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# ION-MOLECULE CHEMISTRY WITHIN TRIPLY CHARGED AMMONIA CLUSTERS

by

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We present in this communication the first observation of "intramolecular" ion-molecule reactions within triply charged clusters produced via electron impact ionization of neat beams of ammonia molecules. The fragmentation pattern strongly suggests that reactions occurring within these triply charged clusters are similar to those previously observed for singly and doubly charged ammonia clusters. This behavior implies that these cluster ions consist of three singly charged ammonia cations which react separately within the bulk neutral cluster. That is either one, two, three or none of the ammonia cations may react with the solvating neutrals within the cluster. We also report for singly charged ammonia clusters the observation that extensive fragmentation can occur within the cluster producing ions with the empirical formulas of $(NH_3)_{n-1}N^+$ and $(NH_3)_{n-1}NH^+$.

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# Ion-Molecule Chemistry Within Triply Charged Ammonia Clusters

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**Abstract:**

We present in this communication the first observation of "intramolecular" ion-molecule reactions within triply charged clusters produced via electron impact ionization of neat beams of ammonia molecules. The fragmentation pattern strongly suggests that reactions occurring within these triply charged clusters are similar to those previously observed for singly and doubly charged ammonia clusters. This behavior implies that these cluster ions consist of three singly charged ammonia cations which react separately within the bulk neutral cluster. That is, either one, two, three or none of the ammonia cations may react with the solvating neutrals within the cluster. We also report for singly charged ammonia clusters the observation that extensive fragmentation can occur within the cluster producing ions with the empirical formulas of $(NH_3)_{n-1}N^+$ and $(NH_3)_{n-1}NH^+$.

## Introduction

Ion clusters provide a unique environment in which to observe ion-molecule chemistry. In the case of singly charged ammonia ion clusters, intracluster ion-molecule chemistry can occur through the formation of the $NH_4^+$ ion[1-9] via the following bimolecular exoergic ($\Delta H^o = -1.1 eV$) reaction:

$$(NH_3)_{n-1}\,[\,NH_3^+ + NH_3\,] \Rightarrow (NH_3)_{n-1}NH_4^+ + NH_2 \qquad (1)$$

A new development in this area has been the characterization of multiply charged clusters in which the very same ion-molecule chemistry can occur. For doubly charged ammonia clusters, a critical size of $n_c = 51$ has been reported[10,11] and attributed to the formation of the $(NH_3)_{n-2}(NH_4^+)_2$ cluster ion. In a recent paper[12], we reported mass spectra which have shown instead, that there are seven stable forms of doubly charged ammonia clusters. This repeated sequence of seven mass peaks, each separated by 1/2 amu, was attributed to chemical processes occurring at two separate and independent cation centers within the doubly charged ammonia cluster.

For the case of triply charged ammonia clusters, a critical size of $n_c = 121$ has also been reported[11] with the assignment being tentatively made as due to the $(NH_3)_{n-3}(NH_4^+)_3$ specie. In this letter, we show that there are also several different triply charged species which are stable, with the dominant forms being that of $\{(NH_3)_{n-3}\,(NH_4^+)_x\,(NH_3^+)_{3-x}\}$, where x is the number of $NH_3^+$ cations which have reacted via reaction 1 to form one, two or three $NH_4^+$ cations (ie. $x = 1 - 3$).

## Experimental Section

The molecular beam apparatus has been described before[12] and consists of a Campargue type beam source[13] where the source chamber is pumped by a $1000 m^3/h$ blower package. The cluster beam is generated by a neat, adiabatic expansion of anhydrous $NH_3$ (Linde, 99.99% pure) at 1.5 atm stagnation pressure (source chamber pressure = 50 mtorr) through a 250 mm nozzle which is kept at 273K by a circulating chiller, as measured by a thermocouple within the nozzle.

Following collimation by a 5 mm diameter skimmer, 7.5 mm from the nozzle, the cluster beam passes into a differentially pumped chamber ($p = 1 \times 10^{-5}$ torr) and travels through a second collimating skimmer before entering the differentially pumped mass spectrometer chamber ($p = 5 \times 10^{-7}$ torr). The collimating and mass spectrometer chambers are each pumped by a 360 l/s turbo pump with the two chambers separated by an electromagnetic gate valve which also serves as a beam flag.

The skimmed beam enters into the mass spectrometer chamber in a direction collinear with the ion optic axis. The electron impact ionizer of the mass spectrometer is located 22 cm from the nozzle. The mass spectrometer used is an Extrel C-50 (200 watt, 3/8" diameter rods, open design ionizer). The emission current and electron energy for all these experiments were kept at 2 mA and 100 eV, respectively. Ions formed in this source are mass filtered (up to 1200 amu) and detected by an off-axis channeltron. The amplified signal from the channeltron is then signal averaged by a LeCroy 9400 digital oscilloscope for 1000 scans. The mass scale of the spectrometer from 0 to 500 amu is calibrated by using a perfluorotributylamine standard. The mass calibration is then extended to 1200 amu by running a neat Ar cluster beam.

## Results and Discussion

Figure 1 shows a typical ammonia cluster mass spectrum where singly, doubly and triply charged clusters can all be observed. The peaks are individually labeled at the top. The cluster number, n, above the bracketed peaks denotes the number of nitrogen atoms within each cluster. The capital letter **P** represents the parent peak (where the cluster is composed entirely of n $NH_3$ monomers units). The numbered peaks to the right of **P** denote the number of $NH_3^+$ cations, (**x** = **1**, **2**, or **3**), which have bimolecularly reacted to form $NH_4^+$ cations within the cluster via reaction (1).

In the case of the singly charged clusters, the peaks to the left of **P** (peaks **a**, **42+** and **a**, **43+**) result from unimolecular fragmentation of $NH_3^+$ cations within the parent cluster via the following reaction :

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-1}NH_2^+ \ + \ H. \qquad (2)$$

We note that this is the first time <u>extensive</u> unimolecular fragmentation has been observed within ammonia cluster ions, with the formation of $NH^+$ within the cluster (Figure 1, peak **b**, **43+**) via reaction (3)

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-1}NH^+ \ + \ 2H \qquad (3)$$

and the generation of $N^+$ within the cluster (Figure 1, peak **c**, **43+**) via reaction (4)

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-1}N^+ \ + \ 3H. \qquad (4)$$

To verify the correctness of our assignments of peaks **c** and **b**, as being due to reactions (3) and (4), we noted the variation of ion intensity as a function of electron energy, as shown in Figure 2. For this particular case we examined ammonia cluster of n = 20 in order to remove any potential overlap with doubly (n ≥ 51) and triply (n ≥ 121) charged clusters. As the figure indicates, the $(NH_3)_{19}N^+$ cluster ion has an appearence at approximately 60eV and the $(NH_3)_{19}NH^+$ cluster ion has an appearence at roughly 40eV. This is consistent with our assignment since the breaking of three N-H bonds will have a higher energy threshold then the breaking of two N-H bonds. This is in contrast to the $(NH3)_{19}NH_2^+$ cluster ion appears at aprximately 25 eV and requires the breaking of only one N-H bond.

The ion peaks to the right of the parent peak (labeled **a′**, **b′**, **c′**) in Figure 1 may arise by two different mechanisms. They may represent either products resulting from further cluster chemistry[9,12] or the presence of water contaminants[14]. Two possible cluster reactions (for the case of singly charged clusters) which could lead to the production of this "$NH_5^+$" product ion species are :

$$(NH_3)_{n+1}^+ \Rightarrow (NH_3)_{n-1}NH_5^+ + NH \qquad (5)$$

or

$$(NH_3)_{n+2}^+ \Rightarrow (NH_3)_{n-1}NH_5^+ + N_2H_4 \qquad (6)$$

The doubly charged clusters (separated by 1/2 amu) are of the form $\{(NH_3)_{n-2}\,(NH_4^+)_x\,(NH_3^+)_{2-x}\}$, where x is the number of $NH_3^+$ cations which have reacted via reaction 1, (ie. x = 0 - 2) as has been previously reported[12]. In addition we observe peaks due to fragmentation (reaction (2)-(4)). The same nonmenclature is also used to label the fragmenation peaks of the multiply charged cluster ions as for the singly charged clusters, though it is expected that peaks **b** and **c** more probably result from reaction (2) occuring at the separated $NH_3^+$ cation centers which did not react, rather then reaction (3) or (4) at a single cation center. Peaks to the right of the parent peak also correspond to either water contamination or addition cluster reactions (reaction (5)-(6)), and we use the same nomenclature as before to label them.

Figure 3 shows an expanded view of Figure 1 such that the triply charged peaks (separated by 1/3 amu) can be clearly distinguished. The ion-molecule products are similar to those of singly and doubly charged clusters in that the major peaks all have the general form $\{(NH_3)_{n-3}(NH_4^+)_x(NH_3^+)_{3-x}\}$, where x = 1, 2 or 3.

Figure 4 illustrates a simple model to explain the appearance of the triply charged peaks observed in Figure 3. Through electron impact ionization, three singly charged ammonia cations are formed within the neutral cluster. If the cluster size is below the critical size of 121, the triply charged cluster undergoes a coulombic explosion which most likely generates a singly and a doubly charged ammonia cluster. However, if the cluster is large enough to accommodate these three cations, reorganization (presumbly by rapid charge transfer) occurs within the cluster to separate the three cation centers as far apart as possible. This accounts for the appearance of the parent ion with the empirical formula $(NH_3)_{n-3}(NH_3^+)_3$ (peak **p**, Fig 1 & 2). Once this cluster ion has been formed, each of the separated cation centers can then react with one of the neutral $NH_3$ solvating it via reaction (1). These reactions can then produce either a singly (peak **1**), doubly (peak **2**) or triply (peak **3**) protonated, triply charged ammonia cation. As before, for the singly and doubly charged ammonia clusters, the smaller peaks to the left of the parent peak can be explained by fragmentation (reaction (2)-(4)) while the smaller peaks to the right are due to either water contamination or an intracluster reaction (reactions (5)-(6)) occuring at any of the cation centers.

We note that for large (n > 30) singly and doubly charged clusters, the parent peak (**P**) is of comparable intensity with the first product peak (**1**). This is different from the case of small singly charged ammonia clusters (n = 2-30) where the product peak dominates almost completely. This effect of peak 1 monotonically decreasing in magnitude relative to the parent peak as a function of n, we feel is due in part to the the bath modes of the larger clusters effectively quenching the ion-molecule reaction (reaction (1)). That is, the additional "solvent" molecules can siphon away the excess energy and dampen the reaction. Therefore the *larger* the ion cluster, the *less facile* the ion-molecule (protonation) reaction. This same effect has also been observed for singly charged cluster of methyl halides [15,16].

However, in direct contrast to large singly and doubly charge ammonia clusters (Figure 1), for the case of triply charged ammonia clusters (Figure 3) the parent peak (at large n) is substantially *smaller* then the product peak (approximately 50%)[16]. We interpret this difference not on the basis of an increase in the efficiency of reaction (1) within a triply charged cluster, but rather to a change in the stabilization of the triply charged cluster ion. On comparing a doubly charged cluster (of $n_c = 51$) to a triply charged cluster (of $n_c = 121$) the separation of the cations within the cluster changes little, representing a sizable net increase in the electrostatic repulsion. As a result, if the triply charged cluster ion is to be stable, the solvation in the case of the three cations must be greater than in the case of two cations. Thermochemical data[17] suggest that *energetically* the solvation of $NH_3^+$ by neutral ammonia's will be less in magnitude than that for $NH_4^+$. We speculate then that the reduced solvation of the three $NH_3^+$ ions contributes to destabilizing the triply charged parent (**P**) cluster relative to the product ion peaks (peaks **1** - **3**), which contain $NH_4^+$'s, thus accounting for the observed intensity change.

It is also interesting to compare the behavior of the triply charged ammonia clusters with that of recent work concerning triply charged water clusters, studied by Stace[18]. In that paper, Stace reported the observation of *two* stable forms of triply charged water clusters assigned as $(H_2O)_nH^{3+}$ and $(H_2O)_nH_3^{3+}$, but did not observe the $(H_2O)_nH_2^{3+}$ ion. In contrast, we observe for triply charged ammonia all *three* product peaks, as shown in Figures 3 and 4. We cannot yet account for this disparity exhibited between the two systems but suggest it may be due to thermochemical differences in the respective ion-molecule reactions[12]. That is since the water reaction is more exoergic then the analogous ammonia reaction, the excess reaction energy at one water cation may in turn trigger the reaction at the second water cation.

In conclusion, we present in this letter the observation that there exists not one but several stable forms of triply charged clusters, which can be explained on the basis of ion-molecule reactions within the cluster. We also have presented the first observation of $N^+$ and $NH^+$ cations generated within an ammonia cluster.

It is tempting to now generalize the mass spectra of multiply charged ($z^+$) ammonia clusters, in that all the major peaks will have the same empirical formula of $\{(NH_3)_{n-3}(NH_4^+)_x(NH_3^+)_{z-x}\}$. That is they can be interpreted as z distinct ammonia cations (peak **P** where x=0) separated within the bulk cluster, each of which which can then undergo bimolecular ion-molecule reactions (where x may run from **1** to **z**). Further work is underway in our labs to observe how these various peaks change as a function of the beam expansion conditions, which in turn would reflect a change in the bulk cluster medium.

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## References

1) Hogg, A. M.; Haynes, R. M.; Kebarle, P., *J. Am. Chem. Soc.* **1966**, *88*, 28.

2) Long, J. W.; Franklin; J. L., *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 403.

3) Odutola, J. A.; Dyke, T. R.; Howard, B. J.; Muenter,J. S., *J. Chem. Phys.* **1979**, *70*, 4884.

4) Cook, K. D.; Taylor, J. W., *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 345.

5) Futrell, J. H.; Stephan, K.; Märk, T. D., *J. Chem. Phys.* **1982**, *76*, 5893;
Stephan, K.; Futrell, J. H.; Peterson, K. I.; Castleman Jr., A. W.; Wagner, H. E.;
Djuric, N.; Märk, T. D., *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 167.

6) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T., *J. Chem. Phys.* **1979**, *70*, 14.

7) Echt, O.; Morgan, S.; Dao, P. D.; Stanley, R. J.; Castleman Jr., A. W., *Ber. Bunsenges. Physik. Chem.* **1984**, *88*, 217;
Echt, O.; Dao, P. D.; Morgan, S.; Castleman Jr., A. W., *J. Chem. Phys.* **1985**, *82*, 4076.

8) Shinohara, H.; Nishi, N.; Washida, N., *Chem. Phys. Lett.* **1984**, *106*, 302;
Shinohara, H.; Nishi, N.; Washida, N., *J. Chem. Phys.* **1985**, *83*, 1939;
Shinohara, H.; Nagashima, U.; Nishi, N., *Chem. Phys. Lett.* *111*, **1984**, 511;
Shinohara, H.; Sato, K.; Achiba, Y.; Nishi, N. Kimura, K., *Chem. Phys. Lett.* **1986**, *130*, 231;
Shinohara, H.; Nishi, N., *Chem. Phys. Lett.* **1987**, *141*, 292.

9) Garvey, J. F.; Bernstein, R. B., *Chem. Phys. Lett.* **1988**, *143*, 13.

10) Shukla, A. K.; Moore, C.; Stace, A. J., *Chem. Phys. Lett.* **1984**, *109*, 324.

11) Kreisle, D.; Leiter, K.; Echt, O.; Märk, T. D., *Z. Phys. D* **1986**, *3*, 319.

12) Coolbaugh, M. Todd; Peifer, W. R.; Garvey, J. F., *Chem. Phys. Lett.* **1989**, in press.

13) Campargue, R.; Lebehot, A., *9th Int. Symp. Rarefied Gas Dynamics, Gottingen*, **1974**, pp. c.11- 1-12;
Campargue, R., *J. Phys. Chem.* **1984**, *88*, 4466.

14) Shinohara, H.; Nagashima, U.; Tanaka, H.; Nishi, N., *J. Chem. Phys.* **1985**, *83*, 4183;
Shinohara, H.; Nishi, N.; Washida, N., *Chem. Phys. Lett.* **1988**, *153*, 417.

15) Garvey, J. F.; Bernstein, R. B., *Chem. Phys. Lett.* **1986**, *126*, 394 ;
Garvey, J. F.; Bernstein, R. B., *J. Phys. Chem.* **1986**, *90*, 3577.

16) This result is independent of n, to the upper mass limit of our mass spectrometer (1200 amu).

17) Keesee, R. G.; Castleman Jr., A. W., *J. Phys. Chem. Ref. Data* **1986**, *15*, 1040.

18) Stace, A. J., *Phys. Rev. Lett.* **1988**, *61*, 306.

19) For the mass scale in Figures 1, 2 and 3, the nominal masses of N = 14 amu and H = 1 amu are used (rather than the actual values of 14.0067 and 1.0078 respectively). That is, by ignoring the mass defect, the doubly charged clusters appear at half-integer masses and the triply charged clusters at 1/3 integer masses, assisting the reader in confirming the assignments of the peaks,. However, in the raw mass spectra all the assigned peaks agree with the true masses.

## Figure Captions

Figure 1) Raw data of electron impact mass spectra[19] of singly, doubly and triply charged $NH_3$ cluster ions. The cluster number, n, above the bracketed peaks denotes the number of nitrogen atoms within each cluster. The nomenclature used to assign the mass spectral peaks is as follows: **P** represents the parent peak (where the cluster is composed entirely of n $NH_3$ monomers units). The numbered peaks to the right of **P** denote the number of $NH_3^+$ cations, (**x** = **1**, **2**, or **3**), which have bimolecularly reacted to form $NH_4^+$ cations within the cluster via reaction (1). The peaks (**a**, **b**, **c**) to the left of **P** result from unimolecular fragmentation of $NH_3^+$ cations within the parent cluster. The primed letters to the far right (**a**′, **b**′, **c**′) represent either products resulting from further cluster chemistry[9,12] or the presence of water contaminants[14].

Figure 2) Raw data of electron impact mass spectra[19] of $(NH_3)_{19}N^+$ (peak **c**), $(NH_3)_{19}NH^+$ (peak **b**) and $(NH_3)_{19}NH_2^+$ (peak **a**) at various electron energies. All mass spectra are normalized with respect to peak **a** .

Figure 3) Figure 1 magnified vertically by a factor of 8 and horizontally be a factor of 2.5, to enhance the resolution of the triply charged clusters. The spectrum was run under similar conditions as Figure 1 for 200 scans. Nomenclature is also the same as in Figure 1 [19].

Figure 4) Schematic which indicates possible mechanism for triply charged ion peaks observed in Figure 3.

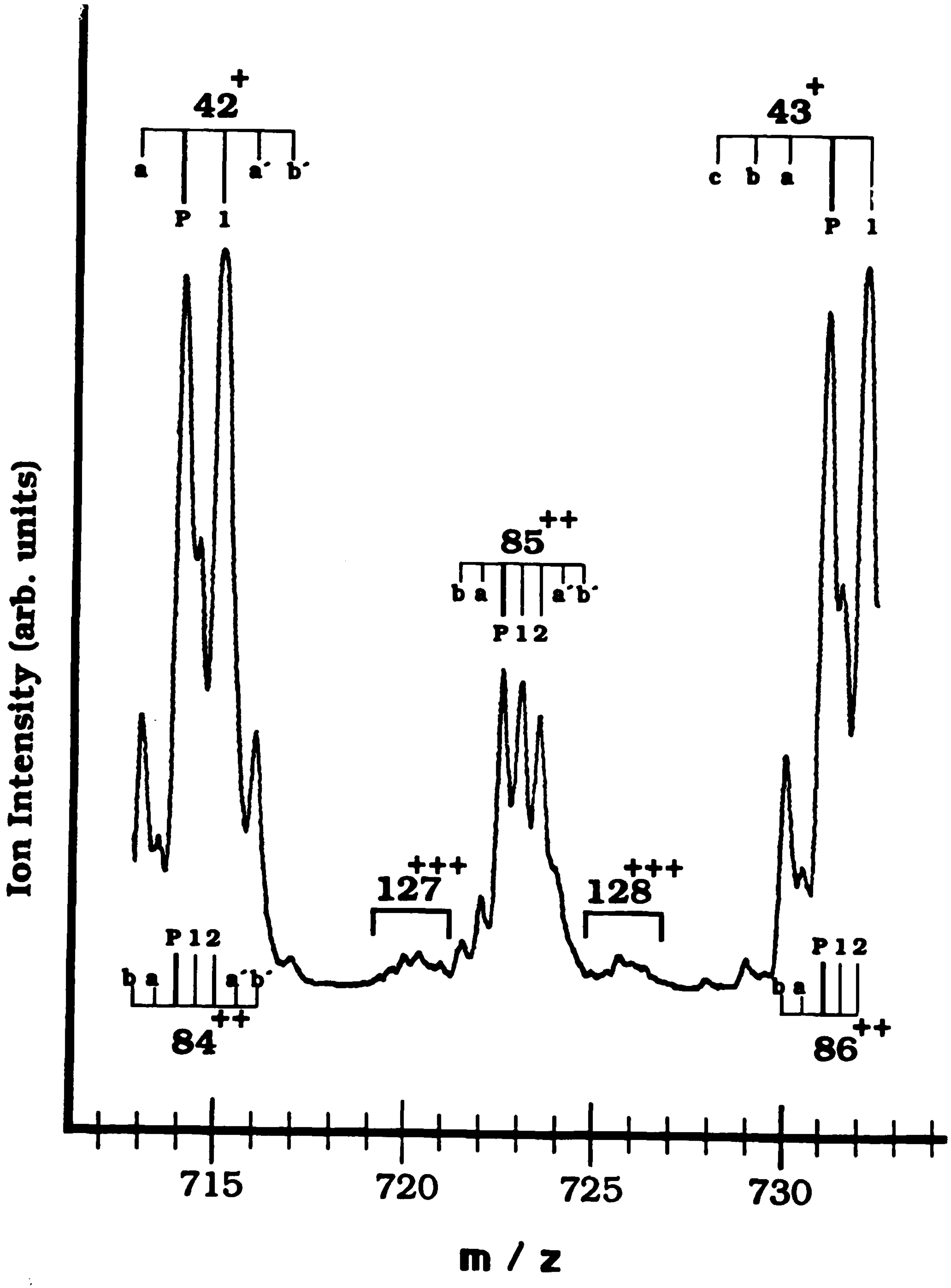

FIGURE 1
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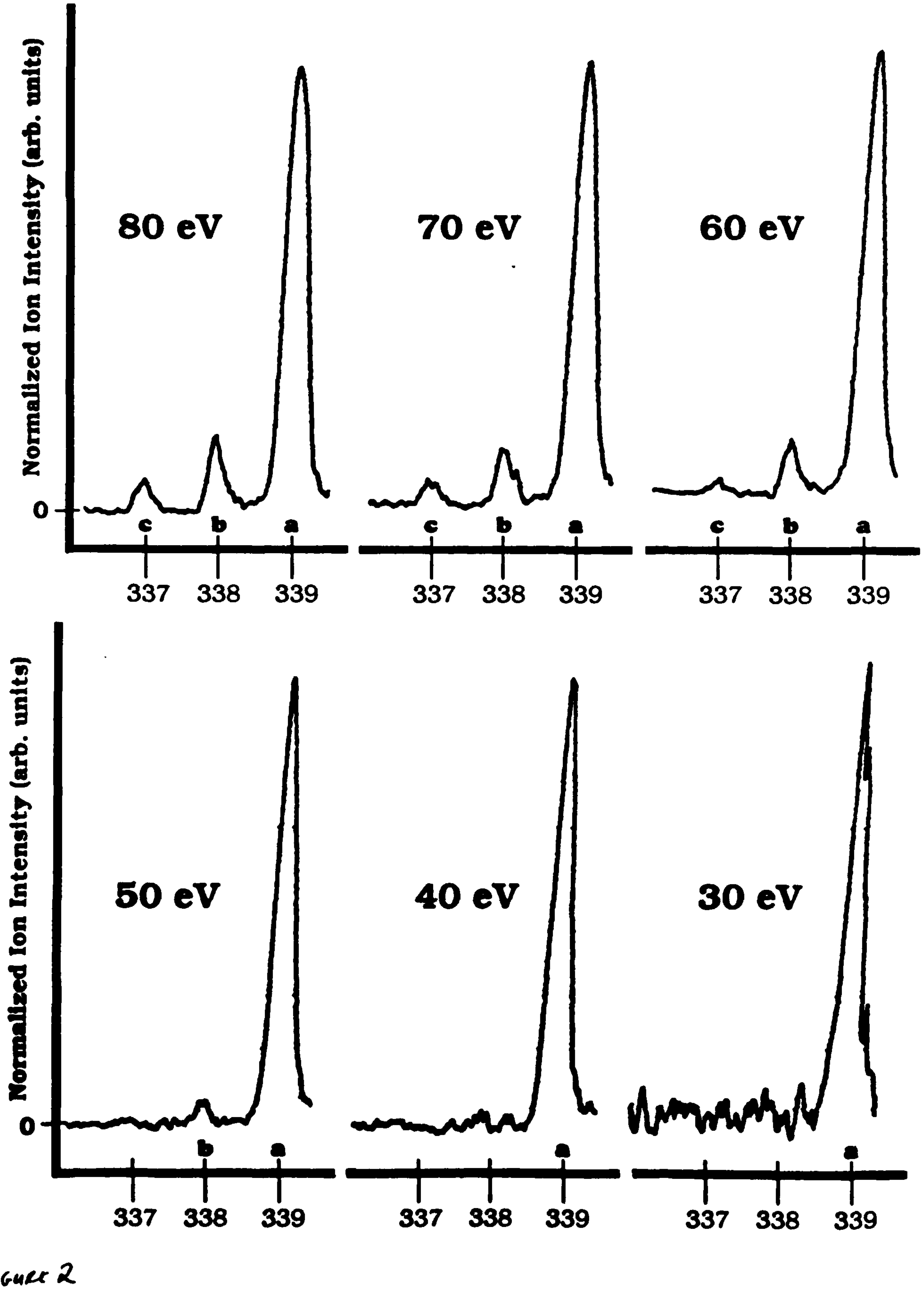

Figure 2

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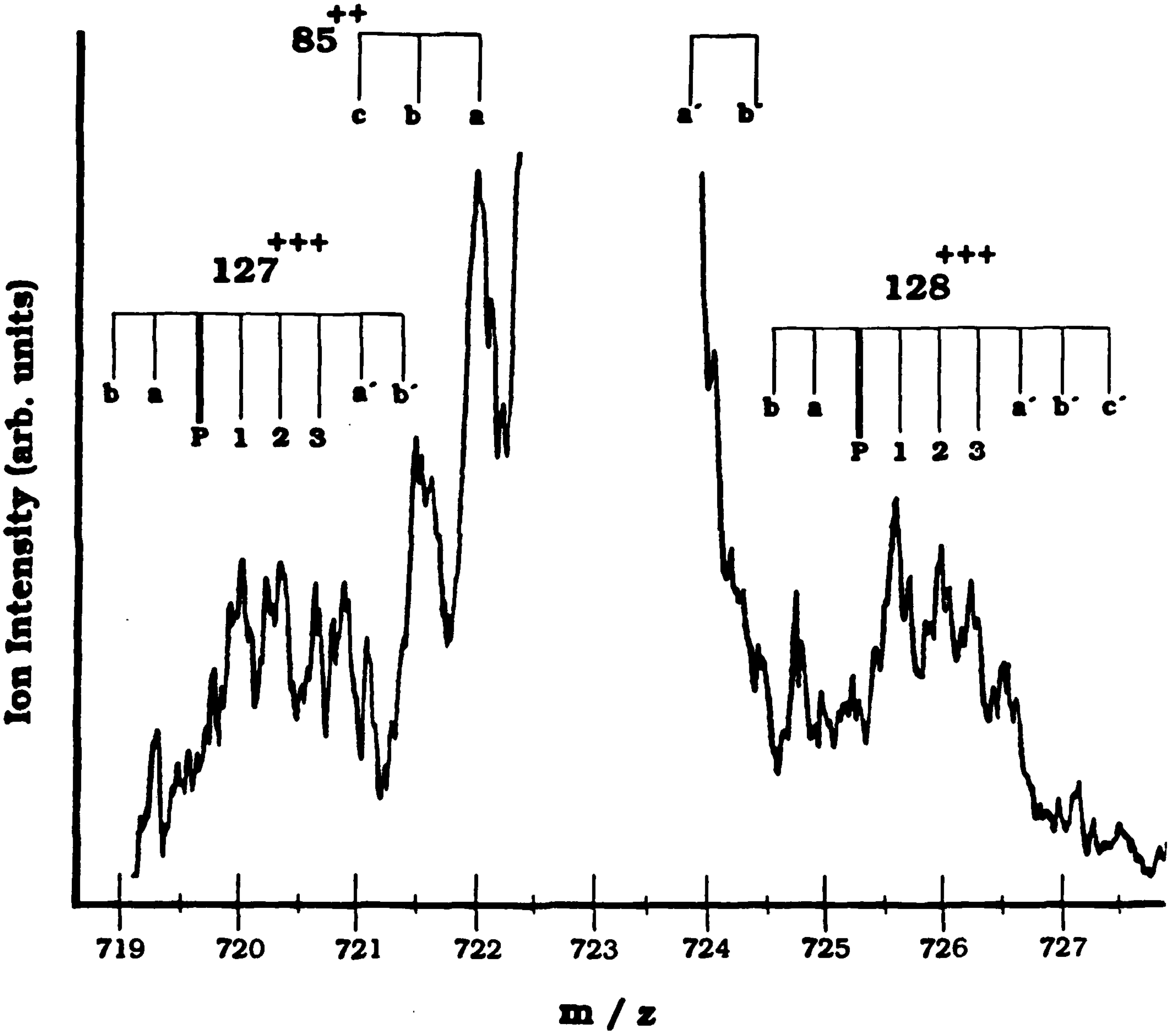

FIGURE 3
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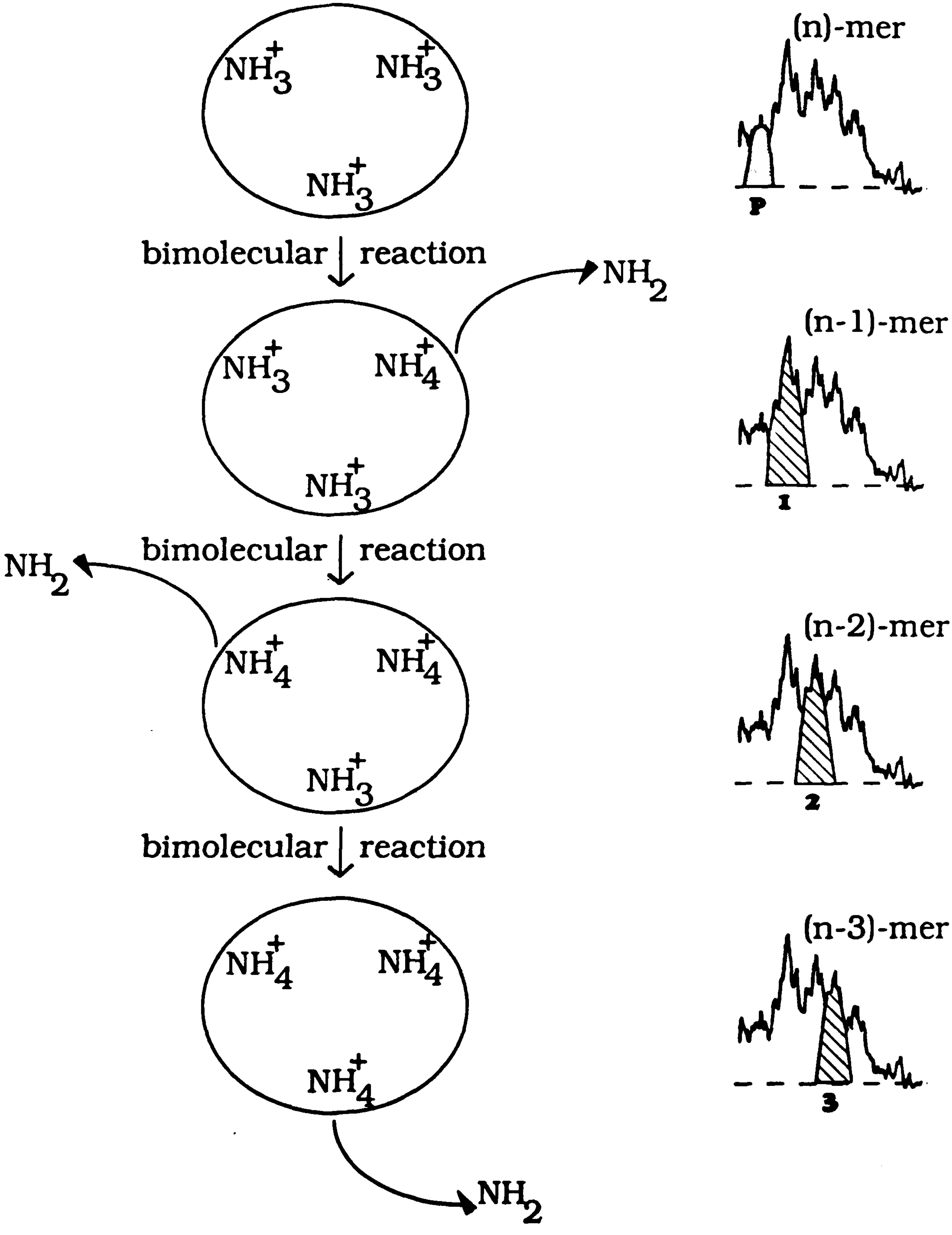

Figure 4
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