Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometric Study on Sodium Azide Cluster Ions

LIU, Han-Qing[a](刘晗青)   GUO, Yin-Long[*,a](郭寅龙)   LU, Hao-Jie[a,b](陆豪杰)
CHEN, Guo-Qiang[a](陈国强)

[a] *Shanghai Mass Spectrometry Centre, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[b] *Department of Chemistry, Fudan University, Shanghai 200433, China*

Sodium azide has rarely been studied in gas phase or in the form of cluster ions and as a model of solid energetic substances and inorganic azide salt was ionized by electrospray ionization (ESI) and studied by high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS) systematically. This paper highlights the effects of experimental conditions on the formation of salt cluster and the collision activation dissociation pathways of cluster ions to develop a microscopic understanding of inorganic azide salt clusters.

Keywords   Fourier transform ion cyclotron resonance (FT-ICR), mass spectrometry (MS), electrospray ionization (ESI), cluster, sodium azide, collision activation dissociation (CAD), magic number, critical size

Introduction

Mass spectrometry (MS) has been an important technique for studying size-dependent cluster properties with unparalleled sensitivity, specificity, and versatility.[1,2] Especially Fourier transform ion cyclotron resonance (FT-ICR) MS offers the benefits of ultra-high mass resolving power, superior mass accuracy, and the ability of affording useful structure information with tandem MS. The introduction of electrospray ionization (ESI) as a gentle mode of ion generation for MS has helped to revolutionize the use of MS for chemical characterization of some special samples.[3,4] Since the combination of ESI with high resolution FT-ICR,[5] ESI/FT-ICR MS has greatly improved the capabilities of MS for chemical and structural analyses in inorganic, organometallic, biological, organic, bioorganic, and polymer chemistry.

Cluster research has attracted a growing number of scientists and cluster science has become an increasingly active discipline. This is due to the fact that these weakly bounded species exist as a state of matter with physical properties so unlike other states of matter that they were called "the fifth state of matter".[6-9] Cluster research is of great significance in many fields. Firstly, for studying mechanism and theory in chemistry, cluster studies can help us understand phase transition, crystal growth, and chemical catalysis.[8,10,11] Secondly, the importance of clusters to environment is still an unacquainted field to humankind. The exhausted gases from energy converters are rich in cluster species. In the current cluster research, the importance of stabilities has become a focus and has been amply illustrated by the electronic shell structure and geometric packing of atoms with experimental and theoretical methods.[12-14]

The inorganic azides are an important class of solid energetic substances, which can be used as explosives, industrial chemicals, and even as useful photographic materials at low temperatures. Fair and Walker presented an excellent overview of physical and chemical properties of azides.[15] Sodium azide is a useful starting material of many important chemicals and often used as an antiseptic, fungicide or mutagen. According to available research reports, most people studied it with quantum chemistry methods[16] and biological methods.[17-19]

To the best of our knowledge, few people have studied sodium azide in gas phase or in the form of cluster ions. The main purposes of our study are to show how to optimize experimental conditions to effectively analyze inorganic salt cluster ions with ESI/FT-ICR MS and to develop a microscopic understanding of inorganic azide salt clusters.

Experimental

Apparatus and conditions

An Apex III[TM] FT-ICR mass spectrometer with 7-T actively shielded superconducting magnet (Bruker Dal-

Mass spectrometry

Chin. J. Chem., 2004, Vol. 22, No. 10 **1165**

tonics, Billerica, MA) equipped with an electrospray ionization source was used. Nitrogen was used as the nebulizing, drying, and collision gas. Following the instrument tune, the capillary and endplate voltages were maintained at -4576 and -3750 V, respectively. Nebulizing gas and drying gas temperatures were 290 and 190 ℃, respectively. The potential of the front trapping plate (PV1) of the ICR cell was 0.85 V and that of the back plate (PV2) was 0.89 V. The mass spectrometer was calibrated externally using PEG 1000 in a 50∶50 (*V/V*) water/methanol solution. Fifty scans were accumulated to obtain a 128 K-point broad-band mass spectrum. The isolation sweep pulse length was 800 usec and sweep attenuation was 18 dB. The pulse lengths of ions activated ranged from 200 to 10000 usec.

Reagents and preparation of the samples

All organic solvents were HPLC grade from Fisher Scientific (Fair Lawn, New Jersey, USA). Deionized water was obtained from a Milli-Q water purification system (Millipore, ElPaso, TX). Solid sodium azide (99.5%; Sigma (St, Louis. MO, USA)) was commercially obtained. Sodium azide concentration was 10 mmol•L^{-1} in a 50∶50 (*V/V*) water/methanol solution unless specific explanation was given.

Results and discussion

Positive ion mass spectra of NaN$_3$

The cluster mass spectra consisted of a series of evenly spaced mass peaks. Figure 1(a) shows the positive ESI full-scan mass spectrum produced from a 10 mM solution (50%*V* water＋50%*V* methanol) of NaN$_3$, and Figure 1(b) highlights the *m/z* ranging from 850 to 1700. The spectrum Figure 1(b) revealed that all singly, doubly, triply, and quadruply charged cluster ions were present. Cluster ion abundance was clearly seen to decrease as charge state increased, thus suggesting that during this ESI process not so many multiply charged ions were produced as singly charged ones. The singly charged cluster ions had the formula $[(NaN_3)_mNa]^+$ (*m* $=3$, 4, 5, ⋯, 35), and formed a series of peaks in the mass spectrum differing by one NaN$_3$ mass unit. The second series of cluster ions corresponded to the doubly charged series of $[(NaN_3)_n(Na)_2]^{2+}$ (*n*$=11$, 12, 13, ⋯, 67). They were evidenced by the middlemost signals between each two singly charged cluster signals. The triply, and quadruply charged cluster ions had the formulae $[(NaN_3)_p(Na)_3]^{3+}$ (*p*$=28$, 29, 30, ⋯, 100) and $[(NaN_3)_q(Na)_4]^{4+}$ (*q*$=29$, 30, 31, ⋯, 131), respectively. Because the spacing of the peaks of the doubly charged clusters was half that of the singly charged counterparts, overlap of the two series occurred at the positions where $n=2\times m$. Overlapping signals were identified with high resolution FT-ICR MS by the distribution of weak isotope peaks for most of the even *n* clusters in the mass spectra. Similarly, the triply charged cluster ion signals

overlapped the singly charged ones and the quadruply charged ones overlapped the singly and doubly charged ones. No peaks of solvated cluster ions were found with high resolution FT-ICR MS. It was ascribed to the high temperature of nebulizing and drying gas, which has the effect of desolvating the ions and so the spectra are not complicated by the appearance of peaks of solvated cluster ions.

Ultra-high mass resolving power of FT-ICR MS not only facilitated us to identify the overlapped peaks, but also provided confident data for the following calculations of magic number.

Effects of experimental conditions on salt cluster formation

Two facets of solution conditions were investigated. Firstly, different sample concentrations were investigated. The concentration of salt solutions appeared to play a key role in the formation of cluster ions, especially that of multiply charged cluster ions. 0.1, 1, 10, 40, and 100 mmol/L solutions of NaN$_3$ in deionized water containing 50% methanol (*V*∶*V*) were investigated. The onset for formation of singly charged cluster ions was found roughly at 1 mmol/L concentration, whereas the formation of singly, doubly charged cluster ions were found perfectly at 10 mmol/L concentration. At the same time, both the triply and quadruply charged cluster ions formed at this concentration although abundance and distribution of them were limited compared to those at 40 and 100 mmol/L concentration. Abundant singly, doubly, triply, and quadruply cluster ions were observed in 40 and 100 mmol/L solutions. Higher concentrations seemed to favor the formation of multiply charged cluster ions, but concentration higher than 40 mmol/L can block the heated capillary by salt crystallization and may lead to tip discharge at the place of capillary exit. So safety was taken into consideration and 10 mmol/L concentration was generally applied.

Secondly, organic solvents (methanol, ethanol, and acetonitrile) were prepared with water at 5 different organic solvent proportions, 0.1, 0.3, 0.5, 0.7, and 0.9 to study the effects of solution composition on the formation of cluster ions. The critical sizes of the doubly charged cluster ions in methanol and ethanol solutions at 5 different organic solvent proportions were all 17 only with two exceptions of 15. The critical sizes of the doubly charged cluster ions in acetonitrile solutions were all 19. The critical sizes of the triply charged cluster ions in methanol and ethanol solutions were all 41 only with one exception of 40. And the critical sizes of the triply charged cluster ions in acetonitrile solutions were all 61 only with one exception of 62. Since all data were acquired under similar conditions, it is plausible to discuss the differences and similarities among these clusters. It was obvious that the critical sizes of multiply charged cluster ions were dependent on the nature of organic solvents. These values almost remained constant throughout the entire solvent concentration range investigated.
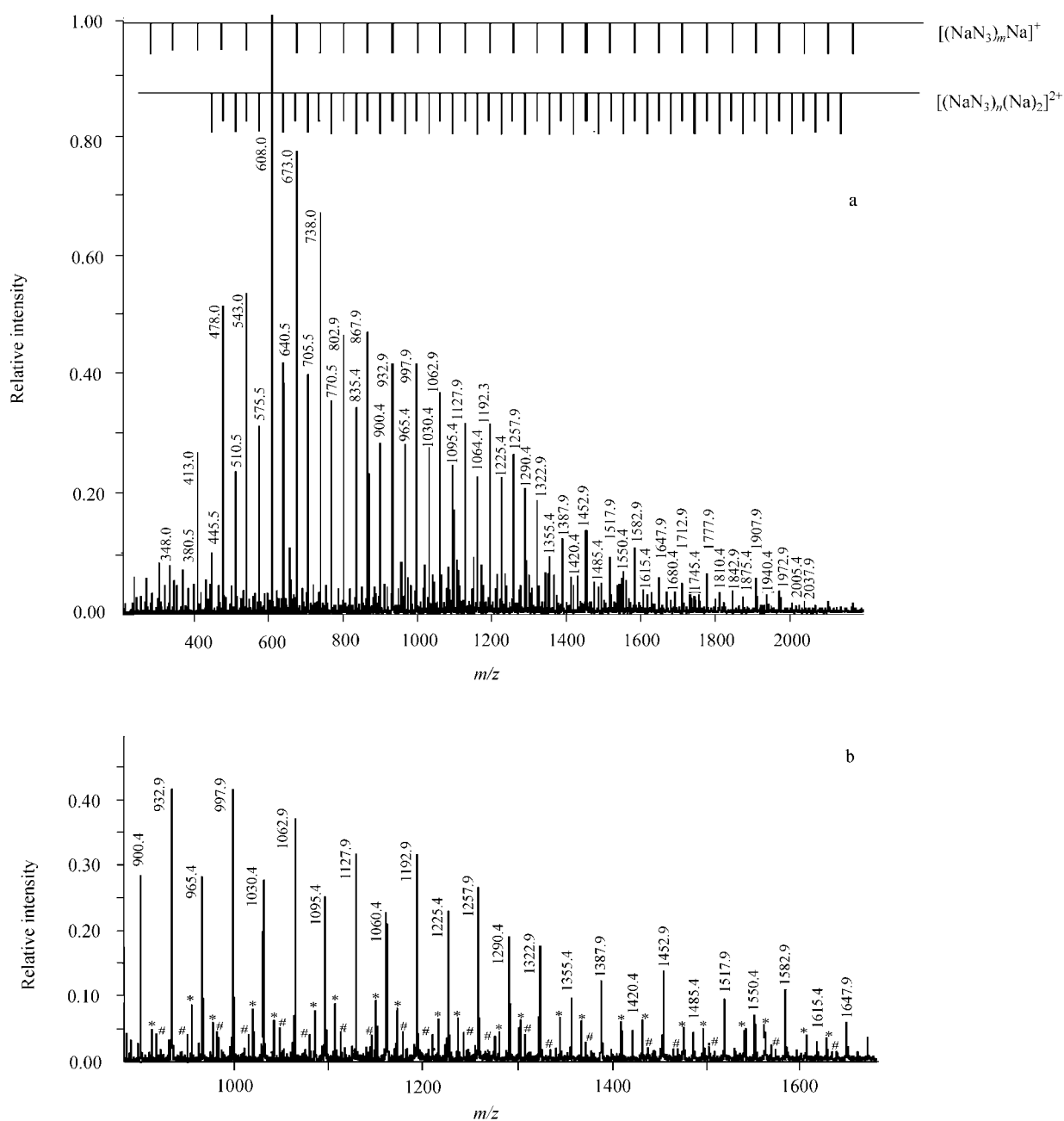
Figure 1   (a) Full-scan mass spectrum of 0.01 mol•L^{-1} NaN$_3$ solution (50%V water$+$50%V methanol) under positive ion electrospray conditions. All singly, doubly, triply, and quadruply charged cluster ions were shown in the range of 200—2200. (b) highlights the *m/z* range 850—1700. Both triply and quadruply charged cluster ions can be easily distinguished from (b). Triply charged cluster ions which are not overlapped by singly ones are marked with *. Quadruply charged cluster ions which are not overlapped by singly and doubly ones are marked with #.

The critical sizes of cluster ions in acetonitrile solutions were much larger than those in other solutions, especially the critical sizes of triply charged cluster ions. The critical sizes of quadruply charged ions were not summarized, because quadruply charged cluster ions were not found in acetonitrile solutions under the same experimental conditions.

Four physicochemical properties of solvents were considered to be related to the critical sizes of multiply charged cluster ions. They were listed in Table 1. Critical sizes seem to increase as the dielectric constant of

solvents increases. Electrostatic attractions and repulsions between ions are small if the dielectric constant of the medium is larger, and ions of opposite charge therefore have a great tendency to dissociate when the dielectric constant is large. So when the dielectric constant is large, the critical sizes are large. Besides that, the larger the dipole moment of solvents is, the more strongly the solvent coordinates towards ions of opposite charge, which leads to a decrease in the electrostatic interaction between them and an increase in the critical sizes. In addition, critical sizes seem to increase with the increase

Mass spectrometry

Chin. J. Chem., 2004, *Vol. 22, No. 10* **1167**

Table 1 Physicochemical properties of pure solvents at 20 ℃

	Water	MeOH	EtOH	MeCN
ε^a	80.4	33.0	25.5	36.1
μ^b (debyes)	1.84	2.87	1.66	3.44
σ^a (dynes/cm)	72.7	22.6	22.7	28.4
η^a (10^5 poises)	1004	599	1154	383

ε: dielectric constant. μ: dipole moment. σ: surface tension. η: viscosity. *a* Values extrapolated from data in Ref. 21. *b* Values extrapolated from data in Ref. 22.

of surface tension and the decrease of viscosity. These physicochemical properties of solvents together resulted in close dependence of the critical sizes on solution compositions. However these correlations have not been summarized in a simple equation.

There are about thirty parameters to control the ESI source, ion transfer, and cell region. Two instrumental parameters were chosen, which often affected cluster ion formation, to study the effects of instrumental conditions on cluster ion formation. These parameters included capillary voltage and drying gas temperature.

The influences of capillary voltage on salt cluster ion formation were studied in the range of -3600 to -6000 V. Absolute intensities of all salt cluster ions had a maximum value at the optimal capillary voltage -4576 V. This phenomenon may be ascribed to different ionization efficiencies. Although absolute intensities had some discrepancies when different capillary voltages were applied, the intensity distributions of cluster ions with the same charge state were quite similar. This indicated that the capillary voltage could influence cluster ions with the same charge state in the same degree and this influence was not size-dependent.

Capillary temperature often has a marked effect on the spectra of inorganic and organometallic compounds.[20] Capillary was heated by drying gas in this instrument. So drying gas temperature from 20 to 300 ℃ was studied. Absolute intensities were very low at 20 and 300 ℃. The critical sizes of doubly charged cluster ions became larger when drying gas temperature was 20 and 300 ℃. The triply and quadruply charged cluster ions were not observed under these conditions. These extreme temperatures may greatly affect the intensities and distributions of cluster ions mainly for two reasons: one is that low temperature may hinder dissolvation processes, and the other is that cluster ions are unstable at high temperature. But it was discovered that distributions of cluster ions with the same charge state were similar when mild temperatures were applied. Intensity distribution of the doubly charged cluster ions at different drying gas temperatures was shown in Figure 2. Although there was an assumption that more energetic conditions decrease the cluster stability, the similar distributions may be ascribed to the relatively strong forces among cluster units. The high temperature cannot result in producing small sizes or low charges of clusters with
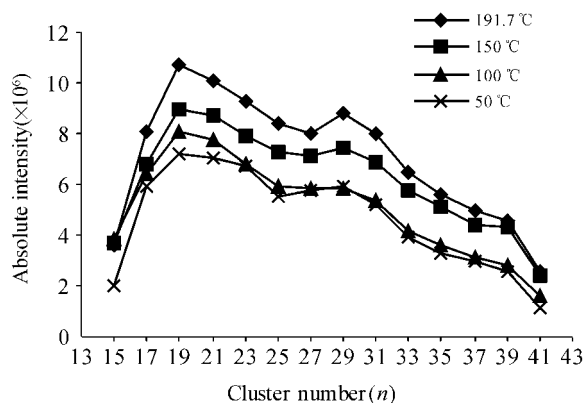

Figure 2 Intensity distribution of doubly charged sodium azide cluster ions at different drying gas temperatures. Distributions of cluster ions were similar when different temperatures were applied.

in-source CID.

Critical sizes and magic numbers of NaN₃ cluster ions

In our experiment, the smallest doubly charged ion observed was $n=11$ with the relative abundance being about 0.07. The smallest triply charged ion observed was $p=28$ and the smallest quadruply charged ion observed was $q=29$.

Because there are not other data of azide salts available for references, these values cannot be compared with others. The critical sizes of quadruply charged ions were much smaller than those of other alkali salt cluster ions reported. For a given charge state, the smallest clusters are expected to be the least stable because repulsive forces between the charged ions increase as the distances between them decrease. The very low critical size of the quadruply charged clusters may be ascribed to the nature of salts studied, the gentle property of the ESI process, and the suitable conditions for formation of quadruply charged cluster ions selected.

To express the size dependence of intensities of singly and doubly charged cluster ions concretely, the intensities of individual clusters were compared to those of their neighbors by plotting $I_m^2/(I_{(m+1)} \times I_{(m-1)})$ and $I_n^2/(I_{(n+1)} \times I_{(n-1)})$ in Figure 3(a) and (b). *I* represents the corresponding absolute intensity of cluster ions and *m* and *n* represent the cluster size. The intensities of singly charged ions used in Figure 3(a) were obtained by subtracting the contributions of the overlapping doubly charged ions from the total intensities. The contributions of the overlapping triply and quadruply charged ions were not subtracted due to the relatively low intensity of them compared to that of both singly and doubly charged cluster ions.

A probability of 100% error was assigned as an indication of a magic number cluster. This treatment, carried out on a single set of data, showed that magic numbers appeared to exist at $m=6, 9, 13, 19$ and 22 and
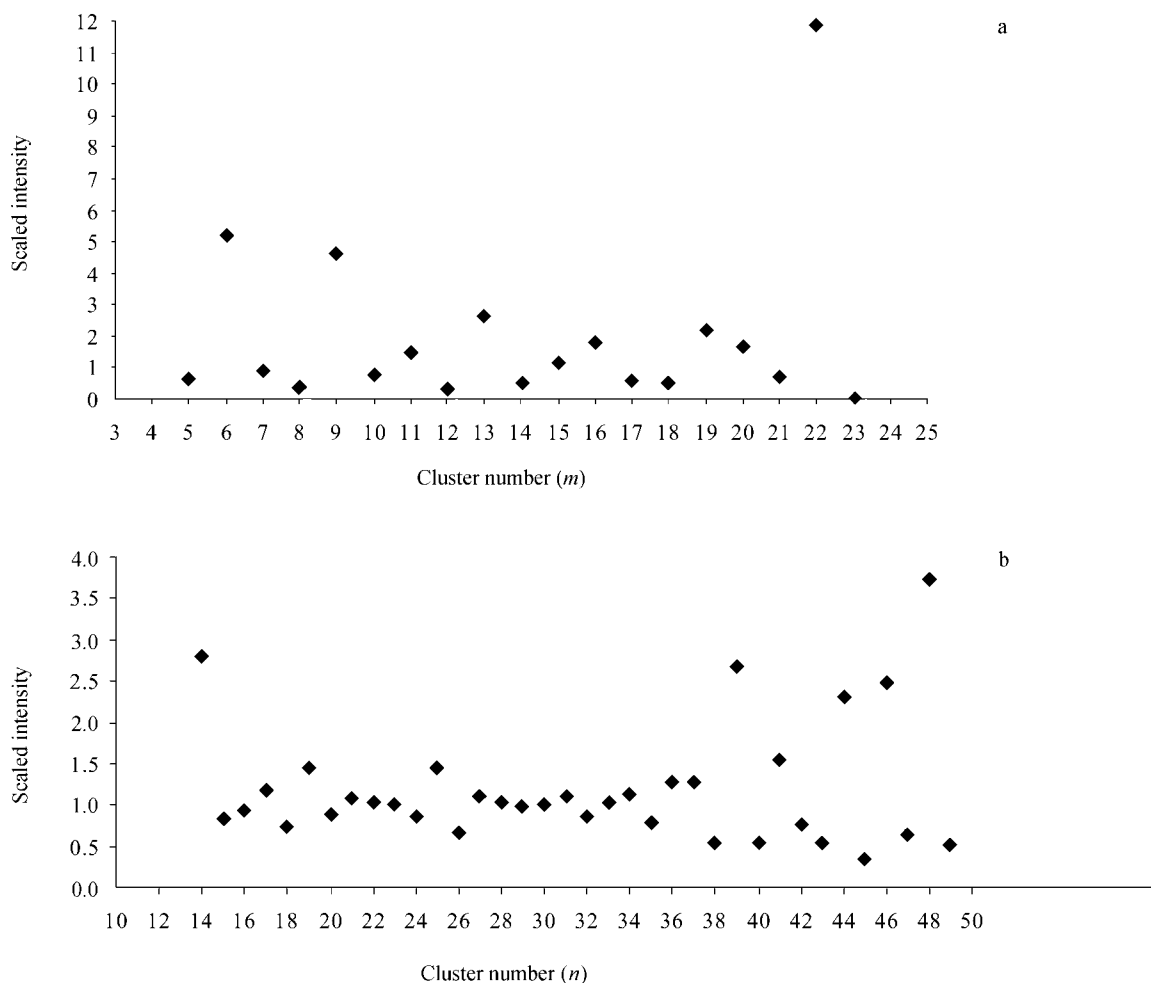
Figure 3   a, The $I_m^2/(I_{(m+1)} \times I_{(m-1)})$ of singly charged clusters observed in the NaN_3 ESI mass spectrum showing magic number effects for certain cluster sizes. b, The $I_n^2/(I_{(n+1)} \times I_{(n-1)})$ of doubly charged clusters observed in the NaN_3 ESI mass spectrum showing magic number effects for certain cluster sizes.

$n=14$, 39, 44, 46, and 48. Because few people studied inorganic azide salts in the form of cluster ions, there are no magic numbers for references.

Collision activation dissociation pathways

Singly charged precursor ions at $m=9$ with the highest intensities in all peaks were further studied in CAD experiments. When pulse length was more than 1000 usec, the precursor ions only generated the product ions with $m=1$. When pulse length equaled to or was less than 1000 us, they generated seven daughter ions, singly charged ions with $m=1$, 2, 3, 4, 5, 6, 7. With the same pulse length, different activation energy was studied, and the analogous distributions of product ions were acquired. The typical CAD spectrum of $m=9$ is shown in Figure 4. From the CAD results, it is evident that singly charged cluster ions generate smaller singly charged cluster ions by losing some neutral salt molecules under CAD conditions.

The main products of these parent ions were the daughter cluster ions with $m=3$ rather than with $m=6$. The parent ions were experimented in different days and the same main products were got. This phenomenon may be ascribed to two reasons. Firstly, the cluster ions

with magic number $m=6$ and $m=9$ have different geometric structures. After cluster ions with $m=9$ were activated, they did not have the tendency to dissociate to form a stable structure with different geometric symmetry. Secondly, the ions with $m=3$ and with $m=6$ had
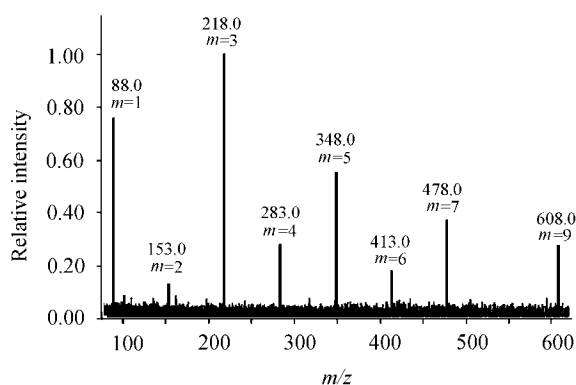

Figure 4   MS/MS spectrum recorded by CAD of singly charged ions $[(NaN_3)_9Na]^+$. The daughter cluster ion with $m=3$ was the main product of singly charged precursor ion with $m=9$. The daughter cluster ions with odd units were observed to have higher intensities than ions with even units.

Mass spectrometry

Chin. J. Chem., 2004, Vol. 22, No. 10 **1169**

different origins, which originated from gas phase and solvents, respectively. Solvent effects may result in this phenomenon. It is a valuable assumption to develop a microscopic understanding of sodium azide clusters. Relative intensities of daughter ions with $m=1, 3, 5$, and 7 were much higher than those with $m=2, 4$, and 6. This may indicate that the cluster ions with $m=9$ had a structure unit of 2 mass units of NaN_3.

The doubly charged ions with odd values of n could be unambiguously identified and isolated. So the doubly charged cluster ions with $n=17$ were selected to do CAD experiments. Under gentle conditions, the singly charged cluster ions with $m=12, 14, 16$ were generated. It can be concluded that the precursor ions were prone to fission in CAD to form singly charged clusters.

Conclusion

Singly, doubly, triply, and quadruply charged clusters of sodium azide, which had the formulae $[(NaN_3)_m Na]^+$, $[(NaN_3)_n (Na)_2]^{2+}$, $[(NaN_3)_p (Na)_3]^{3+}$, and $[(NaN_3)_q (Na)_4]^{4+}$, were generated by positive ion electrospray ionization.

High concentrations seemed to favor the formation of multiply charged cluster ions. Critical sizes of multiple charged cluster ions were supposed to increase with the increase of dielectric constant, dipole moment, and surface tension of solvents or the decrease of viscosity. Distributions of the four charged states of cluster ions were similar when different capillary potentials and mild temperatures were applied.

The critical sizes and magic numbers of cluster ions were studied. It was believed that the results would be helpful for future research of solid energetic substances and inorganic azide salts.

The combination of electrospray ionization with high resolution Fourier transform ion cyclotron resonance has been proved to be a useful technique for producing and studying inorganic clusters.

References

1 Märk, T. D. *Adv. Mass Spectrom.* **1995**, *13*, 71.

2 Stamatovic, A. S.; Märk, T. D. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 51.

3 Whitehouse, C. M.; Dreyer, R. N.; Yamashita, M.; Fenn, J. B. *Anal. Chem.* **1985**, *57*, 675.

4 Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* (*Washington, D. C.*) **1989**, *246*, 64.

5 Henry, K. D.; Williams, E. R.; Wang, B. H.; McLafferty, F. W.; Shabanowitz, J.; Hunt, D. F. *Proc. Natl. Acad. Sci. U. S. A.* **1989**, *86*, 9075.

6 Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589.

7 Castleman, A. W., Jr.; Keesee, R. G. *Annu. Rev. Phys. Chem.* **1986**, *37*, 525.

8 Märk, T. D. *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 1.

9 Garvey, J. F.; Peifer, W. R.; Coolbaugh, M. T. *Acc. Chem. Res.* **1991**, *24*, 48.

10 Märk, T. D.; Castleman, A. W., Jr. *Adv. At. Mol. Phys.* **1985**, *20*, 65.

11 Wang, J.; Wang, J.; Gao, H.; Zhang, Y.-W.; Sheng, L.-S. *Acta Chim. Sinica* **2002**, *60*, 1591 (in Chinese).

12 Echt, O.; Sattler, K.; Recknagel, E. *Phys. Rev. Lett.* **1981**, *47*, 1121.

13 Knight, W. D.; Clemenger, K.; De Heer, W. A., Saunders, W. A.; Chou, M. Y.; Cohen, M. L. *Phys. Rev. Lett.* **1984**, *52*, 2141.

14 Shi, L.; Liu, Z.-Q.; Song, F.-R.; Liu, S.-Y. *Chin. J. Chem.* **2001**, *19*, 1048.

15 Fair, H. D.; Walker, R. F. Eds. *Physics and Chemistry of Inorganic Azides*, Vol. 1, Energetic Materials, Plenum Press, New York, **1977**.

16 Younk, E. H.; Kunz, A. B. *Int. J. Quantum Chem.* **1997**, *63*, 615.

17 Ju, R.; Mao, Y.-H.; Glick, M. J.; Muller, M. T.; Snyder, R. D. *Toxicol. Lett.* **2001**, *121*, 119.

18 Sadiq, M. F.; Owais, W. M. *Mutat. Res.* **2000**, *469*, 253.

19 Hedin, H. L. M.; Fowler, C. J. *Neurosci. Lett.* **2000**, *288*, 203.

20 Dyson, P. J.; McIndoe, J. S. *Inorg. Chim. Acta* **2003**, *354*, 68.

21 Timmermans, J. *Physicochemical Constants of Binary Systems,* Intersciences Publishers Inc., New York, **1960**.

22 Riddick, J. A.; Bunger, W. B. In *Organic Solvents*, 3rd Ed., Vol. 11, Ed.: Weissberger, A., Wiley-Interscience, New York, **1970**.