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We present new data which inidicates that the so-called magic number ion clusters result from neutral clusters which are significantly larger in size.

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'ELECTRON BOMBARDMENT FRAGMENTATION
OF SIZE SELECTED NH₃ CLUSTERS'

by

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Comment on the paper
"Electron bombardment fragmentation of size selected NH3 clusters"

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A recent paper by Buck and Lauenstein[1] utilizing size selection of ammonia clusters with a crossed beam of He atoms, reported some prominent differences in ion intensity as a function of cluster size as compared to the previous work of other authors. We report in this comment new experimental results which demonstrate that the differences they reported can be attributed to Buck and Lauenstein employing a colder molecular beam expansion.

Under the experimental conditions of Buck and Lauenstein[1] (neutral clusters smaller than 12 molecules) they measured fragmentation for ammonia cluster ions up to $n \approx 5$. Interestingly, they observed no maximum in the intensity of $(NH_3)_4NH_4^+$ (n = 5) cluster ion (although they do note that under their conditions it is the largest cluster ion reported). This magic number, at n = 5, has been reported by several other authors[2-5] and is regarded as being due to a closed solvent shell around a NH_4^+ cation. Buck and Lauenstein also observed very little contribution from a sequence of ion clusters corresponding to the general formula, $m/z = 17n + 2$. This sequence of cluster ions has been attributed to either $NH_5^+(NH_3)_{n-1}$ ions[6] or water impurities[7] of the form $NH_4^+(NH_3)_{n-2}H_2O$. This cluster ion has also been recently observed in multiply charged clusters of ammonia[8,9].

The reason for the missing magic numbers as well as the missing $17n + 2$ peaks lies in differences in the expansion conditions in which the starting neutral ammonia clusters are produced (ie., their 60μ nozzle and He-seeded ammonia expansion[1] vs. our 250μ nozzle and neat ammonia expansion[8,9]). To test this hypothesis we have now examined the cluster ion distribution by seeding the expansion with He. Our experimental apparatus has been described previously[10] and consists of a differentially pumped Campargue continuous molecular beam source coupled to an Extrel C-50 quadrupole mass spectrometer. For this paper we used a 250μ nozzle and passed either a neat expansion of ammonia (anhydrous, Linde 99.99%) or a 3% NH_3 in He mixture (Scott Specialty Gases, 99.99% anhydrous ammonia, 99.999% He). Figure 1

shows the resulting cluster ion distribution, for three different cluster ions.

For a neat expansion of ammonia through a 250μ nozzle, we report the previously observed magic number for $(NH_3)_{n-1}NH_4^+$ (Figure 1b, n=5). In addition, we also observe the magic numbers which we had recently reported[11] for $(NH_3)_{n-1}NH_2^+$ (Figure 1a, n=7) and $(NH_3)_nH_2^+$ (Figure 1c, n=8)[12]. In that paper we speculated on possible hydrogen bonded structures for these cluster ions and experimentally observed that these magic numbers did not change upon variations in the electron impact energy (100eV-40eV), the stagnation pressure (P_O=1-5 atm) or the stagnation temperature (T_O=253-313 K).

In this comment we report that seeding of the cluster beam makes a tremendous change in the magic number structure, as shown in Figure 1. By using a He-seeded ammonia expansion, all the magic number structure disappears. Indeed, the ion intensities of the cluster ions, for particular sizes, drops by almost a factor of five.

It is interesting to also note, that this same overall effect is observed if we now change the nozzle diameter. If we again use neat ammonia, but now expand through a 50μ nozzle, we get results which are qualitatively similar to the open square data shown in Figure 1. The expected magic number structure is gone, and the intensities of the $m/z = 17n - 1$ and $m/z = 17n + 2$ peak sequences are now substantially reduced.

We can now speculate as to why these changes in expansion conditions should generate such dramatic changes in the cluster ion distribution. Certainly, under conditions of seeding and a reduced nozzle aperture, the internal temperature of the neutral cluster generated within the expansion is substantially lowered. When this cold cluster is then subsequently ionized, the solvent molecules in this 'solid-like' state are not free to migrate around the newly generated cation, in order to form the stable closed shell hydrogen-bonded structure. As a result, magic numbers are therefore not observed in the ion distribution. However, in an expansion with a large nozzle aperture and a neat expansion, the clusters formed are 'boiling hot'. The individual molecules within the cluster are therefore quite fluxional, and may freely oscillate around the central cation until they find the appropriate stable orientation.

This loss of magic number structure as a function of expansion condition, may therefore represent a phase transition within the cluster, and may be eventually used as a probe of the internal temperature of the cluster itself. We hope to perform further work in this area with other hydrogen bonded systems, in order to see if this is a general result.

An alternative explanation for this effect may lie in that conditions of smaller aperture size and a seeded expansion both make for inefficient

clustering. That is, the distribution of cluster sizes will be concentrated toward small n. This would then suggest that the magic number peaks observed result from extremely large ion clusters which have undergone many successive fragmentation/evaporation processes, until they finally achieve a structure consisting of a closed solvent shell which is hydrogen bonded to a central cation.

In conclusion, for beam conditions of small nozzle aperture and seeded expansions (like the Buck and and Lauenstein experiment[1]) one can expect an absence of magic number structure in plots of cluster ion intensity vs. cluster size due primarily to a colder molecular beam expansion. This loss of magic number structure as a function of expansion condition may in turn be evidence of a phase transition occuring within the cluster.

Acknowledgments

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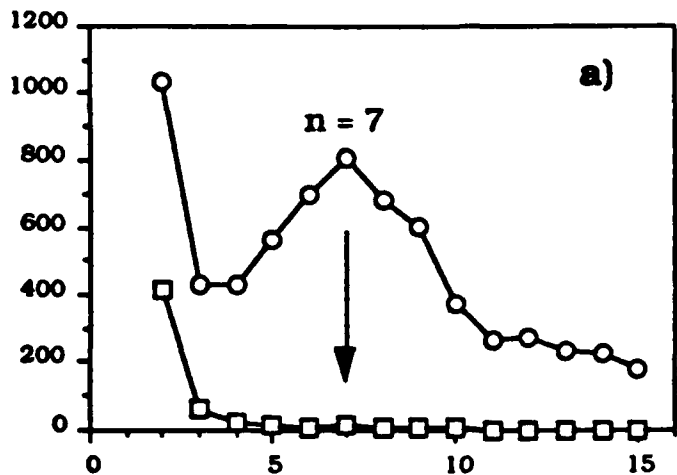
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12) The intensity anomoly at n=5 shown in Fig 1c, is partially due to the ^{15}N contribution of the adjacent $(NH_3)_4NH_4^+$ ion, and should not be considered a magic number.
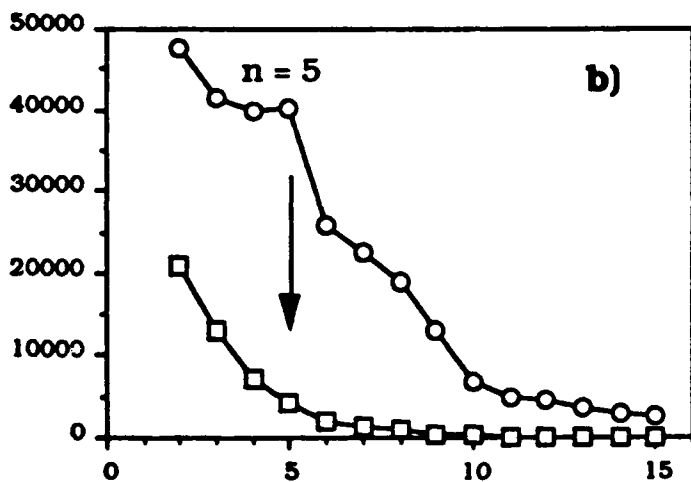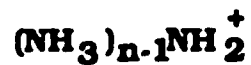
Figure Caption

Figure 1) 70 eV electron impact mass spectra showing cluster ion intensity vs. cluster size using a 250μ diameter nozzle, T_O= 298K. Curves in each graph are quantitatively comparable. Arrows indicate change in magic number as a function of expansion cooling. Open circles : P_O = 1.2 atm, Open Squares : P_O = 2.0 atm,
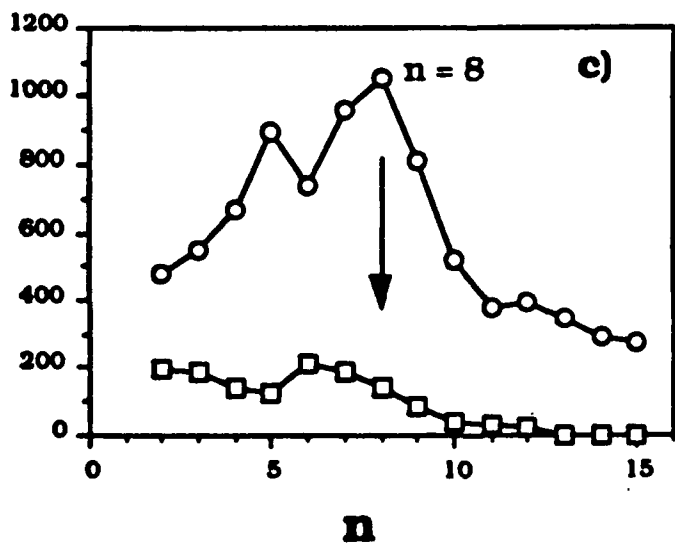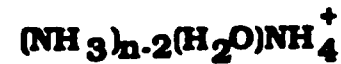
Legend: ○ = neat NH_3 □ = 3% NH_3 in He

a) $n = 7$

$m/z = 17\,n - 1$

$(NH_3)_{n-1}NH_2^+$

b) $n = 5$

$m/z = 17\,n + 1$

$(NH_3)_{n-1}NH_4^+$

c) $n = 8$

$m/z = 17\,n + 2$

$(NH_3)_n H_2^+$ or

$(NH_3)_{n-2}(H_2O)NH_4^+$

Ion Intensity (arb. units)

n