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Davis Highway, Suite 1204, Arlington, VA 22202-4302, a ... (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	**2. REPORT DATE** 01/15/92	**3. REPORT TYPE AND DATES COVERED** Final Report, 3/15/88-9/14/91

4. TITLE AND SUBTITLE
Gallium Arsenide Clusters and Their Interfacial Physics and Chemistry

5. FUNDING NUMBERS
DAAL03-88-K-0039

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MAY 4 1992
S C D

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRES
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 25222.8-CH

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Gallium arsenide clusters have been studied on a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with an external supersonic cluster source. Reaction of $GaAs$ cluster cations with ammonia revealed that all cluster cations larger than seven atoms were most reactive near the 1/1 composition ratio of gallium/arsenic. The results suggest that even at this small size, the clusters begin to adopt the alternating gallium/arsenic bonding arrangement characteristic of bulk $GaAs$ crystal surfaces where gallium-arsenic bonding activates gallium atoms for ammonia chemisorption. With excess NH_3, $Ga_xAs_y(NH_3)_z^+$ with the same $GaAs$ composition (x and y) was observed with several values of z, which is explained in terms of the existence of multiple isomers of $GaAs$ clusters. However, the anions were found to be inert toward NH_3.

Nitric oxide was found to etch singly charged $Ga_xAs_y(x+y=9$ to $16)$ clusters. A pronounced even-odd alternation in cluster ion reactivity towards NO was observed with the odd numbered cluster ions which are believed to be closed shell singlets being much less reactive than the even numbered cluster ions which are of necessity open shell species.

The local density calculations of small $Ga_xAs_y(x+y \leq 10)$ have been carried out. Multiple low energy structures were found, and the electronic properties are in agreement with experimental results.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std 239-18
298-102

Gallium Arsenide Clusters & Their Interfacial Physics and Chemistry

FINAL REPORT

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15 March 1988 – 14 September 1991

U.S. Army Research Office

Contract/Grant Number ARO #DAAL03-88-K-0039

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Houston, TX 77251-1892

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I. Gallium Arsenide Cluster Etched by NO

Reactions of both positive and negative Ga_xAs_y(x+y = 9 to 16) clusters with nitric oxide were studied. Nitric oxide was found to etch singly charged GaAs clusters. The charged species observed after reaction were smaller clusters in which several atoms had been lost. A pronounced even-odd alternation in cluster ion reactivity towards NO was observed with the odd numbered cluster ions which are believed to be closed shell singlets being much less reactive than the even numbered cluster ions which are of necessity open shell species.

1. Introduction

Gallium arsenide continues to grow in importance as a material for semiconductor and laser devices. Because these devices are made of multiple layers of very thin films, surface effects play an important role in determining their performance. In small clusters such as those studied here, surface effects are emphasized and thus experimental studies of small GaAs clusters can provide direct information on surface effects. Surface effects in small GaAs clusters can also be investigated by *ab initio* theoretical calculations, although the number of electrons which must be treated requires the use of approximate methods with presently available computing power. Experimental investigations of these clusters therefore play an important role in providing independent information to verify and calibrate quantum chemical calculations structure and properties of these small clusters. Illustrating this symbiosis between experiment and theory, L. Lou and co-workers[1] in this group have used the local density method to calculate electronic and geometrical structures and energies of small GaAs clusters(1 to 10 atoms). These calculations showed multiple isomers and a large HOMO-LUMO gap for even-numbered clusters in agreement with the experimental results[2, 3, 4, 5].

In this paper, we report new experimental results on the reactions of small GaAs cluster ions with the reagent NO using Fourier Transform Ion Cyclotron Resonance mass spectroscopy (FT-ICR). The high mass resolution and long possible ion trapping time available of FT-ICR provide unique advantages in the study of GaAs clusters and their reactions with various reagent gases. The very high mass resolution is of particular value in differentiating isotopomers. Previous FT-ICR studies have been reported by Reents[6] and this group[7]. Reents studied reactions of HCl with GaAs negative clusters containing up to six atoms and found that the principal reaction was an etching process in which GaCl was lost converting $Ga_xAs_y^-$ to $Ga_{x-1}As_y^-$. This group found that ammonia chemisorbs onto positive GaAs clusters and the clusters near the stoichiometric 1/1 composition of bulk gallium arsenide are the most reactive.

2. Experimental

The apparatus has been described previously in detail.[8, 9] Previously, investigation of reactions of ammonia with gallium arsenide cluster ions[7] have been carried out using this apparatus in a pulse extraction mode. For the present experiments the injection mode was changed to a direct injection mode[10] in which the axis of supersonic cluster beam is coincident with that of the FT-ICR cell. The reasons for this change and the pros and cons of direct injection will now be briefly described.

In pulse extraction mode, the Wiley-McLaren extractor functions as an energy filter. Since all ions entrained in the supersonic cluster beam travel at approximately the carrier supersonic speed (in this case helium is the carrier gas), the extractor is actually a mass filter limiting the mass range of ions that can be efficiently injected into the ICR cell. This is helpful only if it is desirable for an experiment to limit observations to a narrow mass range of clusters. Since the power supply of the extractor is limited to about 700 volts, the maximum mass of ions that can be extracted is about several thousand amu although this limitation can be alleviated by using a tilted extraction stack[11] or higher extraction voltage. However, a better solution to this problem is to use direct injection of the beam. For ions in helium supersonic beam at room temperature, every 100 amu has only about 2 eV of kinetic energy. Therefore, a potential difference of 8 volts between the front door and back door of the ICR cell will easily trap ions with mass range of up to 400 amu. This range is broadened further because there is a distribution of ion velocities[12]. It is thus possible to study simultaneously GaAs clusters over the range from 9 to 16 atoms (about 500 amu). The experimental cycle using direct injection is similar to that described previously[7] except that the pulse extractor is not used and the decelerating voltage is much lower for this mass range (approximately 10 to 20 volts).

There are disadvantages to direct injection mode. In extraction mode, only ions of a single charge polarity in the proper mass range are allowed into the ICR cell, while in direct injection mode, helium carrier gas atoms and cluster ions of both polarities and neutrals enter the cell. The ions injected in a single pulse occupy form a small ion cloud near the axis of the cell and feel a very uniform magnetic field. Multiple injections are usually necessary to build up ions in the cell. As atoms, clusters and ions from later injections pass through the cell, their collisions with the trapped ions enlarge the trapped ion cloud. As a result of this larger ion cloud, the center of the cloud cannot be excited as close as a smaller ion cloud to the detection plates, which leads to weaker signals.

As mentioned in previous work[7], gallium has two naturally occurring isotopes ^{71}Ga (40%) and ^{69}Ga(60%) complicating the mass spectrum. For example, the mass locations of isotopomers in each stoichiometry for Ga_xAs_y $(x + y = 10)$ are illustrated in Fig. 1. All the peaks are approximately 2 amu apart and adjacent stoichiometries

Ga_xAs_y and Ga_{x+1} As_{y-1} overlap x-1 number of peaks (for x>=2). Those overlapping mass peaks cannot be resolved even by the current high resolution FT-ICR mass spectrometer due to signal damping and limited FFT data length. Notice that the pure arsenic cluster peak is 4 amu from the next peak, as will be seen in the experiment to be described below.

For these mass spectra, the concentration for each stoichiometry is obtained from the mass spectrum by least-squares fitting the intensities assuming that the concentration distributions of isotopomers are binomial. This assumption should be valid to a good precision, since isotopic mass effects in the chemical kinetics forming the clusters are expected to be very small because the relative change in mass with isotopic substitution is very small.

3. Observations and results

Singly charged Ga_xAs_y clusters (x+y = 9 to 16) were generated in the direct injection supersonic cluster beam source and trapped in the ICR cell. Then they were exposed to nitric oxide gas with the number of collisions between the reagent and clusters being controlled by time of exposure. Negative and positive cluster ions were studied separately as shown in Fig. 2 and Fig. 3 respectively. A pronounced even/odd alternation in reactivity can be seen in both figures with the even-numbered singly charged clusters being more reactive than the odd-numbered ones. For the odd-numbered singly charged clusters, some of the profiles appear slightly changed after initial exposure to the reagent NO, but the overall profile width does not change much until the fourth panels which are the spectrum after 10 seconds of reaction with $1x10^{-5}$ torr of nitric oxide. We shall see that these initial profile changes for the odd clusters are not caused by reactions of the odd number cluster being studied, but instead are simply due to reaction products from larger clusters.

The reactions of clusters of a given x+y were studied individually. A particular x+y value was selected by sweeping out all the other sizes using SWIFT technology[13] and then NO was introduced. Because of the mass isotope degeneracy described above, it is impossible even with the most sophisticated SWIFT technology to separate out a cluster with a single chemical composition for reaction. Thus only the clusters of given x+y are separated. The mass spectra of negative and positive Ga_xAs_y (x+y = 10) clusters after exposure to nitric oxide are presented in Fig. 4 and Fig. 5 respectively and the mass spectrum of $Ga_xAs_y^-$ (x+y = 14) is presented in Fig. 6. From Fig. 6, we can explain the initial growth in the nine atom cluster between the top and second panel of Fig. 2 as being due to the production of the nine atom clusters from the fourteen atom clusters by reaction: the reaction of $Ga_xAs_y^-$ (x+y = 14) with NO gives a product at size 9 as shown in Fig. 6.

The product ions for $Ga_xAs_y^-$ (x+y = 10) are identified as $Ga_xAs_y^-$ (x+y = 5), $Ga_xAs_yN^-$ (x+y = 8) and the principal product ions of $Ga_xAs_y^-$ (x+y = 14) are $Ga_xAs_y^-$ (x+y = 9) and $Ga_xAs_yN^-$ (x+y = 12). This general pattern of x+y -> x+(y-5) and x+y -> x+(y-2)+N is seen for all negative cluster ions. As_5^- clusters can readily be identified as one of the products as labeled in Fig. 4, standing out because pure arsenic clusters are 4 amu rather than 2 amu from the next mass peak. The product ions for $Ga_xAs_y^+$ (x+y = 10) are identified as $Ga_xAs_y^+$ (x+y = 5), $Ga_xAs_yN^+$ (x+y = 6) and small amount of $Ga_xAs_yN^+$ (x+y = 8). This general pattern of x+y -> x+(y-5) , x+y -> x+(y-4)+N, and x+y -> x+(y-2)+N is seen generally for the positive cluster ions. Thus the cations and anions share two major reaction channels, x+y -> x+(y-5), x+y -> x+(y-2)+N. The cations have the additional channel of x+y -> x+(y-4)+N.

Note that the parent cluster profiles change upon the reaction implying that different stoichiometries have different reaction rates. However, measuring the reaction rates presents some difficulties. Observing an ion requires exciting its cyclotron motion; this gives the ion translational energy changing its reaction rate. Thus, in these experiments, data at only one exposure time is obtained from a single loading of ICR cell. As noted above, the filling is not very reproducible. Therefore, the time zero concentration of a cluster ion, which is needed in order to determine its absolute reaction rate, is not available. However, relative rates can be measured.

In one reaction run, the relative concentrations of the different compositions of unreacted cluster ions can measured by least squares fitting of the profiles with an isotope distribution as described previously[7]. Then relative reaction rates can be determined choosing the most unreactive composition as a reference. Suppose we call this species, r, (for reference) and consider the reaction of a more reactive species, i. Then, if we knew the concentrations of each, we would have

$$k_r = -t^{-1} \ln\left[\frac{I_r(t)}{I_r(0)}\right]$$

$$k_i = -t^{-1} \ln\left[\frac{I_i(t)}{I_i(0)}\right]$$

Thus

$$k_i = k_r + t^{-1} \left(\ln\left[\frac{I_i(t)}{I_r(t)}\right] - \ln\left[\frac{I_i(0)}{I_r(0)}\right]\right)$$

The quantity measured is the concentration of species i relative to species r, $R_i(t)=I_i(t)/I_r(t)$, which varies only slightly from filling to filling. This gives

$$k_i = k_r + t^{-1}\ln\left[\frac{R_i(t)}{R_i(0)}\right]$$

Since the reference species r is chosen to be the least reactive, the quantities

$$t^{-1}\ln\left[\frac{R_i(t)}{R_i(0)}\right]$$

which are presented in the small framed charts inside Figs. 4, 5 and 6 represent lower bounds to the reaction rates. Note that points plotted in the figures should be **added** to the reference rate, k_r, rather than multiplied by it. The reference rate, k_r, can be roughly estimated to be much smaller than most of the other rates making the lower bounds reasonably good estimates of the actual rates. General conclusions, which may be inferred from examinations of Figs. 4, 5 and 6, are that the gallium rich clusters are more reactive and compositions near the stoichiometric 1/1 are least reactive.

The reaction results for $Ga_xAs_y^-$ (x+y = 9) and $Ga_xAs_y^+$ (x+y = 9) clusters are shown in Fig. 7 and Fig. 8 respectively. The positive ions are almost inert with no products observed. The x+y=9 anions are, as is characteristic of odd numbered cluster anions, very unreactive too. Depletion rate constants for the $Ga_xAs_y^-$ (x+y = 9) clusters were calculated with respect to $Ga_3As_6^-$ as described above and are presented in the small inset inside Fig. 7. These rate constants are approximately an order of magnitude smaller than those for the even-numbered anion clusters. As can be seen in the inset, the gallium rich clusters for x+y=9 are again more reactive toward nitric oxide.

From the mass spectrum at a given reaction time, the relative concentrations of all the products to the then unreacted material can be calculated. The relative concentrations of different stoichiometries before and after reaction (corresponding to the bottom panel in the figures) are given in Table I and Table II for Figs. 4 and 5 respectively. These two tables indicate that the ionic products of reactions of negative clusters are arsenic rich and those of positive clusters are gallium rich. The product ions are aligned in rows of the tables according to proposed reaction channels which will soon be described.

Note that in both tables the relative concentration of the unreacted Ga_4A_6 cluster is larger than the relative concentration before reaction, and in Table I for the positive ion, the relative concentration of the $Ga_5As_5^+$ ion after reaction is about twice its relative concentration before reaction. This implies that there must be unobservable products as these reactants can not be increasing in intensity upon treatment with nitric oxide. The low mass limit of the current ICR mass spectrometer is approximately 100 amu; thus there may be unobserved small mass ionic products. The amount of undetected product is difficult to estimate especially as comparison of intensities from a run after some reaction time with intensities from an initial run is made even more unreliable by the changes in intensity caused effects on the ion cloud size by unreactive collisions. However, taking into account the lack of reproducibility between different fillings and such collisional effects, it seems clear that these clusters are almost unreacted at the bottom panel of the Figs. 4 and 5 making the unobservable products about equal to the observable products.

The neutral species are, of course, undetectable. As a result, there is no direct way to correlate the products with reactants from the experiment. As a way of sorting out reaction channels, start with the fact that As_5^- is clearly observed in Fig. 4. All the $Ga_4As_6^-$ appears to be almost unreacted and $Ga_3As_7^-$ is initially only a trace. Thus the only possible source of As_5^- is $Ga_5As_5^-$ and we propose the reaction:

$$Ga_5As_5^- + NO \text{ -> } As_5^- + Ga_2O + Ga_3N$$

Ga_2O and Ga_3N are proposed unobservable neutral products because, recent preliminary results of local density calculations[14,12] indicate that Ga_2O and Ga_3N are very stable species. Generalizing this reaction we have

$$Ga_xAs_y^- + NO \text{ -> } Ga_{x-5}As_y^- + Ga_2O + Ga_3N$$

for x = 6 - 9. The GaAs clusters produced in our supersonic cluster beams are always Ga-rich, this reaction channel provides a means for producing negatively charged As-rich clusters.

Similarly, the only sources of $Ga_2As_6N^-$ product are $Ga_4As_6^-$ and $Ga_3A_7^-$ and $Ga_3As_7^-$ seems to be present initially in too small a concentration to account for it. Thus we propose the reaction:

$Ga_4As_6^- + NO \text{->} Ga_2As_6N^- + Ga_2O$

Generalizing this reaction we have

$Ga_xAs_y^- + NO \text{->} Ga_{x-2}As_yN^- + Ga_2O$

for x = 4, 5 and 6.

These two general reactions account for all the observed products for $Ga_xAs_y^-$ (x+y = 10), and the same scheme can be applied to the anions with x+y=14 in Fig. 6. Two additional small products are seen in Fig. 6, $Ga_xAs_yO^-$ (x+y=10) and $Ga_xAs_yO_2^-$ (x+y=12). The latter can come only from reaction with two NO's or possibly from reaction with background O_2 (the NO pressure is only 10^{-7} Torr). No attempt will be made here to characterize these minor products. It is interesting to note, however, that O containing anion products might be expected instead of pure GaAs or N containing anion products as O has by far the largest electronegativity of any of the atoms present.

There are similarities between the reaction pattern $Ga_xAs_y^+$ (x+y=10) and that of $Ga_xAs_y^-$ (x+y=10). Both anion channels are seen for the cation. However, the x+y -> x+(y-2)+N channel is only a minor channel for the cation being replaced by a x+y -> x+(y-4)+N channel. Ga_5AsN^+ is almost the only product of this channel. The identity of the reactant is speculative. $Ga_6As_4^+$ or $Ga_7As_3^+$ are reasonable choices; $Ga_8As_2^+$ probably could not supply enough material and $Ga_5As_5^+$ certainly could not. We suggest:

$Ga_7As_3^+ + NO \text{->} Ga_5AsN^+ + Ga_2O + As_2$

as As_2 is known to be stable. The general reaction of this sort is

$Ga_xAs_y^+ + NO \text{->} Ga_{x-2}As_{y-2}N^+ + Ga_2O + As_2$

for x = 4, 5 and 7.

If the proposed reactions are correct and the only reactions taking place, the sum of the percentages after reaction at the end of a row in Tables I and II to those before reaction should be unity. In the light of the previous arguments showing that there must be unobserved product ions, the agreement seen for the several of the gallium-rich clusters has to be fortuitous.

4. Discussion

The even/odd alternation in reactivity of singly charged GaAs clusters toward nitric oxide (Fig. 2 and Fig. 3) is strong evidence confirming that the odd-numbered singly charged GaAs clusters have closed-shell singlet ground states. The even-numbered ions, which have an odd number of valence electrons, are necessarily open-shell. The free radical, nitric oxide, is a well-known radical scavenger. Thus it is quite reasonable that NO will react rapidly with the free radical singly charged even-numbered GaAs clusters. In contrast, the closed-shell reagent, ammonia, showed no evident reaction preference between even-numbered and odd-numbered positive GaAs clusters[7]. In earlier work, photoionization studies of the neutral GaAs cluster beam revealed a strong even/odd alternation in the ionization potentials[3] and photodetachment studies of the negative clusters showed corresponding odd/even alternation in the electron affinities[4, 5] of the clusters. Those results suggested that all the even-numbered neutral clusters have closed-shell singlet ground states with substantial HOMO-LUMO gaps. The odd-numbered neutral clusters must be open-shell species as they have odd number of valence electrons. The experiments reported here further confirmed the conclusion that GaAs species with an even number of electrons generally are closed-shell singlets.

The reactions of $Ga_xAs_y^+$ (x+y = 10) and $Ga_xAs_y^-$ (x+y = 10) with NO seemingly require complete reorganization of the bonding. The bonding of NO to the cluster must release enough energy to overcome any activation barrier to dissociation of the NO as the N and O atoms form bonds to gallium atoms, and it will also weaken the NO bond because the LUMO of NO is an anti-bonding orbital. The resulting energy release results in fragmentation of the cluster ion into neutral fragment(s) containing O and sometimes N and a fragment ion, which does not contain O and often not N. Thus these NO reactions with GaAs cluster ions are etching reactions similar to HCl reactions studied by Reents[6] in contrast with the addition reactions of NH_3.

GaAs clusters around 1/1 stoichiometry are less reactive toward NO. This can be seen more clearly in reaction of $Ga_xAs_y^-$ (x+y=14) with NO because there are more data points on the Ar-rich side. A model accounting for this can be constructed by picturing these reactions as involving two stages. In the first, NO is bonded to the cluster ion releasing energy. This energy then "melts" the cluster permitting a more facile attack of the Ga atoms on the NO. Blackemore[15] presented the phase diagram for Ga-As binary system as a function of composition. In this diagram there is a maximum melting temperature at stoichiometric GaAs indicating GaAs compound formation. The two halves of the diagram (Ga-rich and As-rich) each exhibit normal eutectic behavior. The melting temperature of GaAs is 1513 K, that of Ga is 303 K, and that of gray As is 1090 K. If it is assumed that GaAs clusters even at this size have adopted some bulk properties, then GaAs clusters around 1/1 stoichiometry would have a higher melting point and thus not be as readily activated by the energy released by binding NO to the cluster to attack the NO bond. This rationalization is supported by other experiments[5, 7] which have shown indications that GaAs clusters start to adopt some bulk properties at small size.

The bonding of NO to odd-numbered singly charged GaAs clusters should be much weaker because the odd-numbered ions have closed shell structure. Thus these is less energy available from attachment of the NO to provide the "melting" activation energy for attack on the NO bond.

The general tendency observed for the positive ionic products to be gallium rich is in accord with the fact that the ionization potential of Ga is much lower than that of As. Likewise the negative ionic products are generally arsenic rich as might be expected on the basis that arsenic atoms are more electronegative than gallium atoms.

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Table I. Relative stoichiometric concentrations for $Ga_xAs_y^-$ (x+y = 10) before and after reaction with $1x10^{-7}$ torr of nitric oxide for 32 sec. The products are aligned according to the proposed reaction channels. Total is the sum of percentage concentrations over a reaction channel.

Before		**After Reaction**						
Parents	**%**	**Parents**	**%**	**Products**	**%**	**Products**	**%**	**Total**
$Ga_3As_7^-$	0.9	$Ga_3As_7^-$	1.4					1.4
$Ga_4As_6^-$	4.5	$Ga_4As_6^-$	7.4	$Ga_2As_6N^-$	2.7			10.1
$Ga_5As_5^-$	18.0	$Ga_5As_5^-$	6.4	$Ga_3As_5N^-$	6.0	As_5^-	6.9	19.3
$Ga_6As_4^-$	30.4	$Ga_6As_4^-$	3.1	$Ga_4As_4N^-$	11.9	$Ga_1As_4^-$	18.4	33.4
$Ga_7As_3^-$	31.8					$Ga_2As_3^-$	26.8	26.8
$Ga_8As_2^-$	12.5					$Ga_3As_2^-$	8.3	8.3

Table II. Relative stoichiometric concentrations for $Ga_xAs_y^+$ (x+y = 10) before and after reaction with $1x10^{-7}$ torr of nitric oxide for 10 sec. The products are aligned according to the proposed reaction channels. Total is the sum of percentage concentrations over a reaction channel.

Before		**After Reaction**								
Parents	**%**	**Parents**	**%**	**Products**	**%**	**Products**	**%**	**Products**	**%**	**Total**
$Ga_4As_6^+$	3.4	$Ga_4As_6^+$	5.0			$Ga_2As_4N^+$	0.5			5.5
$Ga_5As_5^+$	10.4	$Ga_5As_5^+$	20.5			$Ga_3As_3N^+$	0.5			21.0
$Ga_6As_4^+$	27.9	$Ga_6As_4^+$	9.5			$Ga_4As_2N^+$	0.3	$Ga_1As_4^+$	4.3	14.1
$Ga_7As_3^+$	37.7	$Ga_7As_3^+$	15.4	$Ga_5As_3N^+$	1.1	$Ga_5As_1N^+$	16.4	$Ga_2As_3^+$	2.9	32.9
$Ga_8As_2^+$	18.3	$Ga_8As_2^+$	7.1	$Ga_6As_2N^+$	1.6			$Ga_3As_2^+$	10.2	18.9
$Ga_9As_1^+$	1.6	$Ga_9As_1^+$	1.2					$Ga_4As_1^+$	2.3	3.5

Figure Captions

Fig.1. The mass locations of isotopomers in each stoichiometry for Ga_xAs_y (x+y=10). The overlapping mass peaks cannot be resolved by the current high resolution FT-ICR mass spectrometer.

Fig. 2. $Ga_xAs_y^-$(x+y=9 to 16) clusters reacting with nitric oxide. An even/odd alternation of reactivity is apparent.

Fig. 3. $Ga_xAs_y^+$(x+y=9 to 16) clusters reacting with nitric oxide. An even/odd alternation of reactivity can be seen.

Fig. 4. $Ga_xAs_y^-$ (x+y = 10) clusters reacting with nitric oxide. The inset shows the absolute increase in depletion rate constant of different stoichiometries in the clusters over that of $Ga_4As_6^-$ which is the least reactive composition. The identified products are $Ga_xAs_yN^-$ (x+y = 8), and $Ga_xAs_y^-$ (x+y = 5). The small bump in the top panel, where the peak spacings are twice as dense as original signals, is the second harmonic.

Fig. 5. $Ga_xAs_y^+$ (x+y = 10) clusters reacting with nitric oxide. The inset shows the absolute increase in depletion rate constant of different stoichiometries in the clusters over that of $Ga_5As_5^+$ which is the least reactive composition. The identified products are $Ga_xAs_yN^+$ (x+y = 8), $Ga_xAs_yN^+$ (x+y = 6), and $Ga_xAs_y^+$ (x+y = 5). The small bump in the top panel, where the peak spacings are twice as dense as original signals, is the second harmonic.

Fig. 6. $Ga_xAs_y^-$ (x+y = 14) clusters reacting with nitric oxide. The inset shows the absolute increase in depletion rate constant of different stoichiometries in the clusters over that of $Ga_7As_7^-$ which is the least reactive composition. The identified products are $Ga_xAs_yO_2^-$ (x+y = 12), $Ga_xAs_yN^-$ (x+y = 12), $Ga_xAs_yO^-$ (x+y = 10), $Ga_xAs_y^-$ (x+y = 9).

Fig.7. $Ga_xAs_y^-$ (x+y = 9) clusters reacting with nitric oxide. The inset shows the absolute increase in depletion rate constant of different stoichiometries in the clusters over that of $Ga_3As_6^-$ which is the least reactive composition. The products are very weak and identified as $Ga_2As_3^-$ (between 360 and 370 amu), and $Ga_xAs_y^-$ (x+y = 4, between 290 and 300 amu).

Fig.8. $Ga_xAs_y^+$ (x+y = 9) clusters reacting with nitric oxide. No products were observed and the profile changes little implying that $Ga_xAs_y^+$ (x+y = 9) clusters are very unreactive with NO.

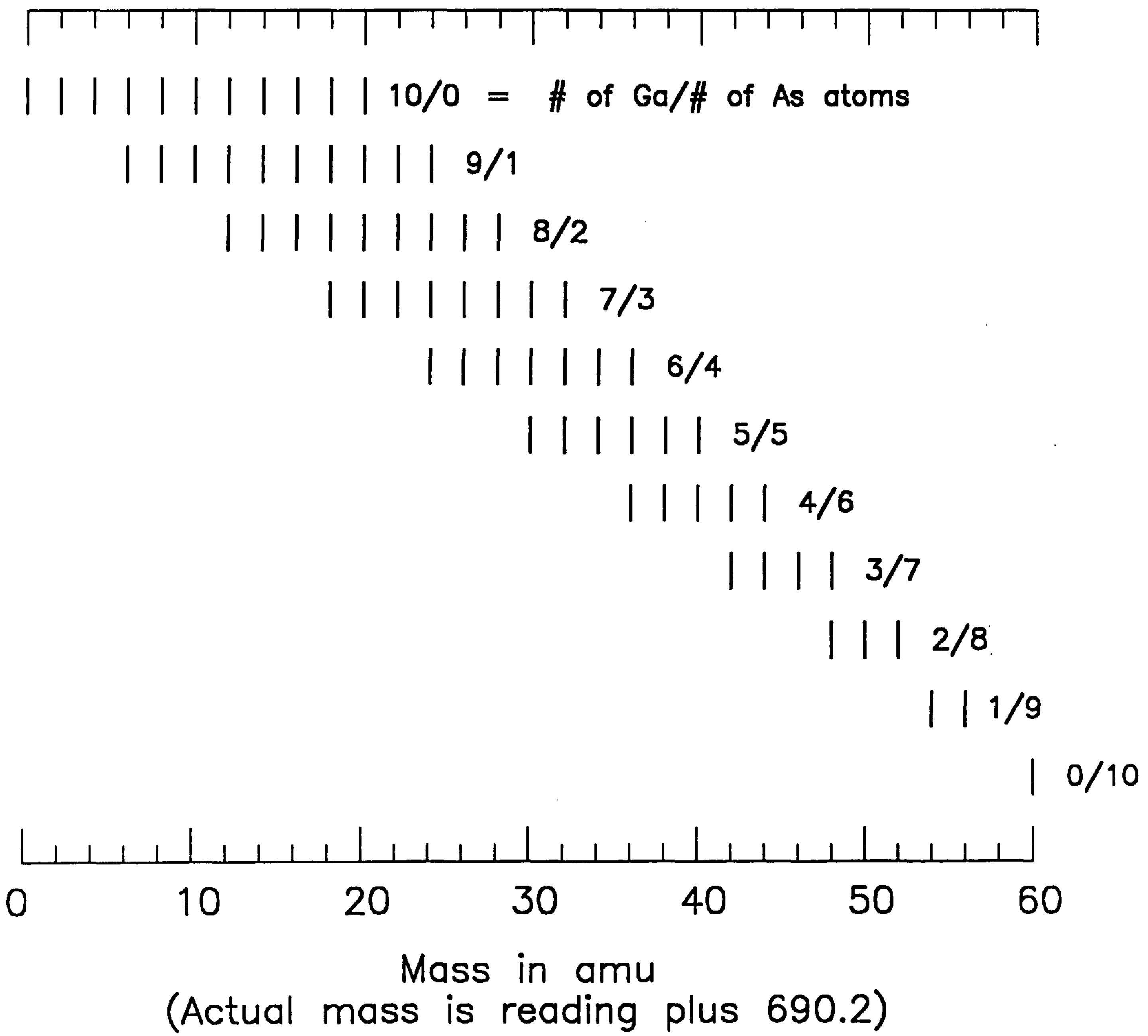
10/0 = # of Ga/# of As atoms
9/1
8/2
7/3
6/4
5/5
4/6
3/7
2/8
1/9
0/10
0
10
20
30
40
50
60
Mass in amu
(Actual mass is reading plus 690.2)

Figure 1

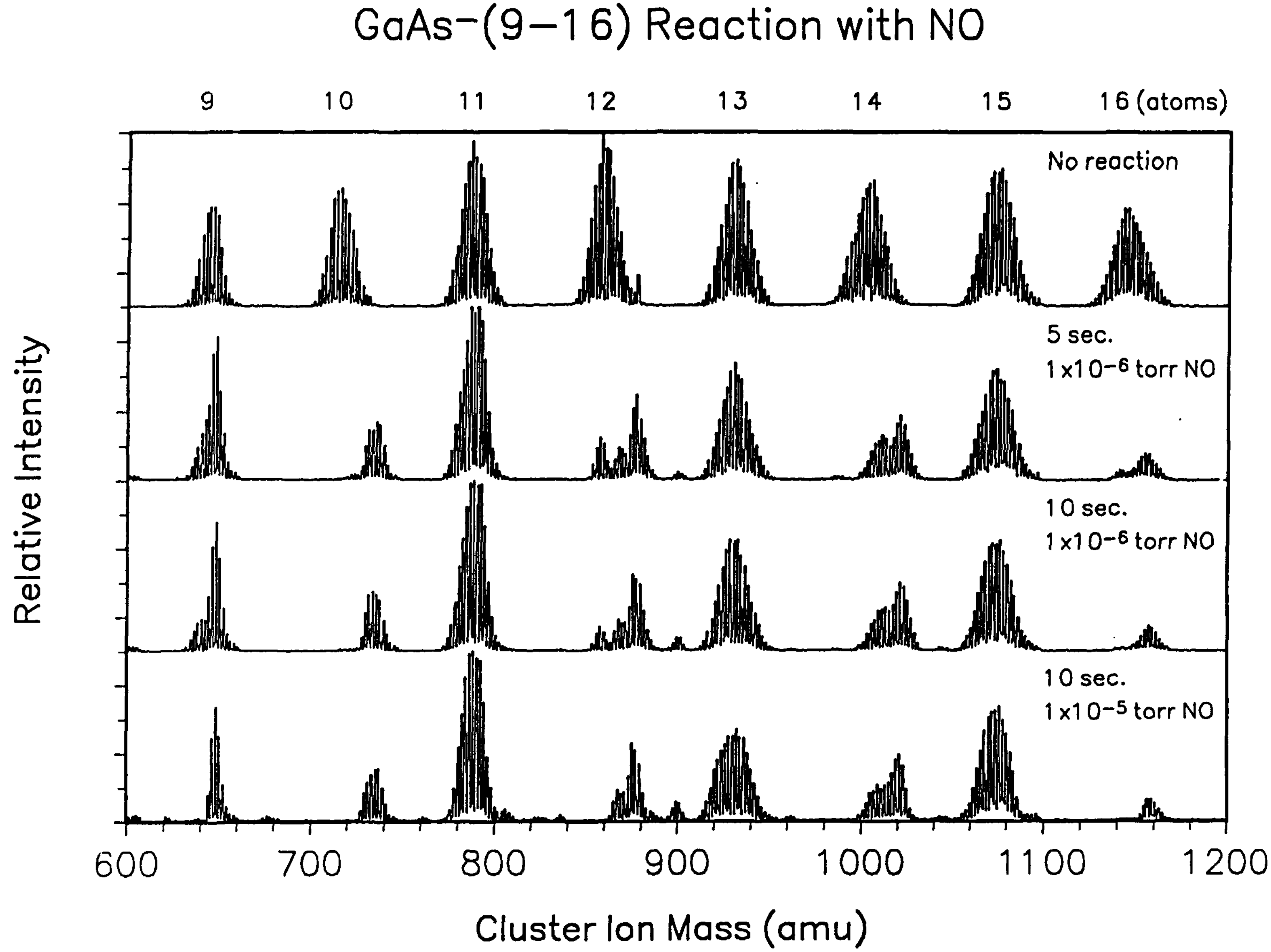
GaAs$^-$(9–16) Reaction with NO
9
10
11
12
13
14
15
16 (atoms)
No reaction
5 sec.
1x10^{-6} torr NO
10 sec.
1x10^{-6} torr NO
10 sec.
1x10^{-5} torr NO
Relative Intensity
600
700
800
900
1000
1100
1200
Cluster Ion Mass (amu)

Figure 2

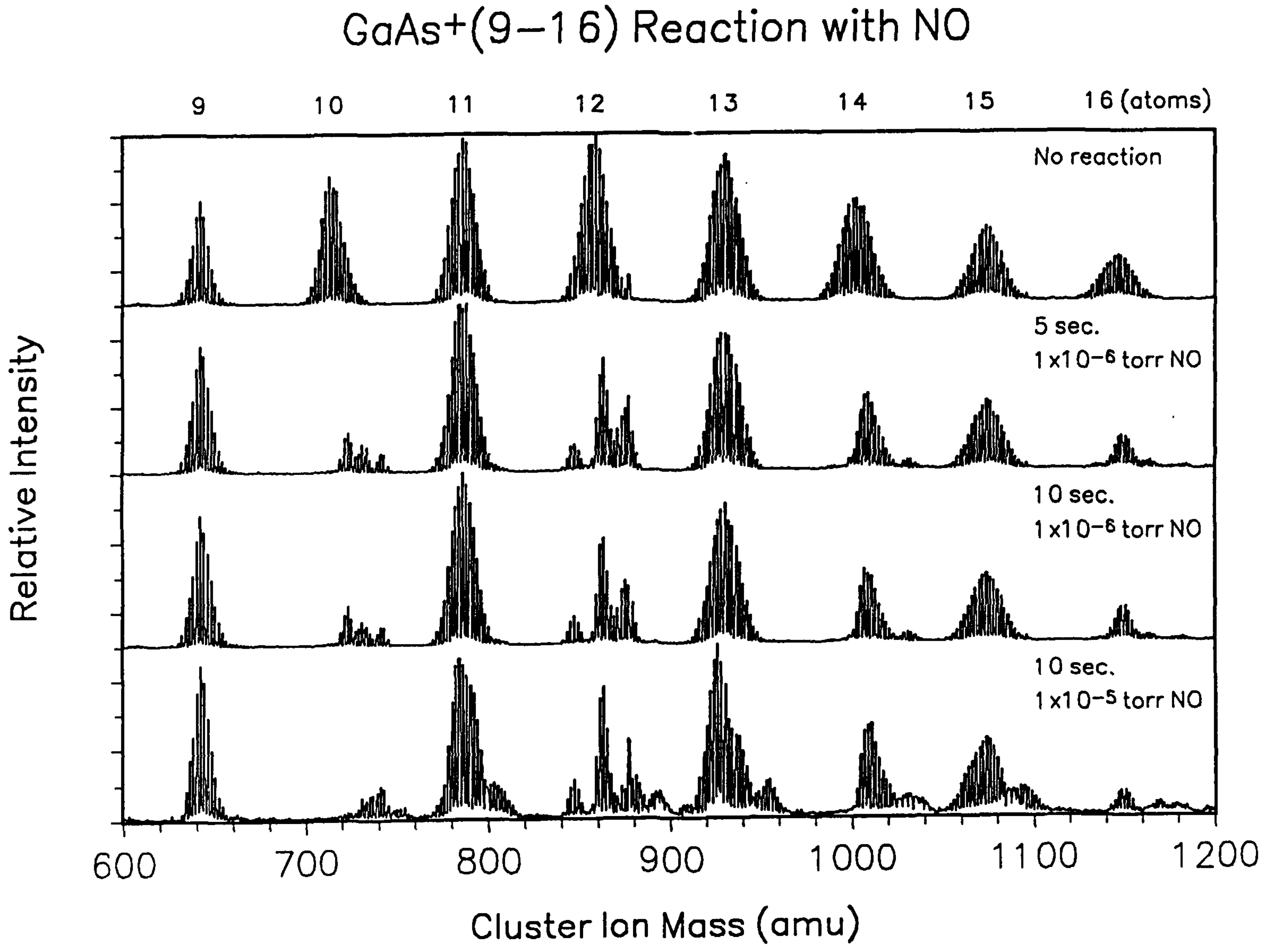
GaAs+(9–16) Reaction with NO
9
10
11
12
13
14
15
16 (atoms)
No reaction
5 sec.
1x10−6 torr NO
10 sec.
1x10−6 torr NO
10 sec.
1x10−5 torr NO
Relative Intensity
600
700
800
900
1000
1100
1200
Cluster Ion Mass (amu)

Figure 3

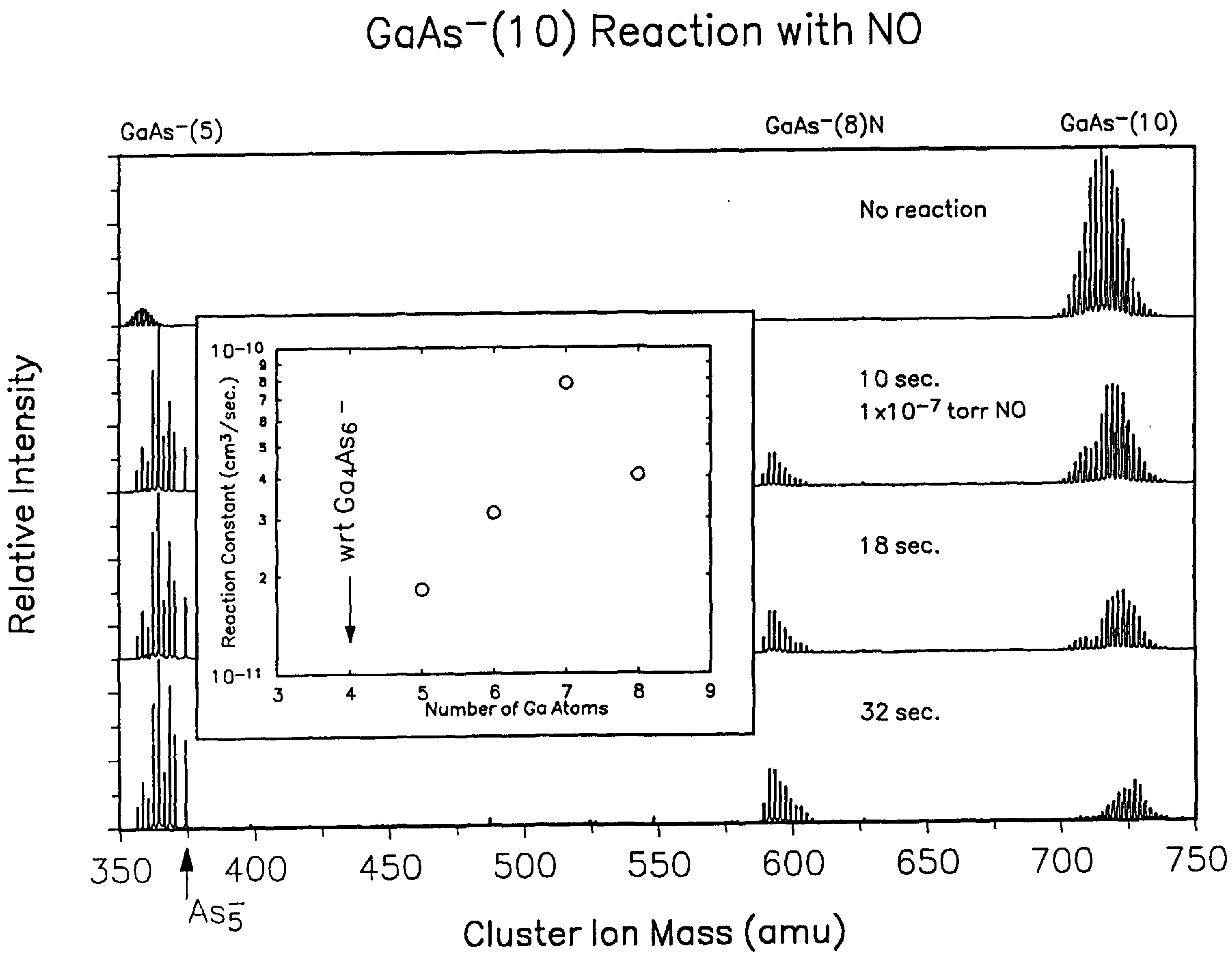
GaAs⁻(10) Reaction with NO
GaAs⁻(5)
GaAs⁻(8)N
GaAs⁻(10)
No reaction
10 sec.
1x10⁻⁷ torr NO
18 sec.
32 sec.
Relative Intensity
Cluster Ion Mass (amu)
350
400
450
500
550
600
650
700
750
As5⁻
Reaction Constant (cm³/sec.)
10⁻¹⁰
10⁻¹¹
9
8
7
6
5
4
3
2
wrt Ga4As6⁻
Number of Ga Atoms
3
4
5
6
7
8
9

Figure 4

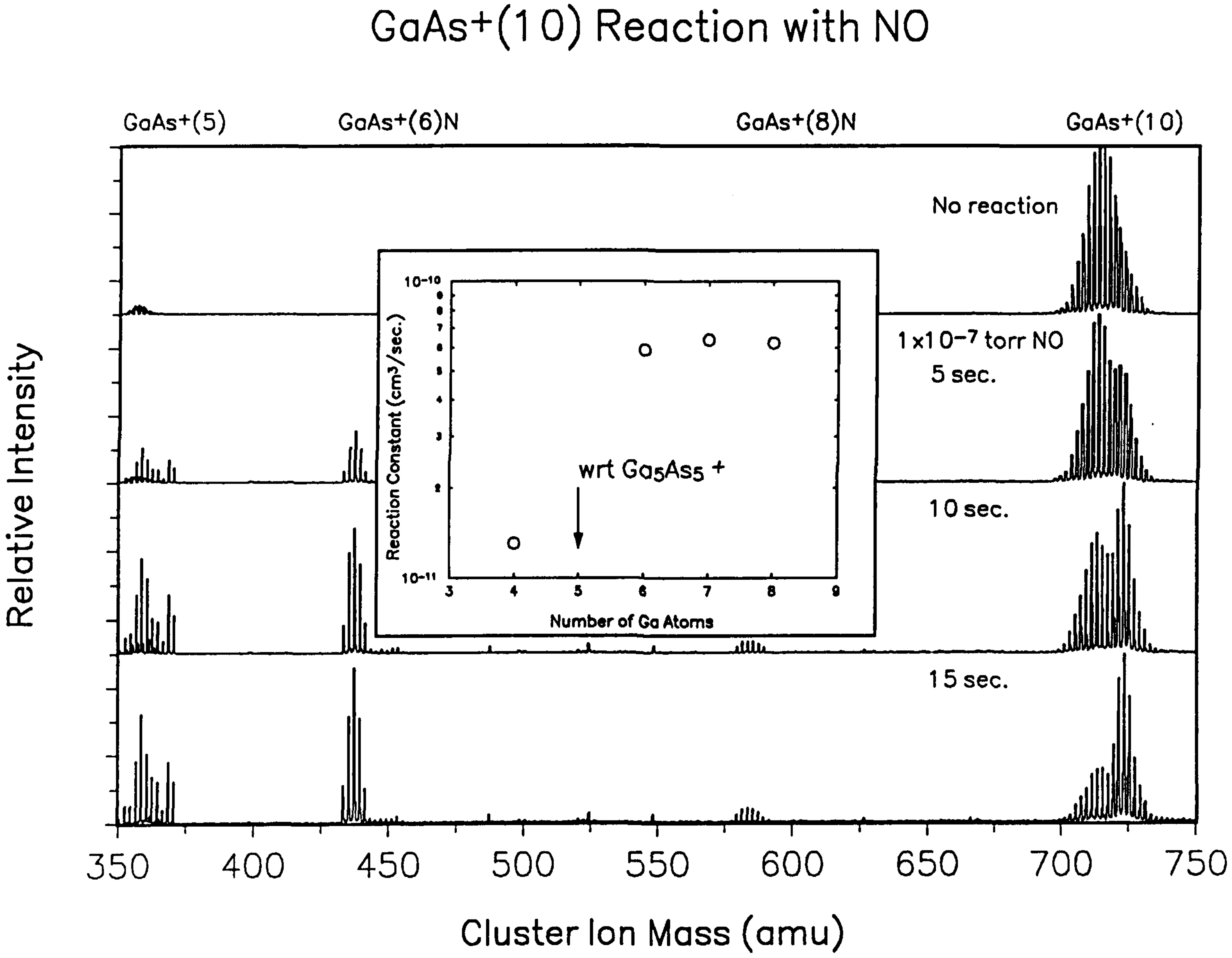
GaAs+(10) Reaction with NO
GaAs+(5)
GaAs+(6)N
GaAs+(8)N
GaAs+(10)
No reaction
1x10^{-7} torr NO
5 sec.
10 sec.
15 sec.
Relative Intensity
Cluster Ion Mass (amu)
350
400
450
500
550
600
650
700
750
Reaction Constant (cm^3/sec.)
10^{-10}
10^{-11}
Number of Ga Atoms
3
4
5
6
7
8
9
wrt Ga$_5$As$_5$ +

Figure 5

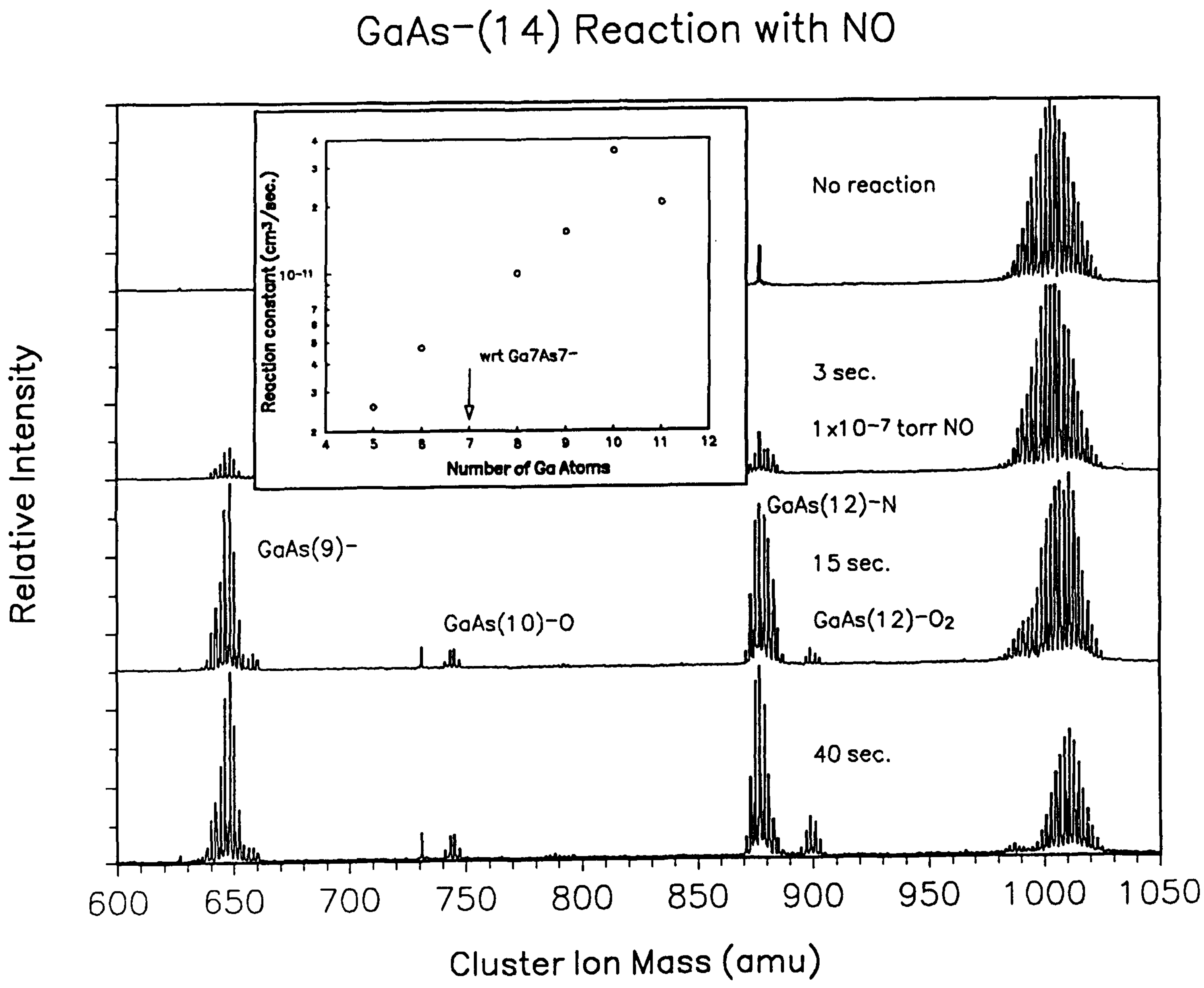
GaAs−(14) Reaction with NO
Relative Intensity
Cluster Ion Mass (amu)
600
650
700
750
800
850
900
950
1000
1050
No reaction
3 sec.
1x10−7 torr NO
GaAs(12)−N
15 sec.
GaAs(12)−O2
40 sec.
GaAs(9)−
GaAs(10)−O
Reaction constant (cm3/sec.)
10−11
Number of Ga Atoms
4
5
6
7
8
9
10
11
12
wrt Ga7As7−

Figure 6

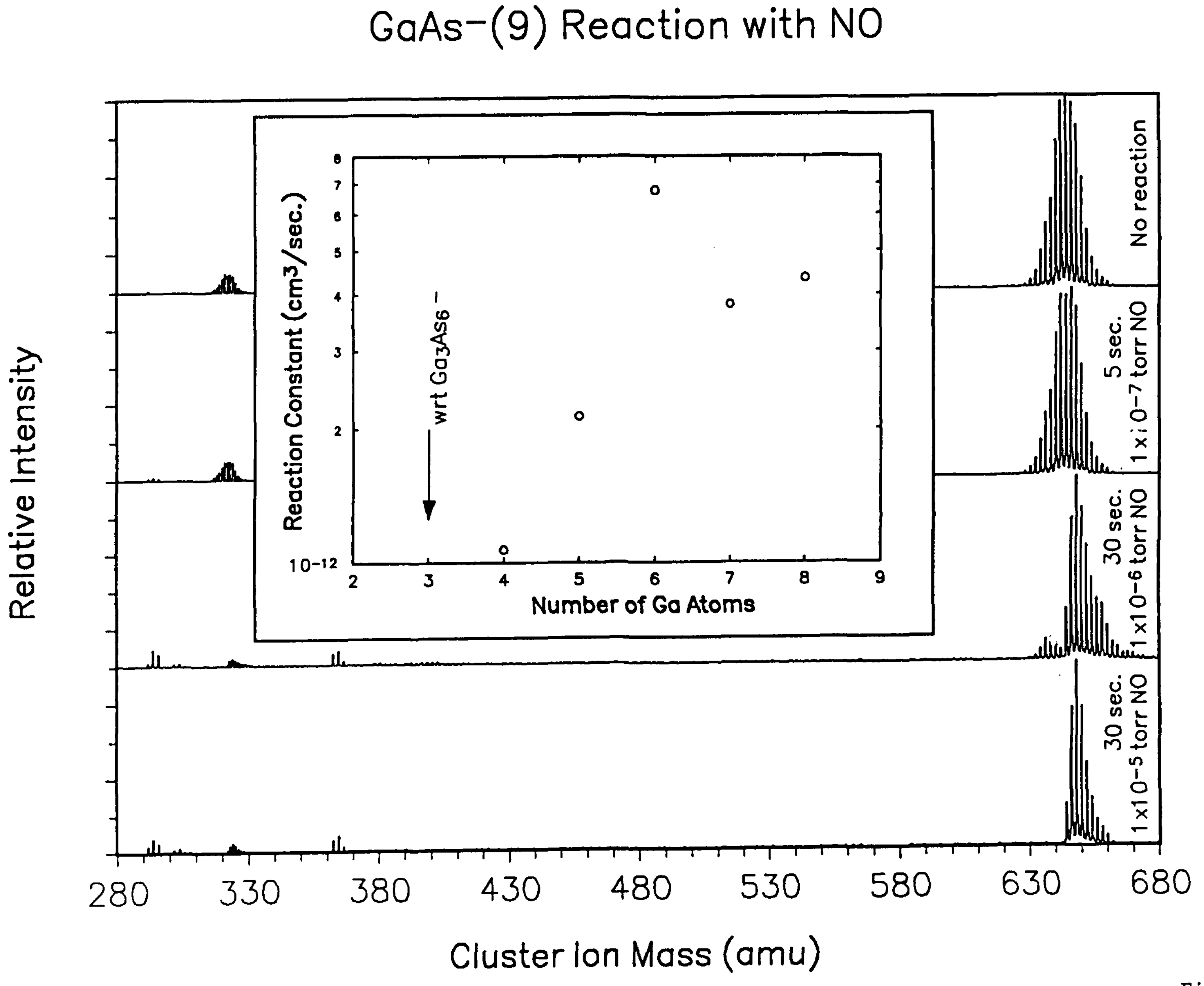
GaAs$^-$(9) Reaction with NO
Relative Intensity
Cluster Ion Mass (amu)
280
330
380
430
480
530
580
630
680
No reaction
5 sec.
1x10^{-7} torr NO
30 sec.
1x10^{-6} torr NO
30 sec.
1x10^{-5} torr NO
Reaction Constant (cm^3/sec.)
10^{-12}
2
3
4
5
6
7
8
Number of Ga Atoms
2
3
4
5
6
7
8
9
wrt Ga$_3$As$_6$$^-$

Figure 7

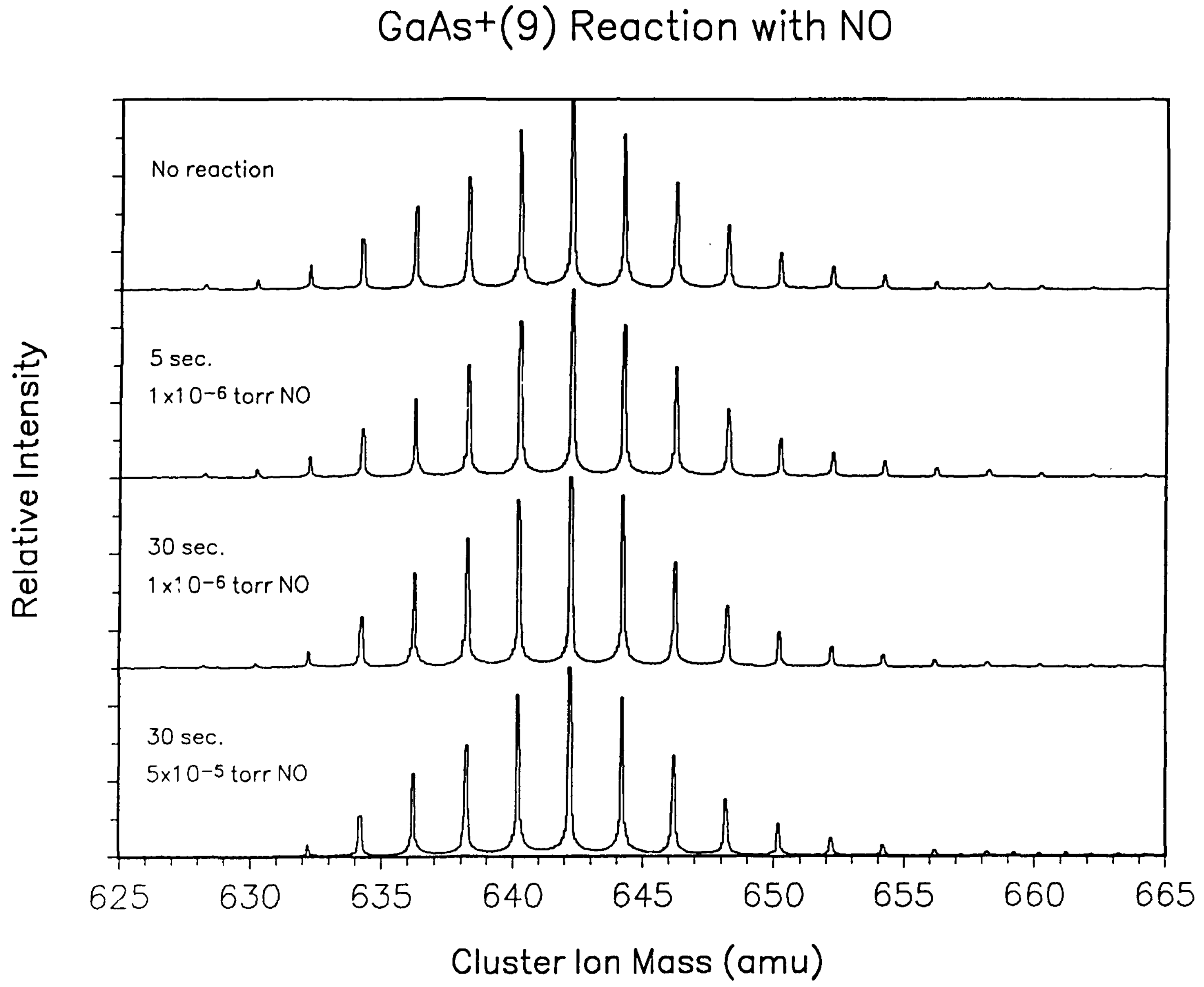
GaAs+(9) Reaction with NO
No reaction
5 sec.
1x10−6 torr NO
30 sec.
1x10−6 torr NO
30 sec.
5x10−5 torr NO
Relative Intensity
625
630
635
640
645
650
655
660
665
Cluster Ion Mass (amu)

Figure 8

II. Isomers of Gallium Arsenide Cluster Ions

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 NH_3 forming addition complexes with the cluster cations. With excess NH_3, $Ga_xAs_y(NH_3)_z^+$ with the same GaAs composition (x+y) was observed with several values of z. This observation of different numbers of chemisorbed NH_3 molecules at completion is explained in terms of the existence of multiple isomers of positive GaAs clusters. Negative $Ga_xAs_y^-$ clusters were found to be inert toward NH_3.

1. Introduction

The kinetics of positive GaAs clusters towards 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 NH_3 and observe for the same reactant composition several final products with different numbers of ammonia molecules attached. This provides strong evidence that the 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 Fourier 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 period, and identified with high mass resolution. The detailed experimental sequence and data processing have been discussed previously[1,6]. In brief, Ga_xAs_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 NH_3 at a pressure of about 10^{-5} Torr for about 30 seconds. 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 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 various chemical compositions and the overlapping isotopes of ^{69}Ga and ^{71}Ga. The following two panels in Fig. 1 show the mass spectra after 30 and 40 seconds of reaction with $6x10^{-6}$ torr of NH_3 respectively. As discussed previously[1], the reaction is chemisorption of 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 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 ten atom positive GaAs clusters, up to four ammonia molecules are chemisorbed. Reaction with the majority of stoichiometries is complete after 30 seconds, 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 $Ga_4As_6^+$ and $Ga_5As_5^+$ clusters are shown in Fig. 2 and Fig. 3 respectively. After 20 seconds, all the parent $Ga_4As_6^+$ and $Ga_5As_5^+$ 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 $Ga_4As_6^+$ clusters reacted to form $Ga_4As_6^+(NH_3)_3$, and the rest generated $Ga_4As_6^+(NH_3)_4$. In Fig. 3, it is shown that about 30% of $Ga_5As_5^+$ clusters reacted to form $Ga_5As_5^+(NH_3)_3$, and about 70% reacted to form $Ga_5As_5^+(NH_3)_4$. Results for other compositions are listed in Table 1. Among those tested, $Ga_4As_4^+$ and $Ga_3As_5^+$ are the only two stoichiometries which adsorb more than four ammonia molecules.

The relative stoichiometric concentrations for $Ga_xAs_y^+$ (x+y = 10) before and after reaction with 6×10^{-6} torr of NH_3 for 40 sec are tabulated in Table 2. The sum of all the products corresponding to one stoichiometry after reaction should be the same as the parent relative concentration before reaction theoretically. In this experiment, they are very close within the fluctuation error of experiment.

To check wether the reaction has reached completion or just an equilibrium, we did the same experiment for 10 atom GaAs cations with 5 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 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 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 $Ga_5As_5^+$ clusters reacted to form $Ga_5As_5^+(NH_3)_3$, and about 40% reacted to form $Ga_5As_5^+(NH_3)_4$, compared with 30% of $Ga_5As_5^+(NH_3)_3$ and 70% of $Ga_5As_5^+(NH_3)_4$ 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 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, because the laser vaporization supersonic cluster beam always generates Ga-rich clusters since As is more volatile, even when the source condition is optimized for generation of As-rich clusters.

We have also trapped negatively charged GaAs clusters in the FT-ICR cell and exposed them to NH_3 gas. No reaction was observed.

4. Discussion

Presumably the NH_3 chemisorption is through formation of a dative bond between the lone pair of the Lewis base, NH_3, and an electron deficient gallium atom. The table for each cluster size 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 NH_3 molecules. Previously[1] it was found that the 1/1 composition reacted most rapidly with NH_3.

In some way As atoms must activate a gallium atom for 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 NH_3 until about 100 °C[8]. Since the data in Table 1 is 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 is obtained that the positive GaAs clusters will adsorb fewer 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 number 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 NH_3 dissociation to produce $-NH_2$ or $=NH$ and surface hydrides such that each 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 $Ga_4As_5^+$ and $Ga_8As_8^+$ adsorb at most four ammonia molecules. The chemisorption mechanism might be further studied by determining whether NH_3 or some other species such as H or NH_2 is photo-desorbed.

Also unexplored is how chemisorption of ammonia changes the electronic structure of the GaAs clusters. An theoretical study of ammonia chemisorption might help explain why

$Ga_4As_4^+$ and $Ga_3As_5^+$ 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 NH_3 is that the electron lone pair of NH_3 will be on the back side of 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.

References

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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, Mat. Res. Soc. Aymp. Proc. 131 (1989) 3.

5 S. Maruyama, L.R. Anderson and R.E. Smalley, Rev. Sci. Instr. 61 (1990) 3686.

6 Lihong Wang, L.P.F. Chibante, F.K. Tittel, R.F. Curl, R.E. Smalley, to be published.

7 L. Lou, Lihong Wang, L. P. F. Chibante, R. T. Laaksonen, P. Nordlander, and R. E. Smalley, J. Chem. Phys., 94(1991),8015.

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1 Lihong Wang, L.P.F. Chibante, F.K. Tittel, R.F. Curl, R.E. Smalley, Chem. Phys. Lett. 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, Mat. Res. Soc. Aymp. Proc. 131 (1989) 3.

5 S. Maruyama, L.R. Anderson and R.E. Smalley, Rev. Sci. Instr. 61 (1990) 3686.

6 Lihong Wang, L.P.F. Chibante, F.K. Tittel, R.F. Curl, R.E. Smalley, to be published.

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8 I.A. Sheka, I.S. Chaus, and T.T. Mityureva, The Chemistry of Gallium, Elsevier Pushlishing Company, 133, (1966).

Table 1. The final products and their relative abundance for some stoichiometries of $Ga_xAs_y^+$ (x+y=7 - 10, 16) clusters after reaction with NH_3.

For $Ga_xAs_y^+$ (x+y=7)

x	y	$Ga_xAs_y^+$	$Ga_xAs_yNH_3^+$	$Ga_xAs_y(NH_3)_2^+$
6	1		46	54
5	2	2	97	1
4	3	85	6	9
3	4	65		35

For $Ga_xAs_y^+$ (x+y=8)

x	y	$Ga_xAs_y^+$	Ga_xAs_y NH_3^+	Ga_xAs_y $(NH_3)_2^+$	Ga_xAs_y $(NH_3)_3^+$	Ga_xAs_y $(NH_3)_4^+$	Ga_xAs_y $(NH_3)_5^+$
6	2	69	31				
5	3	4	3	78	15		
4	4			7	3	75	15
3	5				75	16	9

For $Ga_xAs_y^+$ (x+y=9)

x	y	$Ga_xAs_y^+$	Ga_xAs NH_3^+	Ga_xAs_y $(NH_3)_2^+$	Ga_xAs_y $(NH_3)_3^+$	Ga_xAs_y $(NH_3)_4^+$
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 $Ga_xAs_y^+$ (x+y=10)

x	y	$Ga_xAs_y^+$	$Ga_xAs_y NH_3^+$	$Ga_xAs_y (NH_3)_2^+$	$Ga_xAs_y (NH_3)_3^+$	$Ga_xAs_y (NH_3)_4^+$
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 $Ga_xAs_y^+$ (x+y=16)

x	y	$Ga_xAs_y^+$	$Ga_xAs_y NH_3^+$	$Ga_xAs_y (NH_3)_2^+$	$Ga_xAs_y (NH_3)_3^+$	$Ga_xAs_y (NH_3)_4^+$
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

Table 2. Relative stoichiometric concentrations for $Ga_xAs_y^+$ (x+y = 10) before and after reaction with $6x10^{-6}$ torr of NH_3 for 40 sec. The concentrations of $Ga_3As_7^+$ and Ga_9-As_1^+ are ignored. The sum is the summation of all the products corresponding to one stoichiometry.

Before Reaction			**After 40 sec. of Reaction**							
Ga	**As**	**parent**	**Ga**	**As**	**parent**	+(NH_3)	+$(NH_3)_2$	+$(NH_3)_3$	+$(NH_3)_4$	**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

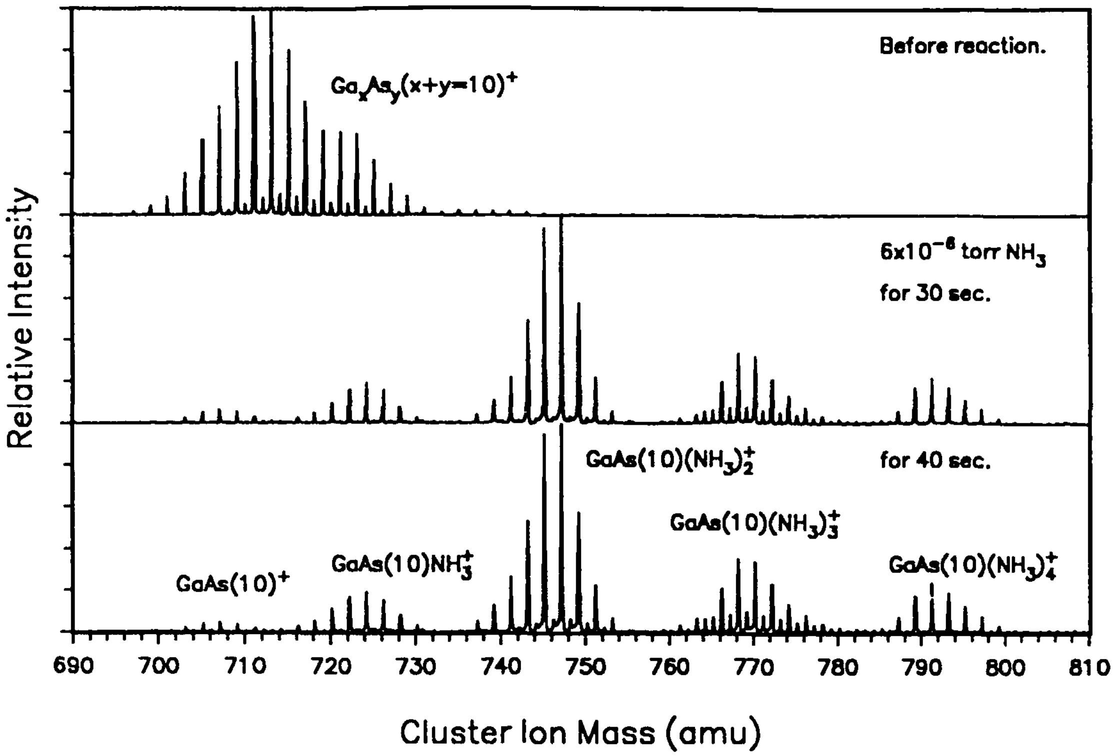
Figure Captions

Fig. 1. The mass spectra of 10 atom positive GaAs cluster reaction with 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 seconds of reaction with 6×10^{-6} torr of NH_3 respectively.

Fig. 2. The relative concentration of $Ga_4As_6^+$ cluster and its products after reaction with NH_3 as a function of reaction time.

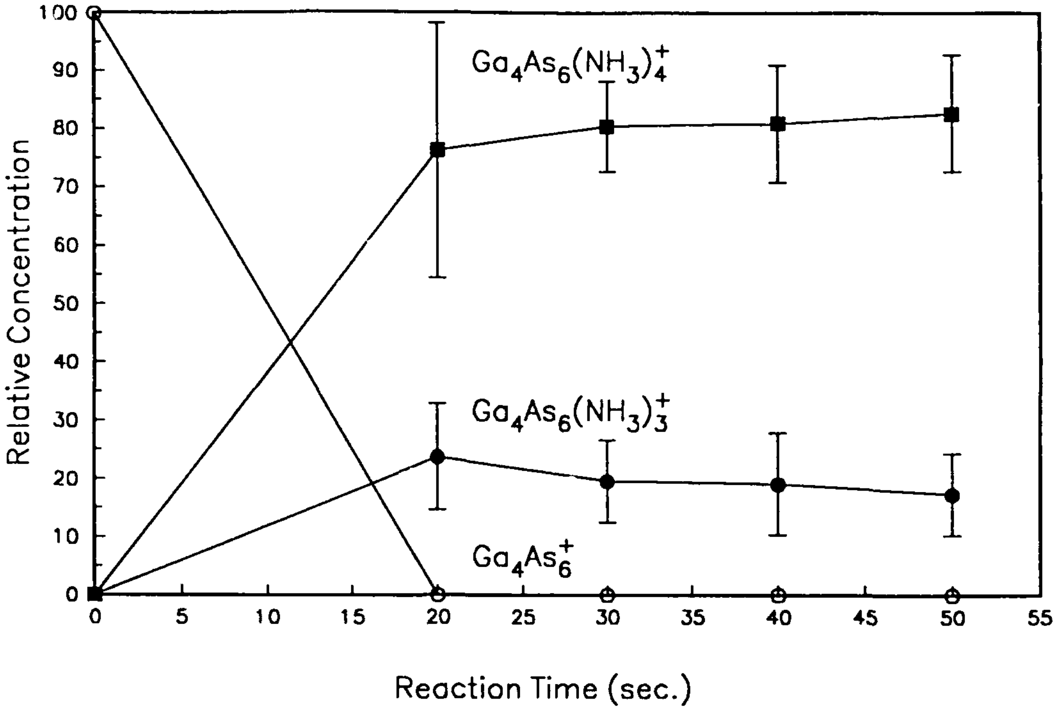
Fig. 3. The relative concentration of $Ga_5As_5^+$ cluster and its products after reaction with NH_3 as a function of reaction time.

Figure 1



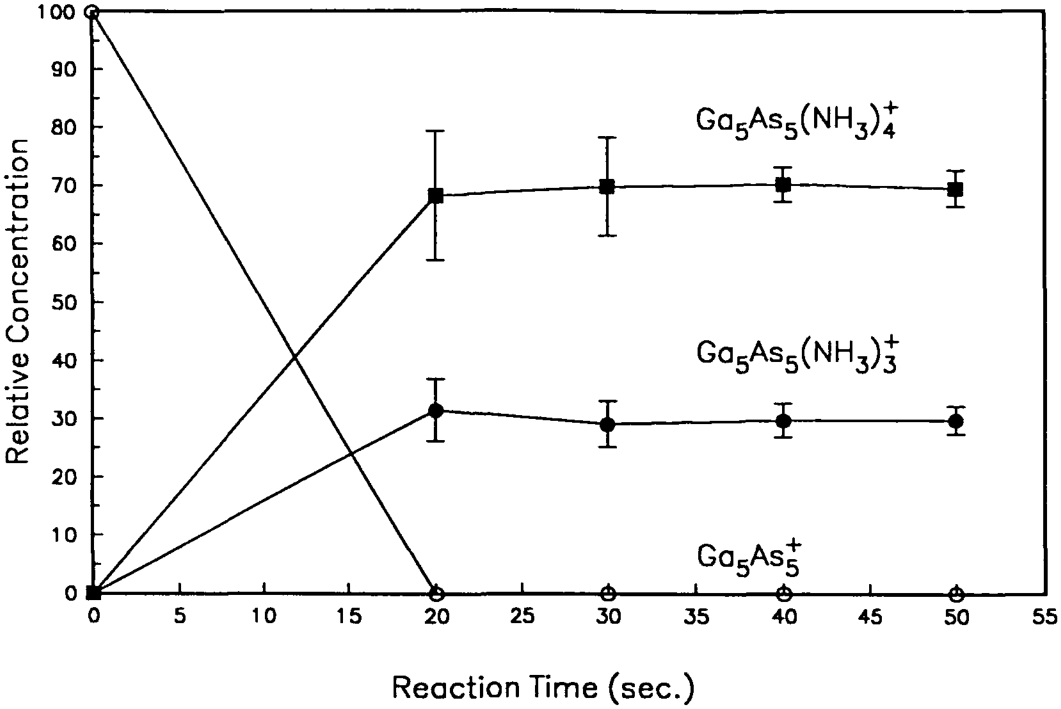
Before reaction.
$Ga_xAs_y(x+y=10)^+$
6×10^{-8} torr NH_3
for 30 sec.
for 40 sec.
$GaAs(10)(NH_3)_2^+$
$GaAs(10)(NH_3)_3^+$
$GaAs(10)NH_3^+$
$GaAs(10)^+$
$GaAs(10)(NH_3)_4^+$
Relative Intensity
690
700
710
720
730
740
750
760
770
780
790
800
810
Cluster Ion Mass (amu)

Figure 2



Relative Concentration
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
55
Reaction Time (sec.)
$Ga_4As_6(NH_3)_4^+$
$Ga_4As_6(NH_3)_3^+$
$Ga_4As_6^+$

Figure 3



Relative Concentration
Reaction Time (sec.)
$Ga_5As_5(NH_3)_4^+$
$Ga_5As_5(NH_3)_3^+$
$Ga_5As_5^+$
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
35
40
45
50
55

C. Publications and Presentations

Publications

1. Lihong Wang, L.P.F. Chibante, F.K. Tittel, R.F. Curl, and R.E. Smalley, "Ammonia Chemisorption on Gallium Arsenide Clusters," *Chemical Physics Letters* **172**, 335-340 (Sept. 1990).
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Presentations

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