SIMS for the exploration of boron / boron-hydrogen Clusters

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Introduction

The study of atomic clusters has grown significantly in recent years, and clusters are now being looked to as a source for new "cluster-assembled" materials which exhibit the novel electronic, optical, magnetic, and structural properties of their cluster constituents . In order to determine what clusters may show promise for an application, it is important to understand the properties of these clusters. This type of study also provides knowledge of the organization of matter in the nano-scale regime.

In this experiment, we use SIMS (secondary-ion mass spectrometry) to examine the stability of boron and boron-hydrogen clusters, which, due to their light weight and high mass percentage of hydrogen, may show promise for application in solid-state hydrogen storage for vehicular use . This provides the basis for future studies into the properties of these clusters.

Procedure

The stability of a cluster is a measure of its ability to form and remain intact; therefore relative cluster stability can be measured by comparing the intensity of each cluster in mass spectra. SIMS was used to generate mass spectra under varying conditions. In high vacuum (3×10^{-8} mbar), an argon ion beam was used to sputter the surface of an isotopically pure boron-11 target. A flow of reactive hydrogen gas applied through a heated platinum wire was directed towards the surface of the target to promote the formation of hydrides. To stabilize higher-energy clusters, a helium gas jet was used to provide collisional cooling to reduce the internal energies of the clusters (see Figure 1).

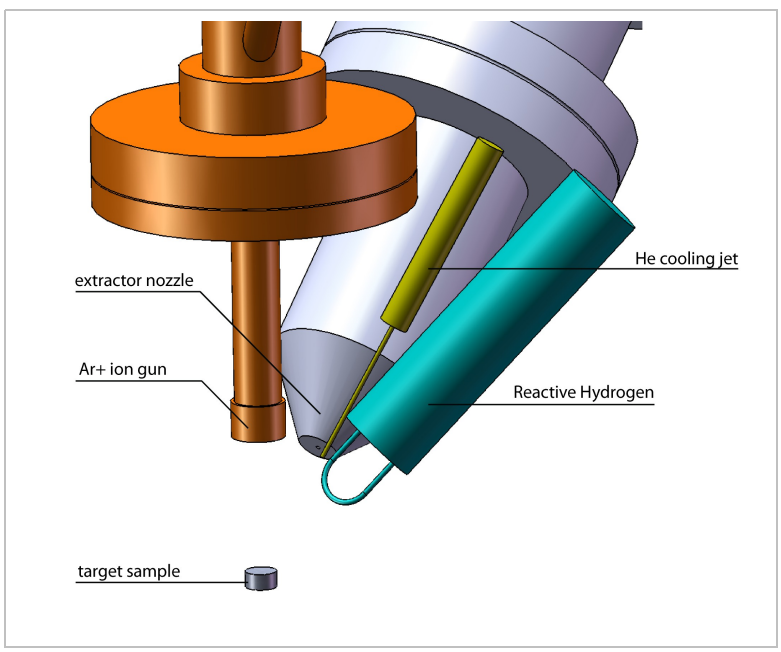


Figure 1. Experimental setup featuring an Ar+ ion gun, reactive hydrogen through a heated platinum wire and helium collisional cooling.

Charged extractor plates pulled ionic clusters through an extractor nozzle and optics, which focused the clusters through a 90-degree biased plate energy filter in which clusters of undesirable energies were

removed. Positive ions were investigated in this experiment, since equipment limitations did not allow for the consistent analysis and measurement of negative ions. A computer-controlled quadrupole and particle counter were used to perform the mass analysis. Figure 2 shows a diagram of the cluster instrument.

With no gases leaked in, the base pressure of the system was 3 x 10^{-8} mbar. Argon was leaked in to 2 x 10^{-5} mbar to maximize current flow through the boron target. For the case in which helium was added, the overall system pressure was brought to 1 x 10^{-4} mbar. Hydrogen was added to bring the total pressure to 2 x 10^{-4} mbar while 14.0 A was driven through the platinum heating wire. (All pressure measurements were recorded with an ion gauge adjusted for air, and are uncorrected).

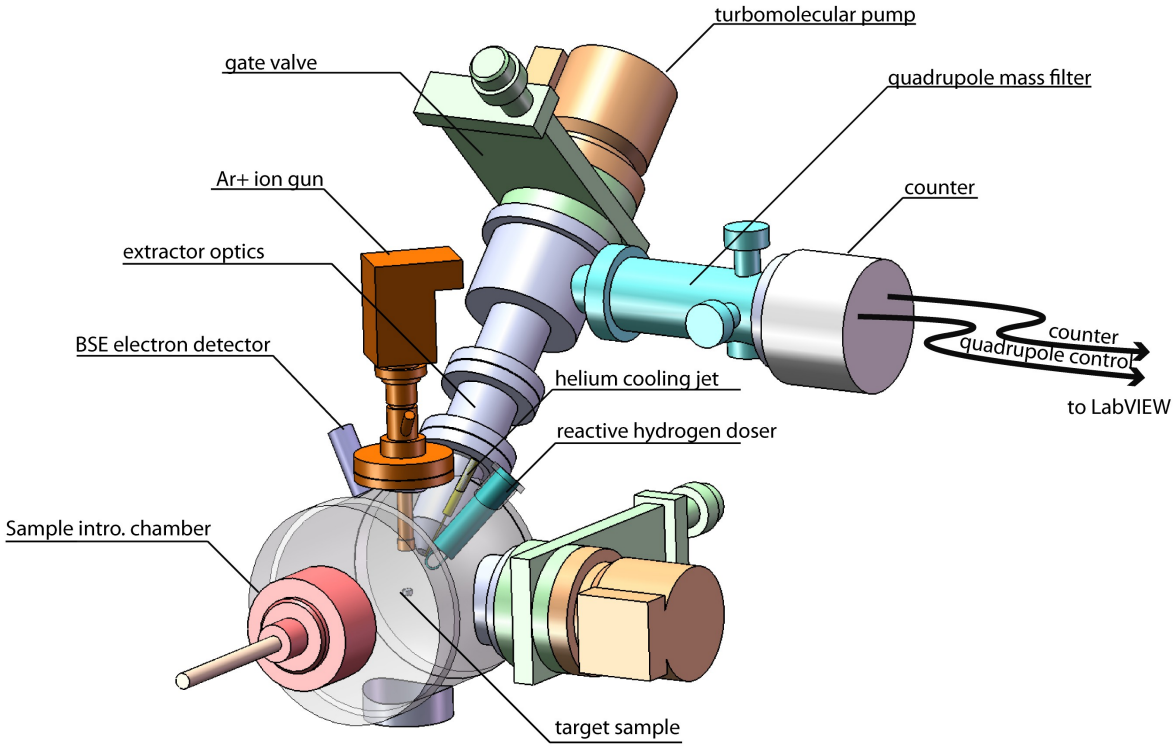
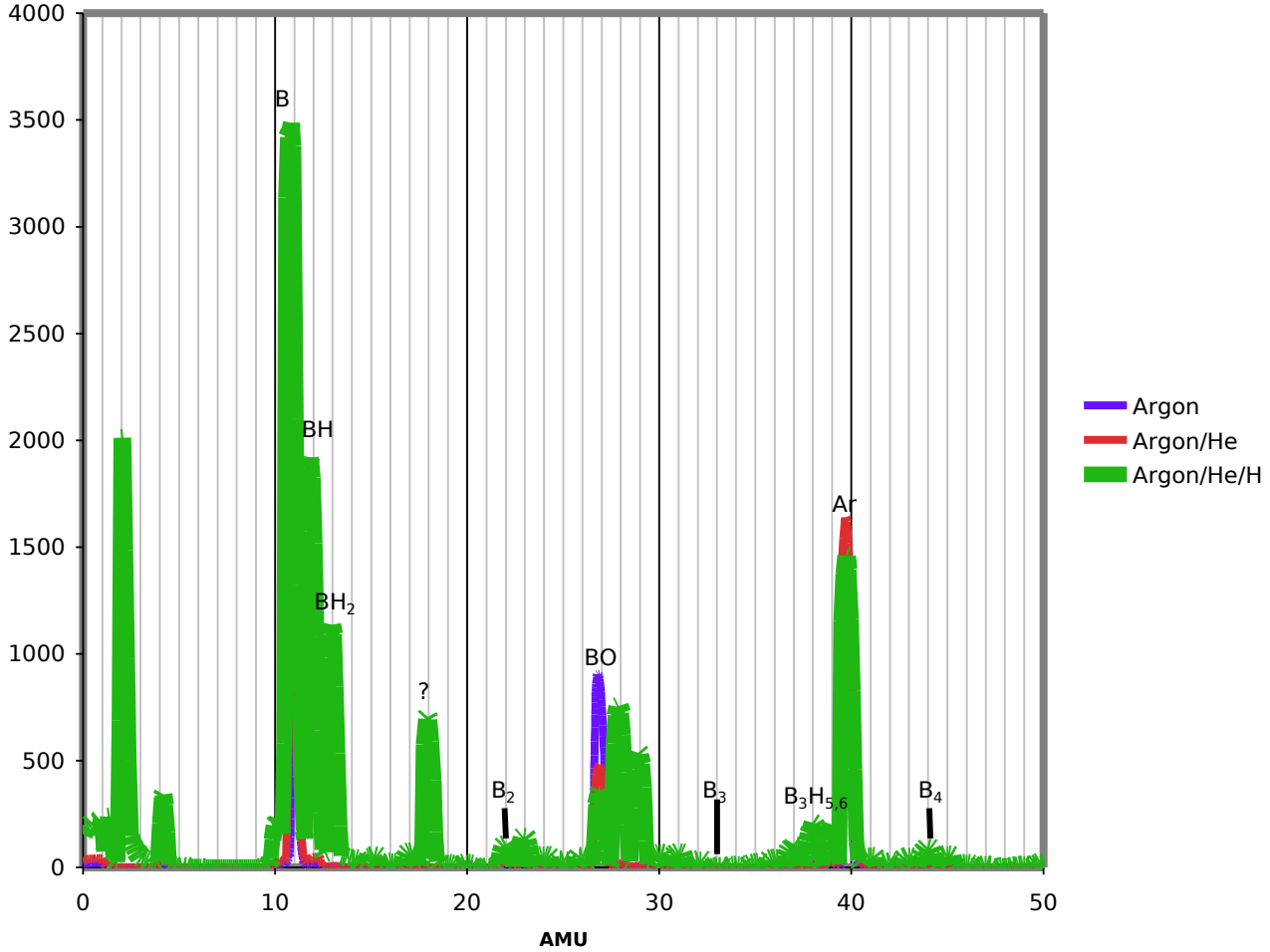


Figure 2. Instrument setup for cluster creation and measurement.

Results

Three sets of data were taken – one with only the ion gun (argon only), the next with helium gas added, and the next with helium and reactive hydrogen added.

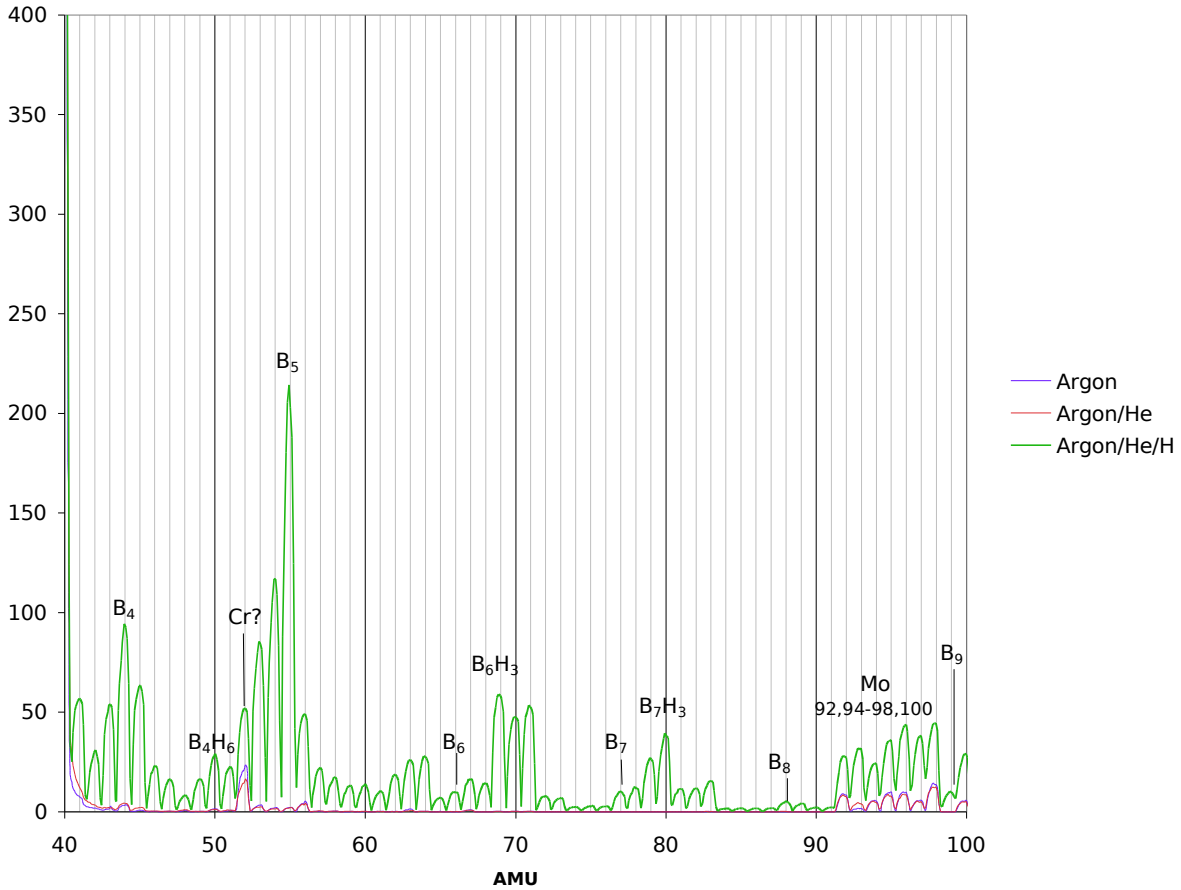
0-50 amu



The purple (Ar) and red (Ar/He) traces show the system without any hydrogen. As expected, these two traces show no evidence of hydrides. Boron oxide forms at 27 amu, with BOH and BOH_2 appearing when hydrogen is added.

Numerous other hydride peaks appear. Notable hydride peaks occur at BH and BH_2. A relatively large unidentified peak occurs at 18 amu – it is possible that two hydrogen molecules are combining with a free oxygen to form H_2O. Interestingly, the peaks at B_2, B_3, and B_4 are significantly smaller than the peak at B. The addition of hydrogen atoms in some cases increases their stability; B_3H_5 and B_3H_6 at 38 and 39 amu appear to be significantly more stable than B_3 itself. 38 amu may also have contributions from B_2O.

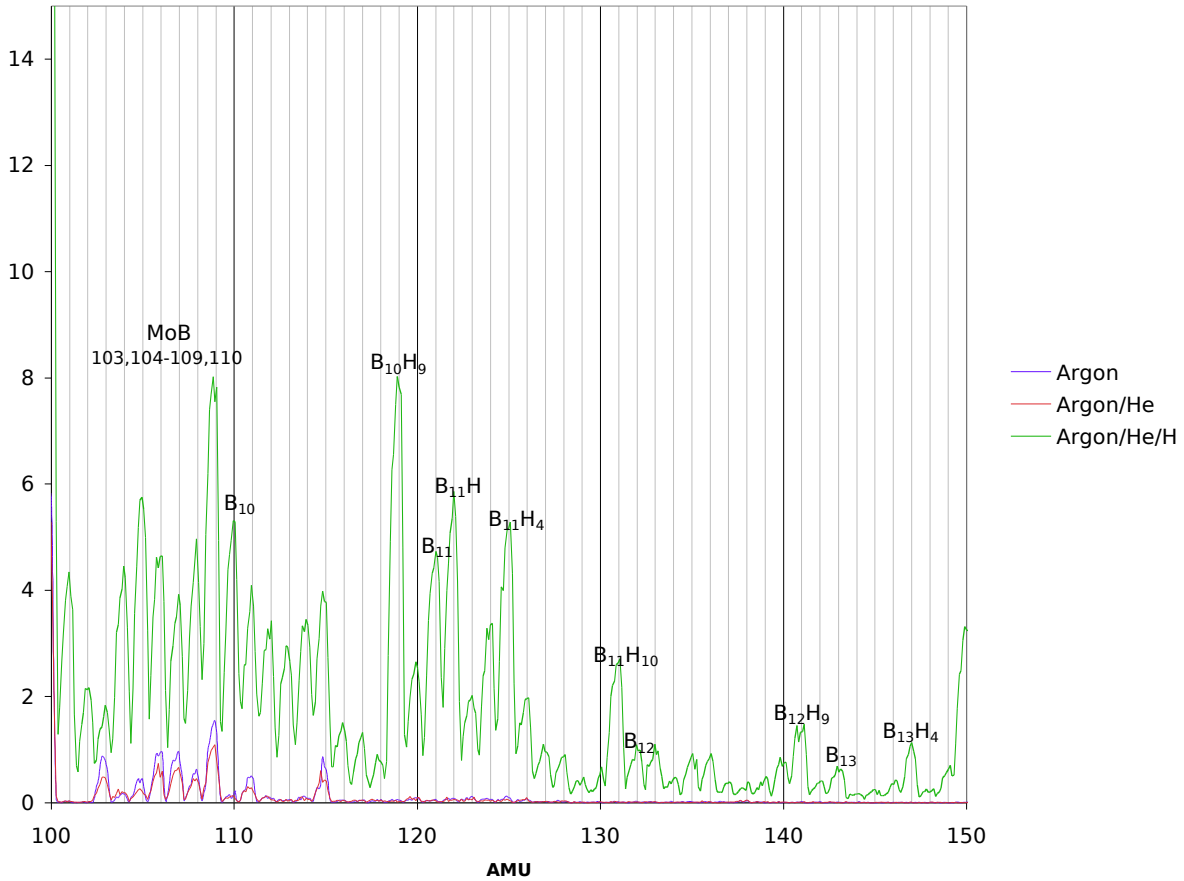
50-100 amu



Aside from the range of molybdenum peaks that occur at 92, 94-97, and 100 amu, the Ar and Ar/He traces are relatively uneventful. A peak occurs at 52 amu in both the hydrogen and hydrogen-free environments – this mass leads one to suspect chromium, although the source of this chromium is unknown. A similar peak occurs at 63 amu, which suggests copper contamination.

The green hydrogen trace shows a number of hydride peaks, and also provides interesting information about B_n clusters. The peak at B_5 is slightly higher than the peak at B_4 and significantly more intense than those at B_6, B_7, or B_8, and. Boron hydride clusters at B_6H_3 and B_7H_3 also show high intensity relative to their neighbors, which suggest that they may be magic number clusters. Although this trend for B_6H_3 and B_7H_3 could not be repeated in later measurements, the resolution of this data set and the apparent signal-to-noise ratio at these peaks suggest it would be worthwhile to further attempt to reproduce these results. A subsequent data set shows a peak of interest at 68 amu, which would correspond to B_6H_2. B_6 is made more stable with the addition of at least one hydrogen atom.

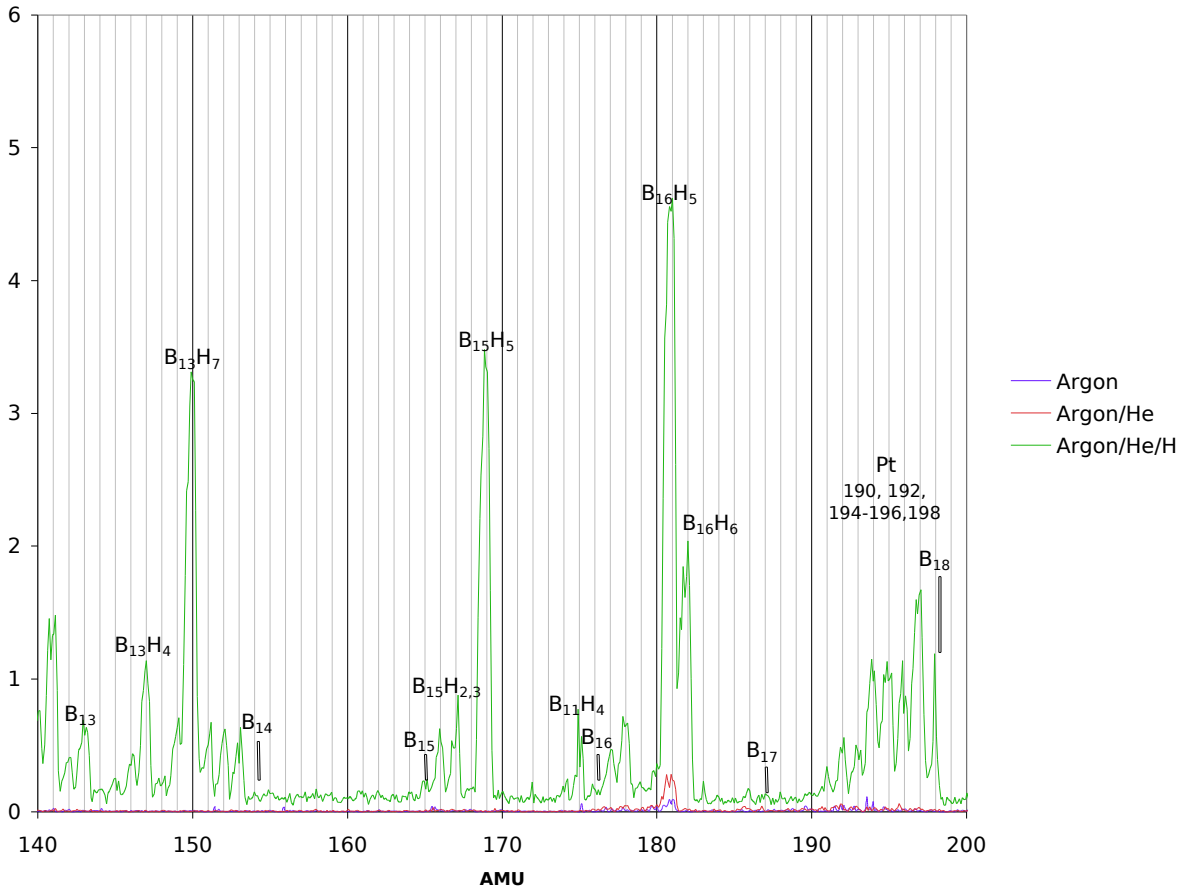
100-150 amu



At atomic masses 103, 104-109, and 110, we see peaks corresponding to molybdenum borides. The peak at 110 amu could have contributions from MoB, B_{10}, and a number of MoB hydrides. Again, the trace for the hydrogenated environment is most interesting, showing many peaks that may be hydrides. Notably, $B_{10}H_9$, $B_{11}H$, $B_{11}H_4$, and $B_{11}H_{10}$ appear to be relatively stable. $B_{12}H_9$ and $B_{13}H_4$ are also noticeably more stable than their neighbors, and are more stable than B_{12} and B_{13}.

Note that coincident masses can make analysis difficult – for example, $B_{11}H_{11}$ is coincident with B_{12}, and $B_{12}H_{12}$ is coincident with $B_{13}H$.

150-200 amu

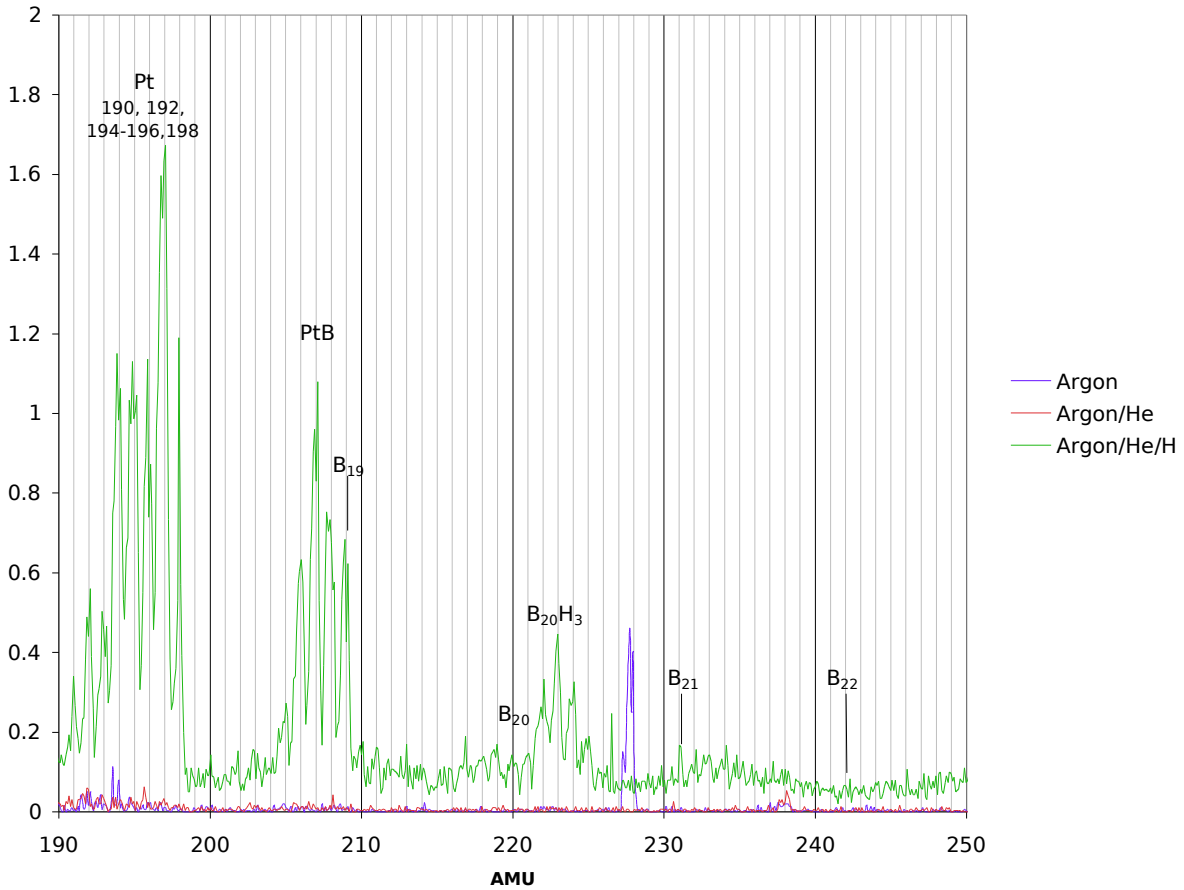


Except for a peak at 181 amu, both hydrogen-free environments show very little activity at the higher masses. $B_{16}H_5$ may contribute to the peak at 181, but it is unlikely that this hydride was formed in the absence of reactive hydrogen gas. The peak at 181 amu for the Ar and Ar/He runs is yet to be explained.

Platinum peaks appear in the 190 amu range as a result of outgassing from the heated platinum wire. Note that B_{13} appears to be significantly more stable than the clusters of $B_{14\text{-}17}$.

In the boron hydrides, $B_{13}H_4$ and $B_{13}H_7$ both appear to be stable, increasing the stability of B_{13}. The same holds true for $B_{15}H_2$ and $B_{15}H_3$, as well as $B_{11}H_4$. With the exception of B_{13} and B_{18}, boron-only clusters show weak intensity in this range.

200+ amu



Signal intensity and signal-to-noise ratio are significantly reduced at higher masses, making it difficult to distinguish which clusters are significant. The peak in the purple trace at 228 amu is likely an artifact from that run, since it does not appear on the other traces.

Note the occurrence of platinum borides, with a pattern that matches the pattern of the platinum isotopes. B_{18} occurs at the same mass at ^{198}Pt, and B_{19} occurs at the same mass as ^{198}PtB. No conclusions about the contribution of each can be made.

Again, in this range the boron clusters seem to be relatively low in intensity compared to the platinum and platinum borides. B_{20} gains intensity when three hydrogen atoms are added ($B_{20}H_3$). Beyond 250 amu, the intensity drops significantly enough that data is no longer usable.

Discussion

The results demonstrate a number of clusters which show marked stability as "magic number" clusters. Boron hydride clusters that showed marked stability are B_3H_5, B_3H_6, B_4H_6, B_7H_3, $B_{10}H_4$, $B_{13}H_7$ and $B_{15}H_5$. It cannot be said for certain that these are magic number clusters, but they show promise as having marked stability. There was nothing in the literature, experimental or theoretical, to suggest that any of these clusters would demonstrate stability. Further study is needed to confirm these results.

Previous experimental work by La Placa et. al suggests that B_{13} may be a magic number cluster , while density functional theory (DFT) of boron clusters suggest that cationic boron clusters B_n^+ may exhibit magic numbers at n= 5, 10, and 13 . Our results confirm that B_5 and B_{13} exhibit higher intensity than nearby B_n^+ clusters. From our data, the same conclusion cannot be made about B_{10}. The intensity of the cluster at 110 amu is slightly higher than the cluster at B_{11} and significantly higher than that at B_{12}, but is small compared to the one at B_9.

Surprisingly, data seems to suggest that the addition of hydrogen improves the stability of many clusters, including those without hydrogen. For example, the intensity of boron at 11 amu is more than doubled when hydrogen is added. Although it is possible that hydrogen has a collisional cooling effect, it is difficult to attribute this intensity boost solely to the addition of hydrogen. The overall increase in intensity is more likely due to inconsistencies with the beam current and power.

This brings into light some of the issues that made the acquisition of consistent data difficult. In order to better examine clusters in the higher mass range, a number of improvements should be made to the instrument to improve the reliability and repeatability of results.

<u>Improved sputtering source</u>

It is recommended that a newer, more powerful, more reliable sputtering source be considered. The Ar+ ion gun was prone to failure. In some tests, the current measured on the target would drift fluctuate as much as 50% over 20 minutes; this significantly effects intensity counts, and makes it difficult to determine the validity of any conclusions drawn when comparing data sets.

Rapid plating of molybdenum on the apertures and ceramic insulators of the gun led to short circuits that adversely affected the gun's stability and performance. When the ceramics were sufficiently plated to cause a high-resistance short, the gun had to be removed from the system and the ceramics etched. This laborious process dictated that the gun be run at half-power to increase the amount of time between etchings; however, target current was limited to around 25 µA. To give better peak intensity and improve signal-to-noise ratio at higher atomic masses, it would be beneficial to be able to run higher target currents and increase sputter rate.

<u>Improvement of leak valves and control</u>

Pressure drift in the system was problematic. Over a 30 minute period, the argon pressure could drift as much as 1e-5 mbar, resulting in a 50% drift in target current. In addition, the leak valve for the hydrogen was sticky and slow, making it difficult to control the pressure of hydrogen leaked into the system (the time for the H pressure to equalize was often as long as 15 minutes).

It may be possible to implement electronically controlled leak valves to maintain stable system pressure, thus keeping beam current more stable and making data more readily comparable. In addition, a replacement leak valve for the hydrogen could significantly reduce dead time while conducting experiments.

LabVIEW hardware timing

The LabVIEW .vi currently uses software timing to control the amount of “dwell” time spent on each mass. Depending on CPU usage, this software timing can be off by a few percent. Although this is not significant, it is an additional source of noise in the data and could be resolved by implementing hardware timing.

Work with a contractor from National Instruments has led to a feasible solution, but so far his program is only compatible with LabVIEW 8.6 and above (the computer in the lab runs version 8.5). The contractor has yet to send a LabVIEW 8.5-compatible version of the code.

Conclusion

There is promise for the usage of SIMS to explore clusters of boron and boron hydrides. The results showed some agreement with previous experimental and theoretical work in boron clusters. In addition, it demonstrated boron hydride clusters that could possibly be magic number clusters.

Although this experiment only explored clusters up to 250 amu, it would be interesting in the future to compare boron and boron hydrides of higher masses and to compare the stability of these clusters to theoretical projections. The suggested improvements to the instrument would aid in the measurement of larger clusters by improving intensity, improving signal-to-noise ratio, and reducing signal noise. In addition, data sets taken on different days would be more easily comparable.

Future studies should examine the electronic and structural properties of the clusters via Raman and gas-phase photoelectron spectroscopy to examine if the clusters exhibit any novel properties that may have use in a particular application.

References