

# Isomers of gallium arsenide cluster ions

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Gallium arsenide cluster ions were generated by laser vaporization in a supersonic nozzle, trapped in a Fourier transform ion-cyclotron resonance mass spectrometer, and allowed to react with  $\text{NH}_3$  forming addition complexes with the cluster cations. With excess  $\text{NH}_3$ ,  $\text{Ga}_x\text{As}_y(\text{NH}_3)_z^+$  with the same GaAs composition ( $x+y$ ) was observed with several values of  $z$ . This observation of different numbers of chemisorbed  $\text{NH}_3$  molecules at completion is explained in terms of the existence of multiple isomers of positive GaAs clusters. Negative  $\text{Ga}_x\text{As}_y^-$  clusters were found to be inert toward  $\text{NH}_3$ .

## 1. Introduction

The kinetics of positive GaAs clusters towards  $\text{NH}_3$  have been discussed previously [1]. In this work, it was shown that ammonia chemisorbs onto positive GaAs clusters and the clusters near the stoichiometric 1/1 composition of bulk gallium arsenide are the most reactive. In the present work, we investigate the final products at completion of reaction with  $\text{NH}_3$  and observe for the same reactant composition several final products with different numbers of ammonia molecules attached. This provides strong evidence that several isomers exist for clusters of the same chemical composition.

The existence of multiple isomers for the GaAs anion clusters has been reported by Reents [2]. Many other clusters have also shown multiple isomers. For example, experiments on silicon clusters done in this group [3] have demonstrated that silicon clusters can be annealed to their most energetically favored isomers by laser excitation as characterized by reactivities towards ethylene or ammonia.

## 2. Experimental

This experiment was conducted on a Fourier

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transform ion-cyclotron resonance (FT-ICR) mass spectrometer in both extraction mode [4] and direct injection mode [5]. Cluster ions can be trapped for minutes, reacted with various reagents for controlled time periods, and identified with high mass resolution. The detailed experimental sequence and data processing have been discussed previously [1,6]. In brief,  $\text{Ga}_x\text{As}_y$  clusters are formed by entraining material pulse-laser-vaporized from the surface of a GaAs disk into a He carrier gas pulse. After undergoing supersonic expansion and being skimmed into a molecular beam, the residual ions from the vaporization plasma are injected into the cell of the FT-ICR. After the cluster ions are trapped in the FT-ICR cell, one particular size can be selected by ejecting all others out of the cell using standard SWIFT technology. Then they are subjected to treatment with  $\text{NH}_3$  at a pressure of about  $10^{-5}$  Torr for about 30 s. In the present experiments, the reaction was conducted for increasingly long reaction times until no further reaction progress was observed, in order to ascertain the final products of the reactions of positive GaAs clusters with  $\text{NH}_3$ .

## 3. Observations and results

The top panel of fig. 1 shows the mass spectrum of 10-atom positive GaAs clusters before reaction. Peaks 2 amu apart are observed arising from the var-

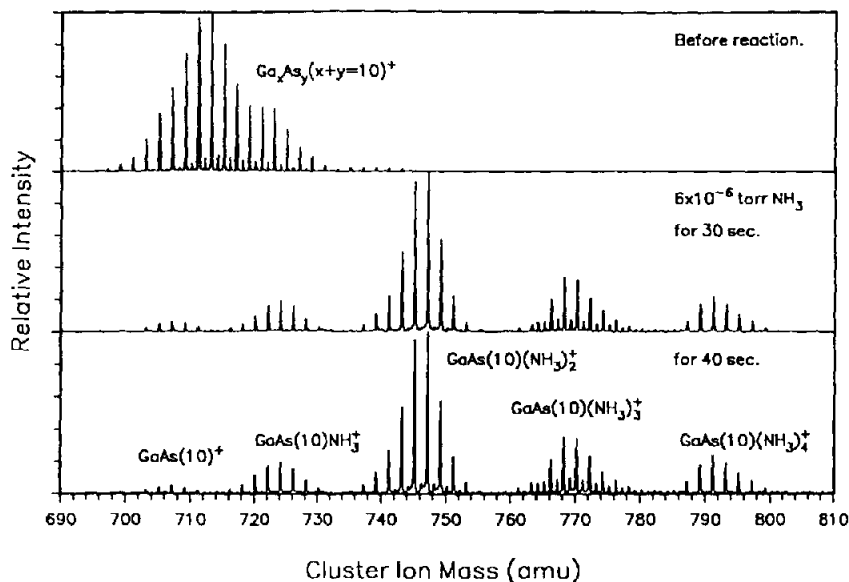


Fig. 1. The mass spectra of 10-atom positive GaAs cluster reaction with  $\text{NH}_3$ . The top panel shows the mass spectrum of 10-atom positive GaAs clusters before reaction. The following two panels show the mass spectra after 30 and 40 s of reaction with  $6 \times 10^{-6}$  Torr of  $\text{NH}_3$ , respectively.

ious chemical compositions and the overlapping isotopes of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$ . The following two panels in fig. 1 show the mass spectra after 30 and 40 s of reaction with  $6 \times 10^{-6}$  Torr of  $\text{NH}_3$ , respectively. As discussed previously [1], the reaction is chemisorption of  $\text{NH}_3$  by the cluster ion. Here, we are concerned with final products. It was also established that the parent cluster ions do not react to form these two kinds of products directly, but sequentially through addition of ammonia molecules [1].

Since the mass of  $\text{NH}_3$  is an odd number (17 amu), the first products can be easily differentiated from the parent clusters, which all have even atomic weights. As the reaction proceeds, ammonia molecules are attached to the clusters successively. For these 10-atom positive GaAs clusters, up to four ammonia molecules are chemisorbed. Reaction with the majority of stoichiometries is complete after 30 s, because the spectrum profiles in the bottom two panels are very similar.

Least-squares fitting as described previously [1] was employed to obtain the relative concentrations of the different stoichiometries in parent and product clusters as a function of reaction time. The results of this treatment for  $\text{Ga}_4\text{As}_6^+$  and  $\text{Ga}_5\text{As}_5^+$  clus-

ters are shown in figs. 2 and 3, respectively. After 20 s, all the parent  $\text{Ga}_4\text{As}_6^+$  and  $\text{Ga}_5\text{As}_5^+$  clusters have reacted away being converted into two forms of products. One product set has three ammonia molecules chemisorbed, and the other four. These two sets of products did not react any further exhibiting the same final relative concentration within experimental error. As shown in fig. 2, about 20% of the  $\text{Ga}_4\text{As}_6^+$  clusters reacted to form  $\text{Ga}_4\text{As}_6^+(\text{NH}_3)_3$ , and the rest generated  $\text{Ga}_4\text{As}_6^+(\text{NH}_3)_4$ . In fig. 3, it is shown that about 30% of  $\text{Ga}_4\text{As}_5^+$  clusters reacted to form  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_3$ , and about 70% reacted to form  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_4$ . Results for other compositions are listed in table 1. Among those tested,  $\text{Ga}_4\text{As}_4^+$  and  $\text{Ga}_3\text{As}_7^+$  are the only two stoichiometries which adsorb more than four ammonia molecules.

The relative stoichiometric concentrations for  $\text{Ga}_x\text{As}_y^+$  ( $x+y=10$ ) before and after reaction with  $6 \times 10^{-6}$  Torr of  $\text{NH}_3$  for 40 s are tabulated in table 2. The sum of all the products corresponding to one stoichiometry after reaction theoretically should be the same as the parent relative concentration before reaction. In this experiment, they are very close within the fluctuation error of experiment.

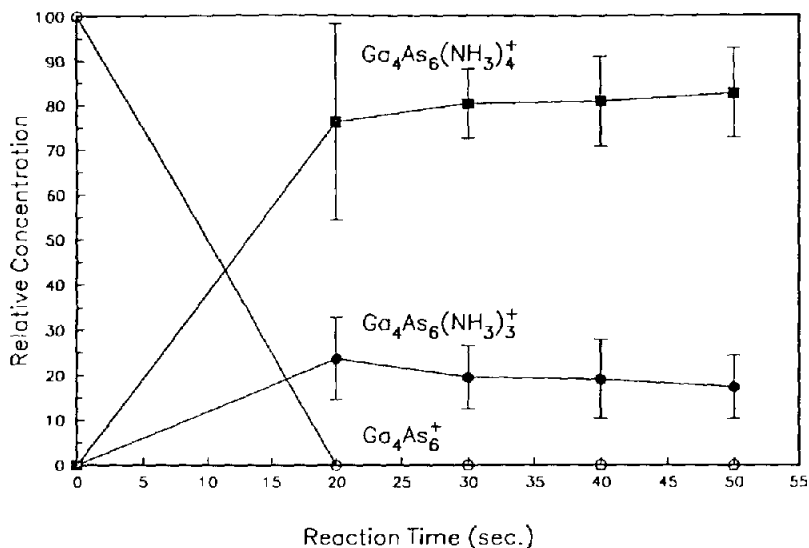


Fig. 2. The relative concentration of  $\text{Ga}_4\text{As}_6^+$  cluster and its products after reaction with  $\text{NH}_3$  as a function of reaction time.

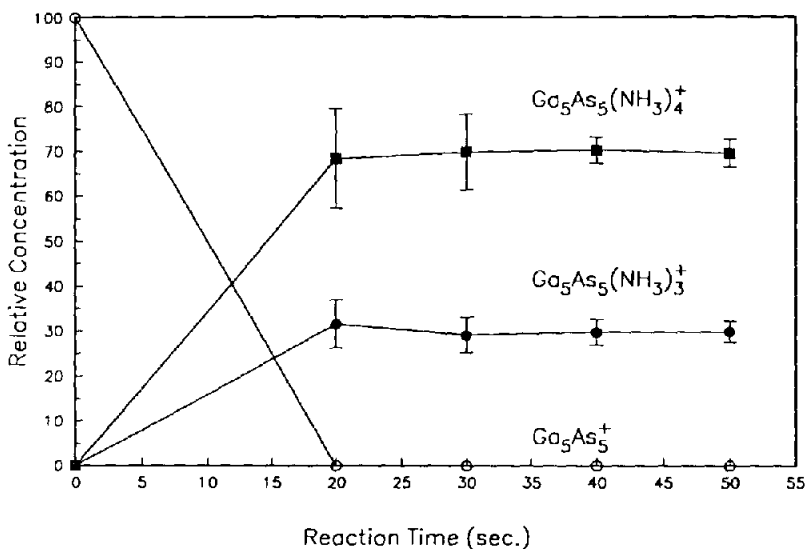


Fig. 3. The relative concentration of  $\text{Ga}_5\text{As}_5^+$  cluster and its products after reaction with  $\text{NH}_3$  as a function of reaction time.

To check whether the reaction has reached completion or just an equilibrium, we did the same experiment for 10-atom GaAs cations with five times higher ammonia pressure. The results showed the same final product distribution within experimental uncertainty, which means the above reaction was at completion and not an equilibrium, otherwise the

product distribution fractions should change with the ammonia reagent pressure.

The results shown in table 1 are from a single typical run for clusters of each size. The relative abundances of the different isomers for each stoichiometry do depend upon source conditions, although the forms of isomers as determined by the number of

Table 1

The final products and their relative abundance for some stoichiometries of  $\text{Ga}_x\text{As}_y^+$  ( $x+y=7-10, 16$ ) clusters after reaction with  $\text{NH}_3$ 

$x$	$y$	$\text{Ga}_x\text{As}_y^+$	$\text{Ga}_x\text{As}_y\text{NH}_3^+$	$\text{Ga}_x\text{As}_y(\text{NH}_3)_2^+$	$\text{Ga}_x\text{As}_y(\text{NH}_3)_3^+$	$\text{Ga}_x\text{As}_y(\text{NH}_3)_4^+$	$\text{Ga}_x\text{As}_y(\text{NH}_3)_5^+$
for $\text{Ga}_x\text{As}_y^+$ ( $x+y=7$ )							
6	1		46	54			
5	2	2	97	1			
4	3	85	6	9			
3	4	65		35			
for $\text{Ga}_x\text{As}_y^+$ ( $x+y=8$ )							
6	2	69	31		15		
5	3	4	3	78			
4	4			7	3	75	15
3	5				75	16	9
for $\text{Ga}_x\text{As}_y^+$ ( $x+y=9$ )							
8	1	8	92				
7	2	51	47	2			
6	3		3	94	3		
5	4		2	39	57	2	
4	5			3	33	64	
for $\text{Ga}_x\text{As}_y^+$ ( $x+y=10$ )							
9	1	5	95				
8	2	12	45	43			
7	3			98	2		
6	4				95	5	
5	5				30	70	
4	6				19	81	
for $\text{Ga}_x\text{As}_y^+$ ( $x+y=16$ )							
14	2	57	43				
13	3	37	54	9			
12	4	1	52	47			
11	5		14	84	2		
10	6		4	88	4	4	
9	7			9	81	10	
8	8			13	67	20	
7	9				72	28	

$\text{NH}_3$  atoms absorbed does not change. The cluster source was miniaturized during this investigation [5]. The reaction of 10-atom GaAs cations generated by the new source showed that about 60% of  $\text{Ga}_5\text{As}_5^+$  clusters reacted to form  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_3$ , and about 40% reacted to form  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_4$ , compared with 30% of  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_3$  and 70% of  $\text{Ga}_5\text{As}_5^+(\text{NH}_3)_4$  with the previous cluster source.

Similar final product reaction studies were conducted for 7-, 8-, 9- and 16-atom positive GaAs clusters. The final products observed after reaction with

$\text{NH}_3$  together with their relative abundances are tabulated for some stoichiometries in table 1. There are more data on the Ga-rich side than on the As-rich side. Even when the source condition is optimized for generation of As-rich clusters, the laser vaporization supersonic cluster beam always generates Ga-rich clusters since As is more volatile.

We have also trapped negatively charged GaAs clusters in the FT-ICR cell and exposed them to  $\text{NH}_3$  gas. No reaction was observed.

Table 2

Relative stoichiometric concentrations for  $\text{Ga}_x\text{As}_y^+$  ( $x+y=10$ ) before and after reaction with  $6 \times 10^{-6}$  Torr of  $\text{NH}_3$  for 40 s. The concentrations of  $\text{Ga}_3\text{As}_7^+$  and  $\text{Ga}_9\text{As}_1^+$  are ignored. The sum is the summation of all the products corresponding to one stoichiometry

Before reaction			After 40 s of reaction							
Ga	As	parent	Ga	As	parent	+ (NH <sub>3</sub> )	+ (NH <sub>3</sub> ) <sub>2</sub>	+ (NH <sub>3</sub> ) <sub>3</sub>	+ (NH <sub>3</sub> ) <sub>4</sub>	sum
4	6	3.3	4	6				0.7	3.2	3.9
5	5	14.1	5	5				4.1	9.7	13.8
6	4	14.5	6	4				15.7	0.9	16.6
7	3	41.4	7	3		0.3	43.1	0.5	0.2	44.1
8	2	20.3	8	2	2.2	8.4	8.1			18.8
9	1	3.7	9	1	0.1	2.4				2.5

#### 4. Discussion

Presumably the  $\text{NH}_3$  chemisorption is through formation of a dative bond between the lone pair of the Lewis base,  $\text{NH}_3$ , and an electron deficient gallium atom. The table for each cluster size except seven in table 1 resembles a band matrix indicating that positive GaAs clusters near the stoichiometric 1/1 composition of bulk gallium arsenide chemisorb the largest number of  $\text{NH}_3$  molecules. Previously [1] it was found that the 1/1 composition of clusters larger than seven reacted most rapidly with  $\text{NH}_3$ . Thus for these clusters there appears to be correlation between composition reaction rate and extent of reaction with rate and extent being largest for the 1/1 composition. In the previous rate study [1], it was found that six and seven atom clusters behaved differently from larger clusters being generally less reactive with the highest reactivity on the Ga-rich side. Here we find extent of reaction also correlates with rate for the seven atom cluster being larger on the Ga-rich side.

In some way As atoms must activate a gallium atom for  $\text{NH}_3$  attack. Probably the activating arsenics are neighbors to the Ga being activated. An attractive hypothesis supported by local functional density calculations of neutral GaAs clusters [7] is that in the cluster structure each Ga atom has as many As neighbors as possible (and vice versa). This arsenic activation model is in agreement with the observation that pure liquid Ga metal does not react with  $\text{NH}_3$  until about  $100^\circ\text{C}$  [8]. Since the data in table 1 are mostly for the Ga-rich side, generally the more As atoms, the more ammonia molecules are absorbed as more Ga atoms are activated into Lewis

acid binding sites for the chemisorption of ammonia. We predict that when As-rich data are obtained that the positive GaAs clusters will adsorb fewer  $\text{NH}_3$  molecules as they approach As-rich side after going through the 1:1 composition.

Almost all stoichiometries show multiple final products. We believe that the only reasonable interpretation for these multiple final products is that they correspond to different isomers as characterized by numbers of chemisorbed ammonia molecules. Local functional density calculations of neutral GaAs clusters [7] have shown multiple energetically favored isomers.

It is as yet unclear whether chemisorption is followed by  $\text{NH}_3$  dissociation to produce  $-\text{NH}_2$  or  $=\text{NH}$  and surface hydrides such that each  $\text{NH}_3$  molecule occupies more than one Ga Lewis acid site. Perhaps, whether this kind of ammonia dissociation happens depends on cluster size and structure as both  $\text{Ga}_4\text{As}_5^+$  and  $\text{Ga}_8\text{As}_8^+$  adsorb at most four ammonia molecules. The chemisorption mechanism might be further studied by determining whether  $\text{NH}_3$  or some other species such as H or  $\text{NH}_2$  is photo-desorbed.

Also unexplored is how chemisorption of ammonia changes the electronic structure of the GaAs clusters. A theoretical study of ammonia chemisorption might help explain why  $\text{Ga}_4\text{As}_4^+$  and  $\text{Ga}_3\text{As}_5^+$  can adsorb the fifth ammonia molecule, where they should have less than five original Lewis active sites before any ammonia adsorption.

A simple explanation for the lack of reactivity of negatively charged GaAs clusters with  $\text{NH}_3$  is that the electron lone pair of  $\text{NH}_3$  will be on the back side of  $\text{NH}_3$  as it approaches with the cluster anion. For positively charged GaAs clusters, the lone pair will

face the clusters on approach. This is consonant with chemisorption through formation of a dative bond involving the lone pair. Reactions of GaAs clusters with other reagents are not strongly dependent upon the cluster charge. Thus the reactions of singly charged GaAs cluster reactions with NO [6] are roughly equally rapid for either anions or cations.

It would be interesting to measure the relative abundance of these multiple isomers after laser annealing [3]. The annealing process should lead to the most stable isomer providing some information about the relative binding energies of the isomers.

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### References

- [1] L. Wang, L.P.F. Chibante, F.K. Tittel, R.F. Curl and R.E. Smalley, *Chem. Phys. Letters* 172 (1990) 335.
- [2] W.D. Reents Jr., *J. Chem. Phys.* 90 (1989) 4258.
- [3] S. Maruyama, L.R. Anderson and R.E. Smalley, *J. Chem. Phys.* 93 (1990) 5349.
- [4] J.M. Alford and R.E. Smalley, *Mater. Res. Soc. Symp. Proc.* 131 (1989) 3.
- [5] S. Maruyama, L.R. Anderson and R.E. Smalley, *Rev. Sci. Instr.* 61 (1990) 3686.
- [6] L. Wang, L.P.F. Chibante, F.K. Tittle, R.F. Curl and R.E. Smalley, to be published.
- [7] L. Lou, L. Wang, L.P.F. Chibante, R.T. Laaksonen, P. Nordlander and R.E. Smalley, *J. Chem. Phys.* 94 (1991) 8015.
- [8] I.A. Sheka, I.S. Chaus and T.T. Mityureva, *The chemistry of gallium* (Elsevier, Amsterdam, 1966) p. 113.