z \exp(-z)$ where $z = \sigma N l$ and σ = helium droplet geometric cross section, N = pickup gas number density and l = length of the pickup zone. The probability of picking up a single Al atom is a maximum when $z = 1$ and so under our experimental conditions (l = 7 cm and $\sigma = 7.2 \times 10^{-13}$ cm^2, assuming a spherical droplet[23]) we predict that the maximum in the pickup of a single Al atom should occur at a vapour pressure of 7.3×10^{-6} mbar. This is in excellent agreement with the vapour pressure deduced for the maximum of the Al^+ signal in Figure 3. It is important to be aware that there are approximations involved here which may make this level of agreement somewhat fortuitous. For example, there is an estimated error margin of ± 20 K in the oven temperature. Also, contributions to the Al^+ signal from the ionization of larger neutral clusters, such as Al_2, have been ignored. Nevertheless, it is clear that our estimated pickup behaviour is in agreement with experimental observations and is distinctly at odds with that presented by Krashnokutski and Huisken. It therefore seems that the absence of Al_n clusters in the experiments of Krashnokutski and Huisken is most likely the result of inadequate pickup of Al atoms, either because the helium droplets were smaller than thought or the Al vapour pressure was lower than claimed.

We note also that the He_2^+ signal shown in Figure 3 undergoes a rapid decline (note the log scale on the vertical axis) once Al_2 starts to form, as deduced by the appearance of the Al_2^+ signal. As mentioned earlier, this type of behaviour is consistent with Al-Al bond formation and provides further evidence against the foam model for Al in liquid helium. The dissociation energy of Al_2 is 0.61 eV[24] and its formation should lead to the evaporation of roughly 1000 helium atoms (the addition of each atom should also lead to evaporation of a further 230 He atoms due to dissipation of their translational energy). As pointed out by Krashnokutski and Huisken,[18] the binding energy per Al atom tends to increase as n increases, at least up until $n = 8$.[24] For example, the binding energy per atom is 2.1 eV for Al_8 and so its formation should result in the evaporation of ~27000 helium atoms. Although this is substantially larger than the mean size of the helium droplets used to record the spectrum in Figure 1, the droplets are expected to follow a log-normal size distribution. The long tail in the log-normal size distribution will provide some helium droplets with sizes far larger than the mean, which could account for the observation of the largest Al_n^+ cluster ions seen in the current study.

To close, the mass spectrometric evidence reported here argues against the formation of an aluminium foam when multiple Al atoms are picked up by helium nanodroplets. Further evidence in support of this suggestion comes from other experiments in our laboratory, where aluminium nanoparticles were observed after growth inside very large helium droplets.[25] These observations were made after collisions of the aluminium-doped droplets with a thin deposition target and then applying transmission electron microscopy. Despite the strong evidence presented here for the absence of an aluminium foam, it would be interesting in future work to explore how aluminium atoms combine in helium nanodroplets and optical spectroscopic studies would be particularly valuable.

Acknowledgements

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References

1. F. Stienkemeier, J. Higgens, C. Callegari, S. I. Kanorsky, W. E. Ernst, G. Scoles, *Z. Phys. D* **38**, 253 (1996).

2. F. Ancilotto, E. Cheng, M. W. Cole, F. Toigo, *Z. Phys. B.* **98**, 323 (1995).
3. A. Nakayama, K. Yamashita, *J. Chem. Phys.* **114**, 780 (2001).
4. J. Higgins, C. Callegari, J. Reho, F. Stienkemeier, W. E. Ernst, K. K. Lehmann, M. Gutowski, G. Scoles, *Science* **273**, 629 (1996).
5. J. Higgins, C. Callegari, J. Reho, F. Stienkemeier, W. E. Ernst, K. K. Lehmann, M. Gutowski, G. Scoles, *J. Phys. Chem. A* **102**, 4952 (1998).
6. J. H. Reho, J. Higgens, M. Nooijen, K. K. Lehmann, G. Scoles, M. Gutowski, *J. Chem. Phys.* **115**, 10265 (2001).
7. F. Stienkemeier, M. Wewer, F. Meier, H. O. Lutz, *Rev. Sci. Instrum.* **71**, 3480 (2000).
8. E. Lugovoj, J. P. Toennies, A. F. Vilesov, *J. Chem. Phys.* **112**, 8217 (2000).
9. C. V. Lovallo, M. Klobukowski, *J. Chem. Phys.* **120**, 246 (2004).
10. A. Hernando, R. Mayol, M. Pi, M. Barranco, F. Ancilotto, O. Bünermann, F. Stienkemeier, *J. Phys. Chem. A* **111**, 7303 (2007).
11. Y. Ren, V. V. Kresin, *Phys. Rev. A* **76**, 043204 (2007).
12. O. Bünermann, M. Dvorak, F. Stienkemeier, A. Hernando, R. Mayol, M. Pi, M. Barranco, F. Ancilotto, *Phys. Rev. B* **79**, 214511 (2009).
13. J. H. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann, G. Scoles, *J. Chem. Phys.* **112**, 8409 (2000).
14. A. Przystawik, S. Göde, T. Döppner, J. Tiggesbäumker, K. -H. Meiwes-Broer, *Phys. Rev. A* **78**, 021202 (2008).
15. J. Navarro, D. Mateo, M. Barranco, A. Sarsa, *J. Chem. Phys.* **136**, 054301 (2012).
16. A. Hernando, M. Barranco, R. Mayol, M. Pi, F. Ancilotto, *Phys. Rev. B* **78**, 184515 (2008).
17. S. Göde, R. Irsig, J. Tiggesbäumker, K. -H. Meiwesr-Broer, *New J. Phys.* **15**, 015026 (2013).

18. S. A. Krasnokutski, F. Huisken, *J. Phys. Chem. A* **115**, 7120 (2011).

19. A. Boatwright, C. Feng, D. Spence, E. Latimer, C. Binns, A. M. Ellis, S. Yang, *Faraday Discuss.* **162**, 113 (2013).

20. L. F. Gomez, E. Loginov, R. Sliter, A. F. Vilesov, *J. Chem. Phys.* **135**, 154201 (2011).

21. R. E. Leuchtner, A. C. Harms, A. W. Castleman Jr, *J. Chem. Phys.* **94**, 1093 (1991).

22. J. H. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann, G. Scoles, *J. Phys. Chem. A* **104**, 3620 (2000).

23. J. P. Toennies, A. F. Vilesov, *Angew. Chem. Int. Ed.* **43**, 2622 (2004).

24. A. K. Ray, B. K. Rao, *J. Phys.: Condens. Matter* **9**, 2859 (1997).

25. D. Spence, E. Latimer, W. York, A. Boatwright, C. Feng, C. Binns, A. M. Ellis, S. Yang, to be published.

Figure captions

1. Mass spectrum obtained at nozzle temperature of 12 K and a helium stagnation pressure of 15 bar, which is expected to produce helium atoms with an average of 12000 helium atoms. The alumina oven was maintained at a temperature of 1100 K for this experiment, which corresponds to a vapour pressure of Al of *ca.* 10^{-6} mbar. Several series of peaks are highlighted, the most prominent being from Al_n^+ ions. Also shown are the aluminum oxide ions Al_2O^+ and $[(Al_2O)Al_n]^+$.

2. An expanded view of the mass spectrum in Figure 1 highlighting peaks assigned to the $AlHe_n^+$ and $Al_2He_n^+$ series of ions. Note that the peaks for the latter series of ions are weak and this assignment should therefore be regarded as tentative.

3. Response of the He_2^+, Al^+ and Al_2^+ signals as a function of oven temperature for a fixed helium droplet size (mean size 10^4 helium atoms). The sharp decline in Al^+ and Al_2^+ signals at high temperature is attributed to the preferential formation of larger neutral Al_n clusters at these temperatures.

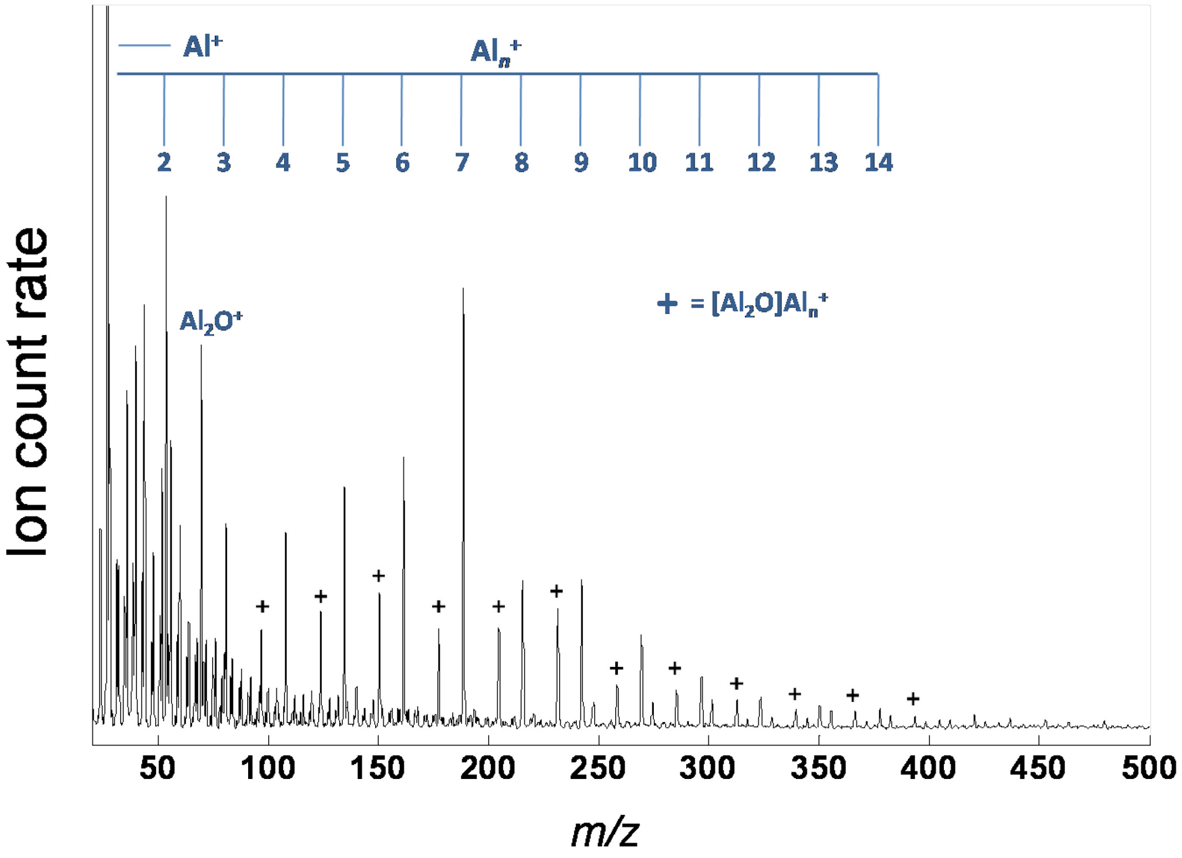

Al+
Aln+
2
3
4
5
6
7
8
9
10
11
12
13
14
Al2O+
+ = [Al2O]Aln+
Ion count rate
50
100
150
200
250
300
350
400
450
500
m/z

Figure 1

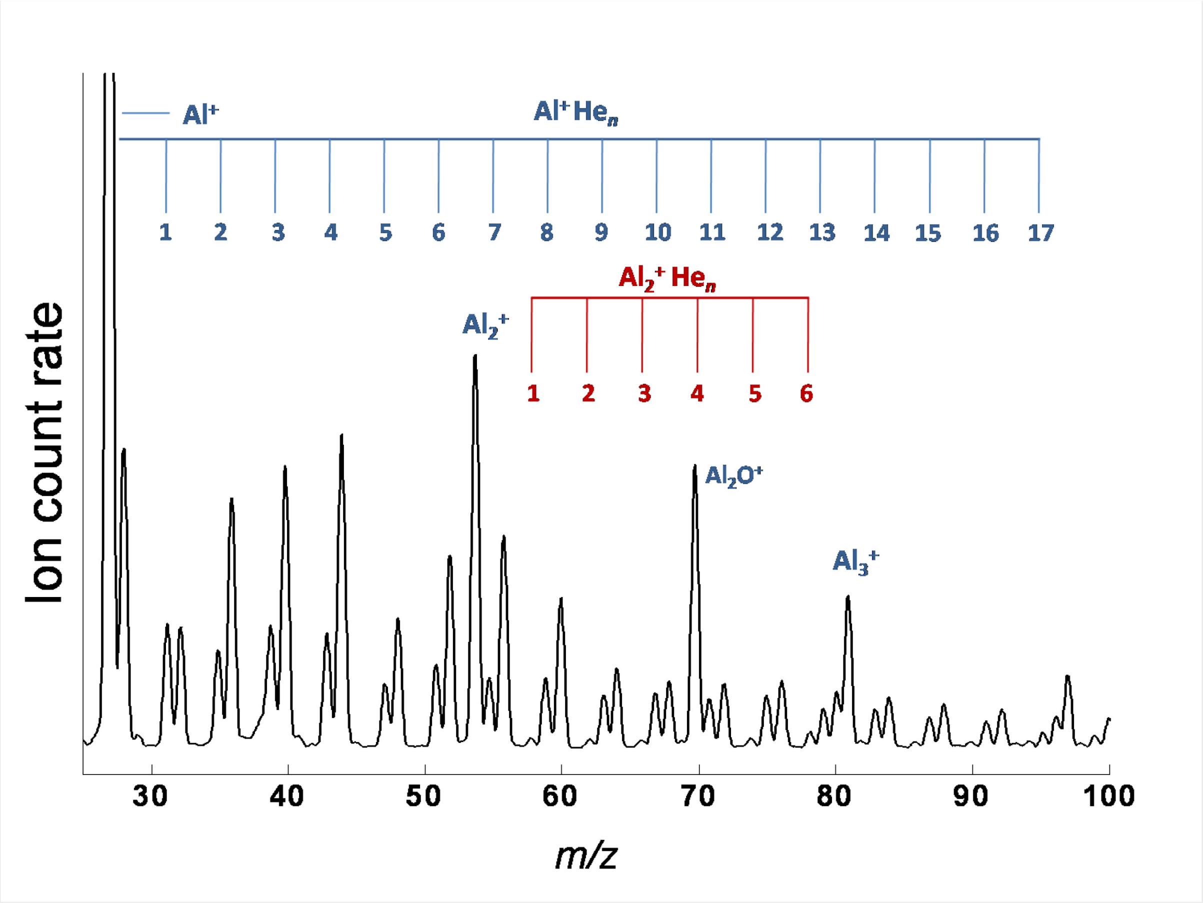
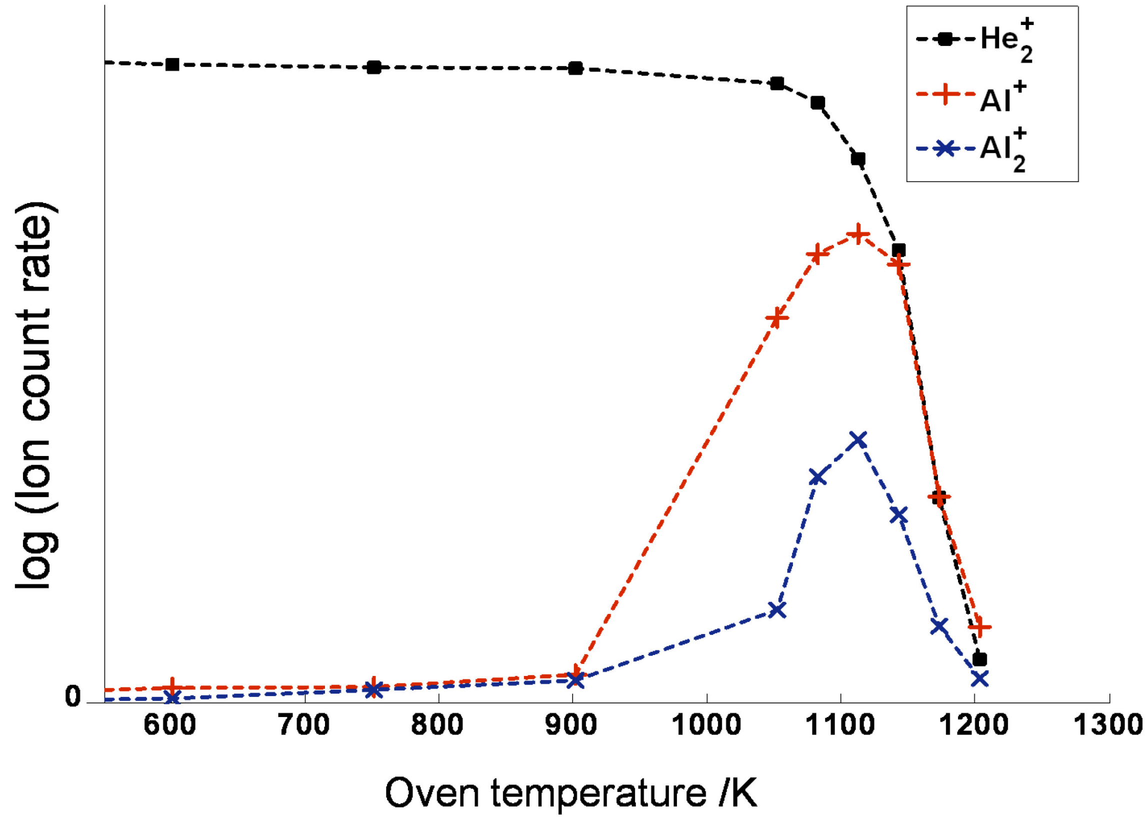

Al⁺
Al⁺He$_n$
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Al$_2$⁺He$_n$
1 2 3 4 5 6
Al$_2$⁺
Al$_2$O⁺
Al$_3$⁺
Ion count rate
30 40 50 60 70 80 90 100
m/z

Figure 2



log (Ion count rate)
0
600
700
800
900
1000
1100
1200
1300
Oven temperature /K
He_2^+
Al^+
Al_2^+

Figure 3