

sion 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 Lauenstein experiment<sup>1</sup>) 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 occurring within the cluster.

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<sup>10</sup>M. T. Coolbaugh, W. R. Peifer, and J. F. Garvey, *J. Phys. Chem.* **94**, 1619 (1990).

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<sup>12</sup>The intensity anomaly at  $n = 5$ , shown in Fig. 1(c), is partially due to the <sup>15</sup>N contribution of the adjacent (NH<sub>3</sub>)<sub>4</sub>NH<sub>4</sub><sup>+</sup> ion, and should not be considered a magic number.

## Reply to the comment on: "Electron bombardment fragmentation of size selected NH<sub>3</sub> clusters"

Udo Buck, Reinhard Krohne, and Harold Linnartz  
Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D3400 Göttingen,  
Federal Republic of Germany

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In our original work<sup>1</sup> we measured the fragmentation probabilities of electron bombardment ionization of neutral size-selected (NH<sub>3</sub>) <sub>$n$</sub>  clusters,  $n = 2, 3, 4$ , and 5, utilizing a crossed beam arrangement with He atoms. The largest fragment in all cases is the NH<sub>4</sub><sup>+</sup> ion, which is the result of a fast exothermic reaction within the cluster and which leads for larger clusters than the dimer to the additional evaporation of monomers. For dimers it was also shown that the fragmentation probability did not depend on the internal excitation of the clusters which was varied by the scattering process.<sup>2</sup> In order to get an idea what happens with larger clusters, angular dependent mass spectra were measured that contain contributions from all clusters  $n \leq 11$ . The re-

sults exhibit the same trends as were observed for the fully size-selected clusters up to  $n = 5$ . The largest contribution is still from the NH<sub>4</sub><sup>+</sup> and the first measurable intensity is seen at (NH<sub>3</sub>)<sub>4</sub>NH<sub>4</sub><sup>+</sup> indicating a loss of at least 5 monomers.

These results are at variance with those reported by several authors.<sup>3-8</sup> They all see a prominent peak or rapid dropoff of the intensity at the mass corresponding to (NH<sub>3</sub>)<sub>4</sub>NH<sub>4</sub><sup>+</sup>, but, in contrast to our method, no size selection is used. In addition, also the sequence of cluster intensities at  $m/z = 17 \cdot n + 2$  is only weakly present in the results of Ref. 1 and does not show any maximum, in contrast to the results of Ref. 8.

In the preceding comment,<sup>3</sup> the authors claim that the

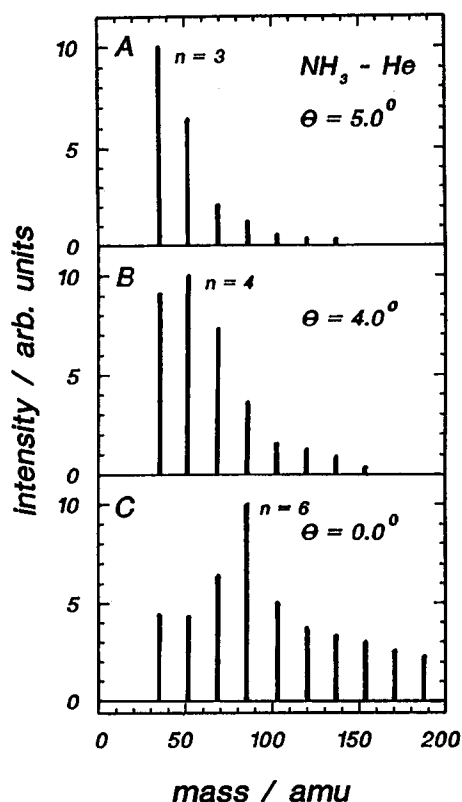


FIG. 1. Angular dependent mass spectra of scattered  $(\text{NH}_3)_n$  clusters observed at A:  $\Theta = 5.0^\circ$  with  $n < 12$ , B:  $\Theta = 4.0^\circ$  with  $n < 10$ , and C:  $\Theta = 0.0^\circ$  (no scattering) with no restriction in cluster size. The bars correspond to ion intensities at  $(\text{NH}_3)_{n-2}\text{NH}_4^+$ . The beam conditions for all three experiments are: Nozzle diameter  $d = 150 \mu\text{m}$ , stagnation pressure 1.0 bar, pure  $\text{NH}_3$ .

reason for this discrepancy lies in differences in the expansion conditions of the two experiments. Indeed, when they repeated the experiment in their machine without size selection but under the beam conditions of Ref. 1 (small nozzle diameter, 3% mixture in He), they found no intensity maximum for  $(\text{NH}_3)_4\text{NH}_4^+$ , but they confirmed it with neat expansions and large nozzle diameters. They presented an appealing explanation for the result. The different internal temperatures caused by the different expansion conditions lead to a more rigid and less reactive behavior in the Göttingen experiments and a more fluxional and more reactive behavior in the Buffalo experiment. However, there is still the possibility that the different behavior is mainly caused by the different cluster sizes in the two experiments. To test this hypothesis, we have repeated the experiments with partly size-selected clusters in our machine under the beam conditions of the Buffalo experiment. For that purpose a neat  $\text{NH}_3$  expansion through a  $150 \mu\text{m}$  nozzle at 1 bar stagnation pressure is used.

Figure 1 shows the resulting cluster ion intensities for

three different deflection angles after the scattering with a He beam. The scattering process successively excludes the larger clusters. At  $\Theta = 0^\circ$  with no scattering [Fig. 1(c)] there is no restriction on the cluster size and we confirm, indeed, the results of the Buffalo experiment and many others before: A nice peak at  $(\text{NH}_3)_4\text{NH}_4^+$ . If we increase the scattering angle, the cluster size is restricted. In Fig. 1(b) taken at  $4.0^\circ$  the maximum cluster size is  $n = 12$  and in Fig. 1(a) taken at  $5.0^\circ$  the maximum cluster size is  $n = 10$ . The intensity distributions change considerably. In the first case the maximum appears at  $(\text{NH}_3)_2\text{NH}_4^+$  and in the second case at  $(\text{NH}_3)\text{NH}_4^+$ . The latter spectrum resembles the published results of Ref. 1 very much, although in that case  $n = 11$  was assumed. This discrepancy can be explained by the lower resolution of the present experiment which slightly extends the mass range, since the width of the velocity distribution of the neat  $\text{NH}_3$  expansion is 14.0% compared with 6.6% of the seeded expansion. In any case, the trend is convincing. We conclude that the missing ion intensity maxima in  $(\text{NH}_3)_n$  cluster spectra are a consequence of the cluster size. This result also explains the differences found in Ref. 3. Neat expansions through large nozzle diameters produce larger clusters than mixtures with He through smaller nozzles. This suggests (as was already mentioned as the second possibility in Ref. 3) that the peaks result from larger ion clusters which have undergone many successive fragmentation and evaporation processes until they reach this stable structure. Experiments, taken also at other angles, indicate that at least clusters  $n > 25$  are necessary to produce the peak at  $(\text{NH}_3)_4\text{NH}_4^+$ . Further experiments will hopefully reveal the same trends for the other observed maxima.

We note that the ion intensities of neutral clusters after ionization are not simply correlated with their neutral precursors. They undergo a complicated process depending crucially on the structural charge when going from the neutral to the ionized species. Detailed experimental information on these processes can only be obtained in experiments with size-selected neutral clusters.

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