

## The Formation of the Cluster Ions $\text{NH}_5^+$ and $(\text{NH}_3)_2\text{H}_2^+$ and *ab initio* Calculation Study of Their Structures

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**Abstract:** The mass spectra of cluster ions  $(\text{NH}_3)_n\text{H}_2^+$  with  $n < 4$  were measured for the first time using a MPI mass spectrometer. The structures of the cluster ions  $\text{NH}_5^+$  and  $(\text{NH}_3)_2\text{H}_2^+$  were calculated using GAUSSIAN-94 package, and stable structures for both of them were found.

**Keywords:** Ammonia, cluster, multiphoton ionization, proton transfer, *ab initio* calculation.

Ammonia cluster has been widely studied by many groups<sup>1-3</sup>. The main ions measured in the mass spectra are protonated ammonia cluster ions, which are produced from the ion-molecule reactions in the ionized ammonia clusters.

Shinohara and Nishi<sup>4,5</sup> found the ions whose mass were 1 amu. larger than the protonated ammonia cluster ions by the method of MPI MS. They attributed these ions to the binary cluster ions  $[(\text{NH}_3)_n\text{NH}_4^+ \text{H}_2\text{O}]$  coming from water as the impurity in the ammonia sample.

Bugaets and Zhogolev<sup>6</sup> predicted theoretically the probability of the existence of the hypervalence ion  $\text{NH}_5^+$  using SCF MO LCAO method. Garvey and Bernstein<sup>7</sup> reported the existence of the hypervalence cluster ion series  $(\text{NH}_3)_n\text{H}_2^+$  for the first time, but the only cluster ions they measured were those with  $n \geq 4$ .

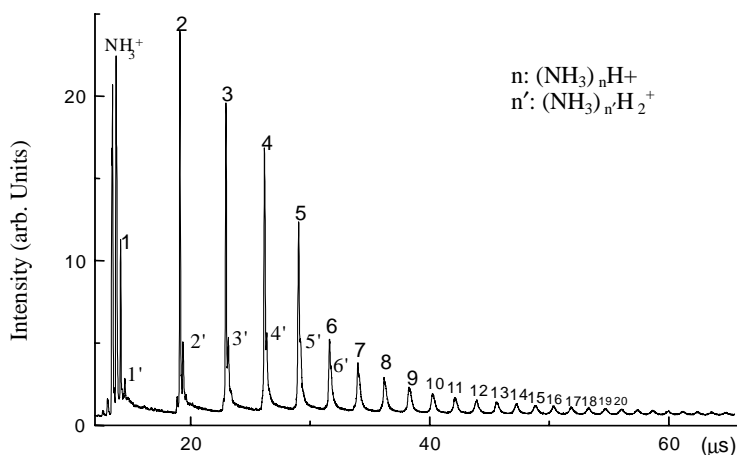
The structures of this kind of cluster ions were calculated by Kassab *et al*<sup>8</sup> using MONSTERGAUSS program, and were considered that a core of  $\text{H}_3\text{NH-HNH}_3^+$  formed first and the other ammonia molecules solvating around the core in turn.

The equipment used in this experiment is a typical time-of-flight mass spectrometer which contains a pulse molecule beam, an ionization area, a free drift section and the ion detector.

The purity of the ammonia is 99.99%. The wavelength of the laser is 355 nm.

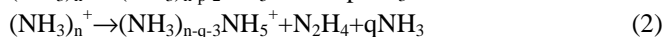
**Figure 1** shows the MPI mass spectrum of ammonia cluster measured with a mixture of the 10% ammonia and 90% He. There is a weak series of cluster ions besides the predominant protonated ammonia cluster ions, the mass of the former being 1 amu. larger than the relevant protonated ions.

**Figure 1.** MP1 MS of 10% NH<sub>3</sub> and 90% He  
(Pressure: 3.16×10<sup>5</sup>Pa, Intensity of the laser: 6mj/pulse)



The water content of the ammonia sample we used is less than 0.01%, and the effect of the isotope of N and H are less than 0.36% and 0.015% respectively. So we can reasonably conclude that this series of cluster ions are (NH<sub>3</sub>)<sub>n</sub>H<sub>2</sub><sup>+</sup> (1≤n≤6), which is different from Garvey results<sup>7</sup> where only the ions with n≥4 could be measured.

Because the pressure of (1~3.5)×10<sup>-3</sup>Pa was maintained during the measurement in the TOF MS, the mean free path of the molecule is large enough to avoid collision induced reaction between ions and other molecules. Therefore we consider the production mechanism of these ions is that pointed out by Garvey<sup>7</sup>:



In the *ab initio* calculation, we optimized the structures of the ions NH<sub>5</sub><sup>+</sup> and (NH<sub>3</sub>)<sub>2</sub>H<sub>2</sub><sup>+</sup> at HF/STO-3G and MP2/6-31G\*\* level, using GAUSSIAN-94 package, and verified the results with frequency analysis.

Considering various possible structures of the ion NH<sub>5</sub><sup>+</sup>, under aforementioned conditions, only one stable structure was found, as shown in **Table 1**. From it, the ion NH<sub>5</sub><sup>+</sup> can be considered as being composed by ion NH<sub>4</sub><sup>+</sup> and a H atom. The length between atom H2 and H6 is 2.2897Å, and the angle of N1-H2-H6 is almost 180°. It can be deduced that the bond between the H6 and NH<sub>4</sub><sup>+</sup> is obviously weak. **Table 2** shows the energies of various ions, radicals and complexes at MP2 / 6-31G\*\* level. From it, it can be seen that the energies of NH<sub>3</sub>+H<sub>2</sub><sup>+</sup> and NH<sub>3</sub><sup>+</sup>+H<sub>2</sub> are 152.9 kcal/mol and 24.4 kcal/mol higher than that of NH<sub>5</sub><sup>+</sup> respectively, so the ion NH<sub>5</sub><sup>+</sup> is stable comparing to these two dissociation channels. It can also be seen from **Table 2** that the energy of NH<sub>4</sub><sup>+</sup>+H is only 0.01 kcal/mol higher than that of NH<sub>5</sub><sup>+</sup>, so the bond of the NH<sub>4</sub><sup>+</sup> and H in NH<sub>5</sub><sup>+</sup> is weak. If there is enough internal energy left after the ionization-dissociation,

the vibration excited by the energy can make  $\text{NH}_5^+$  dissociate into  $\text{NH}_4^+$  and H. This is probably the reason why the ion  $\text{NH}_5^+$  can not be measured in common experiment.

The structure of the ion  $(\text{NH}_3)_2\text{H}_2^+$  is also shown in **Table 1**. From calculation, it can be seen the energy of it is 29.9 Kcal/mol lower than that of  $\text{NH}_3 + \text{NH}_5^+$ , so the structure of it is also stable.

As for the structure  $\text{H}_3\text{NH-HNH}_3^+$  put forward by Kassab for ion  $(\text{NH}_3)_2\text{H}_2^+$ , we verified it with the two basis sets mentioned above. It is considered that the structure is stable at HF/STO-3G level through frequency analysis. But a negative frequency appears with frequency analysis at MP2/6-31G\*\* level, so the structure obviously is not stable at this level. Therefore, our conclusion is that such a structure may be not stable after all.

**Table 1.** Structural parameters of the ions  $\text{NH}_5^+$  and  $(\text{NH}_3)_2\text{H}_2^+$  at MP2 / 6-31G\*\* level

	bond length(°)	bond angle(°)	dihedral angle(°)
$\text{NH}_5$	N1H2 = 1.0238	H3N1H2 = 109.4887	H6H2N1H3 = -101.8696
	N1H3 = 1.0223	H4N1H2 = 109.4489	
	N1H4 = 1.0224	H5N1H2 = 109.4509	
	N1H5 = 1.0224	H6H2N1 = 179.7685	
	H2H6 = 2.2897		
	N1H2 = 1.0173	H3N1H2 = 112.7368	H6H2N1H3 = -127.7302
$(\text{NH}_3)_2\text{H}_2$	N1H3 = 1.522	H4N1H2 = 106.0412	H2N1H3N7 = 41.3657
	N1H4 = 1.0172	H5N1H2 = 106.0608	N1H3N7H8 = -101.7807
	N1H5 = 1.0172	H6H2N1 = 169.5842	N1H3N7H9 = 18.2051
	H2H6 = 2.6597	N1H3N7 = 179.9975	N1H3N7H10 = 138.2205
	H3N7 = 1.1395	H3N7H8 = 110.7602	
	N7H8 = 1.019	H3N7H9 = 110.7823	
	N7H9 = 1.019	H3N7H10 = 110.7842	
	N7H10 = 1.019		

**Table 2.** The energies of various ions, radicals and complexes at MP2 / 6-31G\*\* level

	E ( hartrees )	$\Delta E$ ( Kcal/mol )
H	-0.498233	
$\text{H}_2$	-1.147165	
$\text{H}_2^+$	-0.589602	
$\text{NH}_3$	-56.347769	
$\text{NH}_3^+$	-55.994953	
$\text{NH}_4$	-56.798807	
$\text{NH}_4^+$	-56.682788	
$\text{NH}_5^+$	-57.181041	0.0
$\text{H} + \text{NH}_4^+$	-57.181021	0.0126
$\text{H}_2 + \text{NH}_3^+$	-57.142118	24.4246
$\text{H}_2^+ + \text{NH}_3$	-56.937371	152.9055
$(\text{NH}_3)_2\text{H}_2^+$	-113.576399	

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