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LETTERS

Covariance Mapping of Ammonia Clusters: Evidence of the Connectiveness of Clusters with Coulombic Explosion

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Direct evidence is reported of the connectiveness of charged clusters with highly charged species (N^{4+}, N^{3+}, and N^{2+}) produced upon the interaction of molecular ammonia clusters with an intense femtosecond laser beam ($\sim 10^{15}$ W/cm^2 at 120 fs). The value of covariance analysis as a general technique for studying dynamical processes in clusters is demonstrated through elucidating the details of various Coulomb explosion events. Positive covariance determinations identify concerted processes such as the concomitant explosion of protonated cluster ions of unsymmetrical size, while anticovariance mapping is exploited to distinguish competitive reaction channels such as the production of highly charged nitrogen atoms formed at the expense of the protonated members of the cluster ion ensemble. The present study demonstrates the great potential which covariance analysis offers in identifying the precursors and products of dynamical events in clusters and in the present case provides further support to the ignition model as a mechanism contributing to the initial ionization events in clusters leading to highly charged atomic species.

Introduction

The study of multidimensional correlation of mass spectra has been an evolving topic for the past 32 years.[1] The original concept of photoion−photoion correlations (PIPICO)[1−7] has blossomed into photoion−photoelectron correlations (PEPICO),[8−15] photoelectron-photoelectron correlations (PEPECO),[16] and photoneutral−photoneutral correlations.[17] The addition of a third dimension extended the PEPICO and PIPICO techniques to photoelectron−photoion−photoion correlation methods (PEPIPICO).[18−30]

Recognition of the value of these methods has been tempered by realization of their difficulty in implementation. An alternative, but related, approach has developed from the statistical concepts of covariance. Codling and co-workers[31−38] demonstrated the power of this method in a series of papers devoted to a study of multicharged processes involving small molecular species such as N_2, N_2O, and CO. The technique requires extensive data analysis and large computational times and has to date attracted only rather limited attention.[31−41] Despite the computational requirements, the method is very powerful and is an especially attractive one for application to the study of molecular clusters.

The purpose of the present paper is to demonstrate the value of covariance analysis through the study of ammonia clusters subjected to intense pulsed radiation in the femtosecond time domain. The role which clusters play in effecting the formation of species of high charge state has only become recognized very recently;[42−47] indeed, to the best of our knowledge, we were the first to observe the formation of multicharged atoms arising from Coulomb explosion processes in molecular cluster systems. In this paper, we take advantage of the concept of covariance analysis to definitively establish the connectiveness of Coulomb explosion with the evolution of various charged species following the ionization of clusters via high-intensity laser fields.

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The value of considering anticovariance in conjunction with more conventional positive covariance mapping is also discussed.

Experimental Section

The equipment used in the present study, which has been described in detail earlier,[48] consists of a femtosecond laser ionization system coupled to a molecular beam-reflectron time-of-flight (TOF) mass spectrometer. Briefly, a femtosecond pulse is created when a continuous-wave argon ion laser is impinged on a dye solution of rhodamine 6G in a colliding pulse mode-locked arrangement; the beam is mode-locked with a DODCI dye solution. The beam is amplified with sulforhodamine 640 dye by using the second harmonic of a 10 Hz Nd:YAG laser focused into a six-pass Bowtie amplifier and thereafter with a series of three (2 mm/6 mm/12 mm) Bethune cell amplifiers. Pulse recompression is achieved using gratings. After amplification, the laser beam is roughly 2.5 mJ/pulse and provides a fluence of about 10^{15} W/cm^2 at the point where it is focused onto the molecular cluster beam.

Ammonia clusters are produced by expanding ammonia at 2300 Torr through a pulse valve into a vacuum environment (7×10^{-6} Torr), and the laser pulse ionizes a packet of ammonia clusters at the center of the TOF grids. The TOF grids were set at a 1600 V difference, and the reflectron was operated in a hard reflection mode whereby the ions were directly reflected to the detector without penetrating into the reflecting electric field of the reflectron. A steep voltage gradient in the TOF lens assembly was purposely employed in this initial study in order to superimpose the dual set of peaks which arise in the Coulomb explosion process, one from the backward and the other from the forward ejected species. We recognize the additional value to be obtained by undertaking a covariance analysis of associated forward and backward ejected peaks, but we leave this as a topic for the next paper. The present study, which represents a test case, incorporated a large number of parent and daughter species, and, even with the superimposed peaks, we needed to cross-correlate 5000 points for 25 million covariance values. The ion intensity was measured with a microchannel plate detector, and the electrical impulses were read via a digital oscilloscope coupled to a personal computer. Neat ammonia (99.98% minimum purity) was used without additional purification.

After a neutral cluster is ionized, it is accelerated in the TOF lens assembly from its point of formation toward lower electric potential. Ions with long lifetimes remain intact until they exit the TOF ionization region, and those which are metastable in this time regime are detected as parent masses when the reflectron is operated in the hard reflection mode. However, ions with short lifetimes decay into smaller fragments prior to departure from the TOF region. All species then traverse a drift region of 2.1 m and are detected at the microchannel plate

Results and Discussion

The primary objective of the present study is to identify various associated species ejected in the Coulomb explosion of clusters following their irradiation at high intensity, and to establish the possible existence of competitive versus concerted reaction channels. The species involved in this process are ejected over a broad distribution of angles away from the point of formation, and those which are refocused following backward ejection proceed toward the detector along with ones which are initially ejected in a forward direction. Hence as mentioned above, to explore connectiveness in the Coulomb explosion phenomena, we used a large potential difference in the birth region to preclude the occurrence of split peaks which normally arise due to these two sets of Coulomb explosion particles (CEPs).[49] Thus, in the arrangement employed, only phenomena occurring within the TOF region can affect the system and cause deviations to an ion's intensity.

In most applications of laser TOF mass spectrometry to cluster studies, advantage is taken of the fact that the ion intensities arising from various processes produce *average intensity* values which can be analyzed and interpreted. However, deviations in the ion intensity do occur because of slight fluctuations in the laser pulse or pulsed nozzle, and advantage is taken of these fluctuations in implementing the technique of covariance mapping.

In order to discuss the measurements reported herein, an overview of the overall phenomena occurring in the ammonia cluster system must first be given. Briefly, as reported earlier,[49] both singly charged protonated cluster ions as well as nitrogen atoms in various charge states are observed. These observations have been found to be consistent with the following model:

$$(NH_3)_x + h\nu \rightarrow (NH_3)_x^{z+} \rightarrow (NH_3)_m H^+ + (NH_3)_n^+ + NH_2 \quad \text{(clusters)}$$

$$(NH_3)_x^{z+} \rightarrow NH_3^+ + NH_2^+ + NH^+ + N^{p+} + H^+ \quad \text{(CEPs)}$$

Although the full range of x and z are not precisely known, p is found to range from 1 to 7 and m and n from 1 to 15.

During the course of our experiments, the intensities of the singly charged clusters were found to vary inversely with the intensities of the CEPs. Also, a change in the ratio of their relative abundances was seen when the focal point of the laser was varied. The processes responsible for their production are parallel and competitive, suggesting a rate dependence on the laser fluence. However, as discussed further below, the species do not arise by mutually exclusive reactions.

A rough schematic of the overall reaction and Coulomb explosion phenomena is given in Figure 1. (Clearly, this figure is not intended to represent a single reaction surface nor the specific electronic states of ammonia, but instead to depict the competitive processes operative at different energies.) By translating the focal point of the laser, we are able to change the fluence that the clusters experience. As the fluence is varied (by employing different focusing conditions), we can increase the energy distributed per neutral cluster and excite the cluster further; at sufficiently high values this opens the Coulomb explosion channel (state I). Conversely, defocusing distributes the power to more clusters and leads to lower excitation, enabling only singly charged clusters to be formed (state III). A midrange of focusing was selected to explore the threshold region between these processes (state II). The fluctuations in the intensities of the various measurements were exploited to investigate the competitive reaction channels which were first seen during the course of our initial observations employing the use of covariance mapping.

Covariance mapping compares the changes in one measurement with another measurement, via a shot-by-shot analysis. If this involves a large number of repetitive measurements (e.g. 10 000 times), then the results are statistically relevant. Covariance is defined as the deviation in two measurements of two different species, just as the variance is the deviation in two measurements of the same species. Thus the covariance analysis provides a measure of connectiveness between two different parameters, namely two different ionic species in the present case.

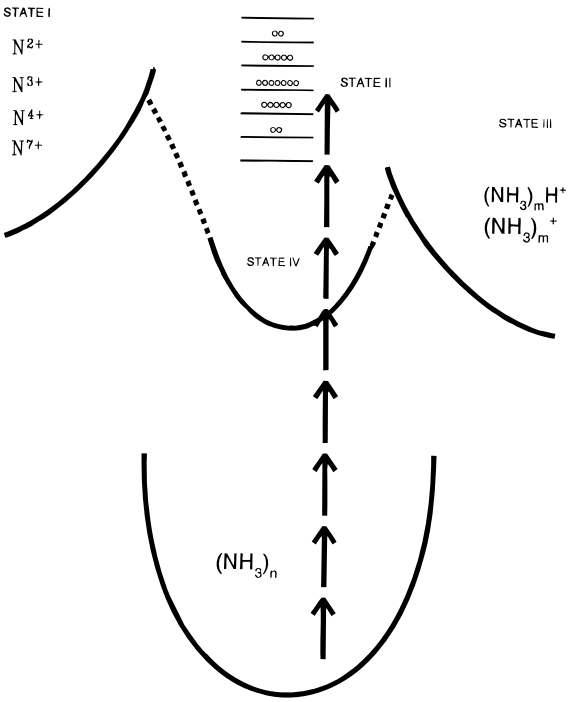

Figure 1. Reaction schematic of the excitation of a neutral ammonia cluster to ionization. State I represents an excited state capable of inducing the Coulomb explosion process. State II is the threshold region where moieties of Coulomb exploded particles and singly charged clusters are seen. State III is the ionized cluster state where only singly charged clusters are prevalent as products. State IV is the state in which the cohesive energy of the cluster overcomes the Coulomb repulsion caused by the charges within the cluster.

Mathematically, the covariance, $C(x,y)$ can be expressed by[31,50,51]

$$\begin{aligned} C(x,y) &= \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle \\ &= \langle XY \rangle - \langle X \rangle \langle Y \rangle \\ &= \frac{1}{N}\sum_{i=1}^{N} X_i(x) \cdot Y_i(y) - \left[\frac{1}{N}\sum_{i=1}^{N} X_i(x)\right]\left[\frac{1}{N}\sum_{i=1}^{N} Y_i(y)\right] \end{aligned}$$

where $X_i(x)$ and $Y_i(y)$ represent the intensities at some trace position i for a particular ionization period or shot and for specific species x and y. $C(x,y)$ is termed the covariance.[50]

Another closely related term to the covariance is the correlation coefficient, $\rho(x,y)$. It is a "direct measure" of the similarity of the changes in trace intensity[33,41,50] and is defined as

$$\rho(x,y) = \frac{C(x,y)}{\sqrt{C(x,x) \cdot C(y,y)}} \quad \text{where} \quad |\rho(x,y)| \leq 1$$

If $\rho(x,y)$ equals 1, 0, or -1, the peaks of x and y are considered perfectly correlated, not correlated, or anticorrelated, respectively.[50] Since the variance of a measurement is always a positive quantity, the sign of the correlation coefficient is clearly dependent on that of the covariance. When $\rho(x,y)$ is less than 0, $C(x,y)$ is less than 0, and conversely.

In terms of a chemical reaction, two peaks are obviously correlated if both increase or decrease with each other. On the other hand, two peaks are anticorrelated if one is seen to increase when the other decreases, and if a peak remains unchanged when the other either increases or decreases, they are, of course, uncorrelated.

Competitive reactions are ones which deplete a reactive species by two or more channels. Unless two reactions are competitive, the products of all reactions will result in correlations (or no correlations) as opposed to anticorrelations. In the present work, the dependent variable is the decay rate of the multiply charged cluster. However, the rate is a function of the laser intensity or the cluster size (the fluctuating variables in the system). There are two limits to the phenomena under study, namely situations where the species produced become either all CEPs or solely singly charged clusters. Fluences which lead the system to adopt a condition resulting in one of these two limits eliminate observable coupling between the two measurements (i.e. without a measurement, there are no covariances or correlations) and place the system essentially in one charge state. Snyder et al.[43] and Wei et al.[49] presented data for experiments conducted under conditions corresponding to states I and III; Wei et al. also presented data showing the attainment of a condition leading to stable multicharged clusters (state IV).[52]

The abscissa and ordinate inserts of Figures 2 and 3 display a plot of the TOF mass spectrum for the present study and enable an analysis of the covariance map. The time-of-flight mass spectrum represents the conditions of intermediate state II in Figure 1. As seen, there are abundant amounts of both CEPs and singly charged clusters.

The center portion of Figure 2 is a covariance map where numerical values of $C(x,y)$ greater than 1 are plotted; this plot enables insight to be gained into the coupling between the reactants or products. The line of symmetry, namely the $x-y$ axis, which is the line defining the variance of the intensity measurements, can be seen beginning in the lower left corner. The positive covariance values for this study ranged from 0 to about 3700. Positive values less than 1 corresponded with base line noise and were ignored. Similarly, the positive correlation data, $\rho(x,y)$, varied from 0 to 1, and values less than 0.1 were ignored as base line noise.

Voids in the covariance map of Figure 2 indicate that no correlation is found between the higher clusters and the CEPs, which implies that they are *not* produced simultaneously. Beginning with $(NH_3)_8H^+$ and lower order clusters, a steady increase in cross-correlation is seen. This clear transition regime where smaller clusters are created along with CEPs would be expected in the threshold region studied.

Figure 3 is a similar map of covariances less than -1, which represents product coupling through competitive reactions. A similar line of symmetry, the $x-y$ axis, can be seen on this plot as well—albeit since the variance is positive, this line of symmetry is actually a void. Negative covariances ranged from about -1000 to 0. Values between -1 and 0 were indistinguishable from background noise and hence were ignored. The intense anticovariance displayed between the higher order clusters and the CEPs, where the void exists in Figure 2, confirms the competitive model presented. To the best of our knowledge, no other researcher, except for Amoruso et al.[41] who studied species evolved from a surface, has explicitly explored a system via anticovariance mapping.

Comparing Figure 2 and 3, $(NH_3)_{15}H^+$ is found to display a covariance with the series $(NH_3)_nH^+$, where $n = 1\cdots5$, and with H^+. The absence of any covariance of $(NH_3)_{15}H^+$ with the protonated hexamer discounts that any protonated hexamer is produced with $(NH_3)_{15}H^+$ through a concerted Coulomb explosion event. These species would be considered uncorrelated with $(NH_3)_{15}H^+$. This finding is quite cogent, because otherwise

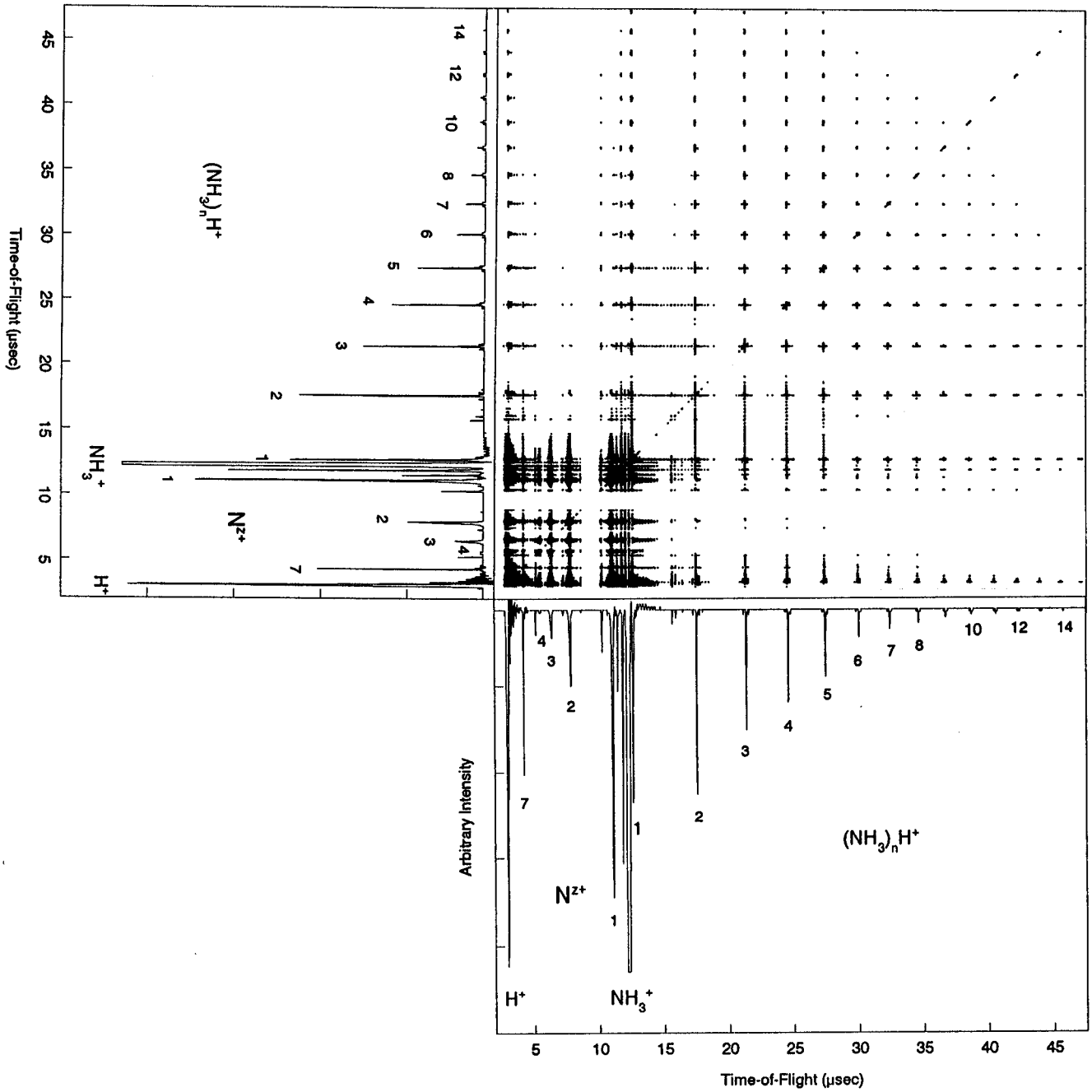

Figure 2. Covariance map of ammonia clusters. The abscissa and ordinate display a TOF spectrum of ammonia clusters averaged over 10 000 single-shot spectra. The center of the figure displays the calculated covariance map as described in the text. Symmetry is clearly visible on the $x-y$ axis starting at the lower left corner. Coupled species are identified by their covariance.

larger singly charged clusters would likely have been found in the study.

A comparison of correlated cluster events with other clusters is made in Figure 4, using the peak correlation values. By using the correlation coefficient values, the influence of individual peak intensity is removed and a comparable value is achieved ($-1 \leq \rho(x,y) \leq 1$). Since a higher correlation coefficient value implies a more common connectiveness, the data indicate that all singly charged clusters are more prevalent in their occurrence along with smaller singly charged cluster siblings. The fact that more clusters are favored under these circumstances could imply that they are just more stable in general, that larger clusters are less common under the present beam expansion conditions, or that the processes under study are entropy driven.[53]

The trend in Figure 4 serves to substantiate the inference of a neutral cluster size of at least $(NH_3)_{21\pm4}$ being involved in the Coulomb explosion process. If the clusters $(NH_3)_nH^+$ where $n = 1\cdots5$ coexisted along with $(NH_3)_{15}H^+$ in each laser shot, then $\rho(x,y)$ would be 1 for every correlation between the species and they would be perfectly correlated. Since $(NH_3)_{15}H^+$ occurs, the neutral cluster must be composed of at least $(NH_3)_{16}$. On the other hand, since $(NH_3)_{15}H^+$ is correlated with other clusters, it must occur in coincidence with them. Therefore, the neutral cluster must be at least $(NH_3)_{21\pm4}$, which would allow for a binary Coulomb explosion event giving rise to these observed species.

The fact that singly charged clusters are sibling products lends credence to the earlier evidence that the instability of the multicharged cluster is due to the existence of an unsymmetric charge distribution[43,49] at the time of ionization. Clearly, if the charge distribution of the multicharged clusters was perfectly symmetric, then a cluster of $(NH_3)_{2n+1}^{2+}$ would break up solely

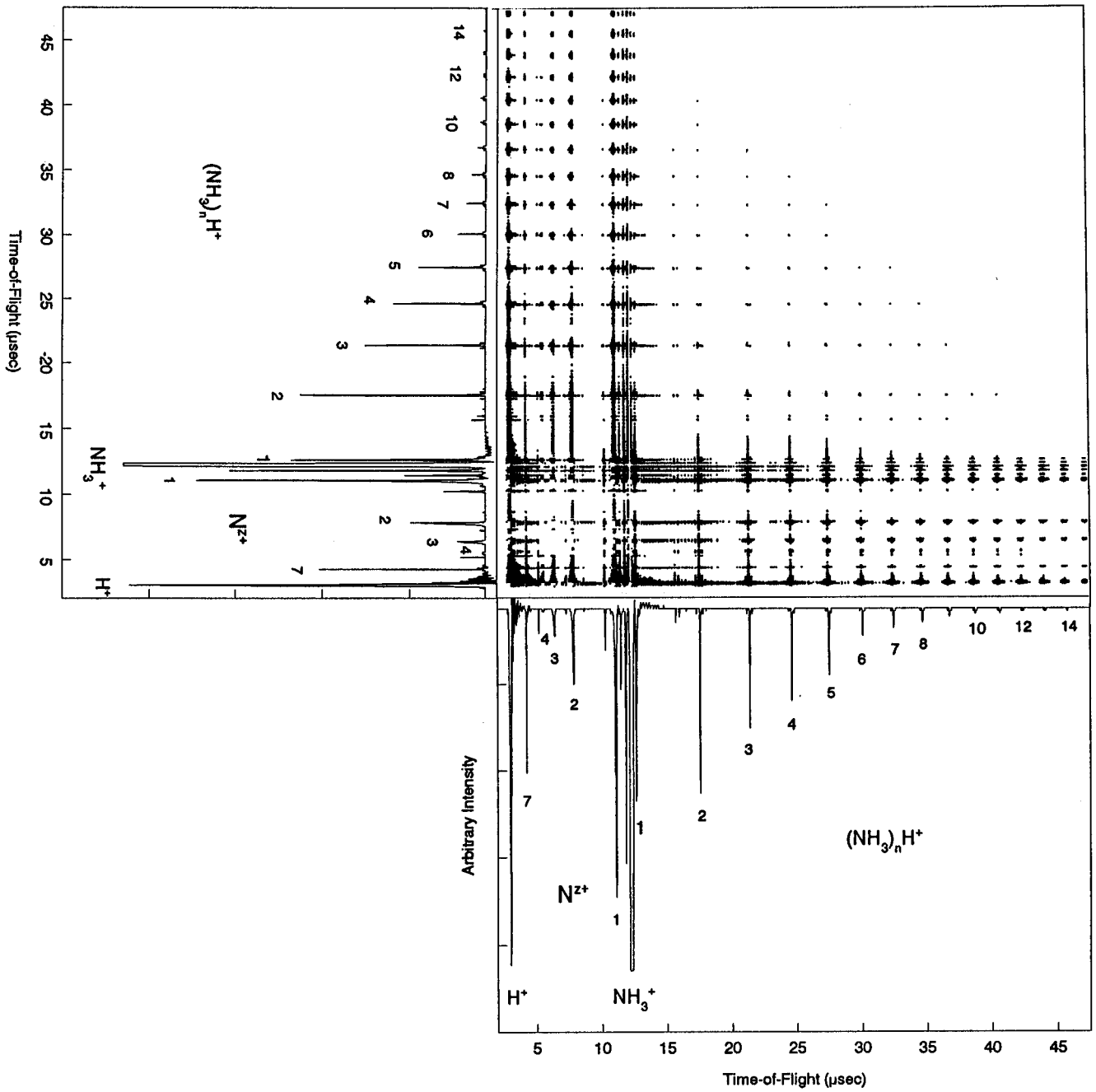

Figure 3. Anticovariance map of ammonia clusters. The abscissa and ordinate display the TOF spectrum averaged over 10 000 single shots. Proof of the competitive reaction is seen in the CEP cluster covariance field which was absent in the similar domain of Figure 2. Although the covariance and anticovariance maps appear to overlap, each data point (x,y) is distinct and is found on only one map.

into two $(NH_3)_nH^+$. Then, the correlation coefficient of this species would be 0 with all other species. Accounting for an even neutral cluster, $(NH_3)_{2n}^{2+}$ would break up into $(NH_3)_nH^+$ and $(NH_3)_{n-1}H^+$; hence, these species would have a correlation coefficient of 1 and display no correlation coefficient with other cluster sizes. These relationships are not seen in Figure 4. Thus the multicharged cluster must have an unsymmetric charge distribution. Logically, increasing the fluence on a neutral cluster to achieve CEPs would also result in an unsymmetric charge distribution.

A plot of the peak correlation values for the submonomer species versus the size of the protonated clusters is seen in Figure 5. Since the correlation values are negative, the plot represents an anticorrelation comparison. As these species' correlation value approaches 0, there is less connectiveness with higher clusters. This demonstrates a gradual trend toward less competition between higher cluster species and CEPs as cluster sizes increase.

Conclusion

The findings presented herein provide direct evidence of competitive parallel reactions involving singly charged clusters and Coulomb exploded particles that form when matter interacts with intense radiation in the ultrafast time region.

The connectiveness of protonated singly charged clusters of different sizes establishes that they arise from the Coulomb explosion of parent clusters of larger size. Although multiply charged clusters smaller in size than those stabilized by their cohesive energy are too unstable to be seen directly in the parent mass distribution, the correlations provided by covariance mapping set lower limits of the size of the neutral cluster species.

The correlations also show good agreement with earlier

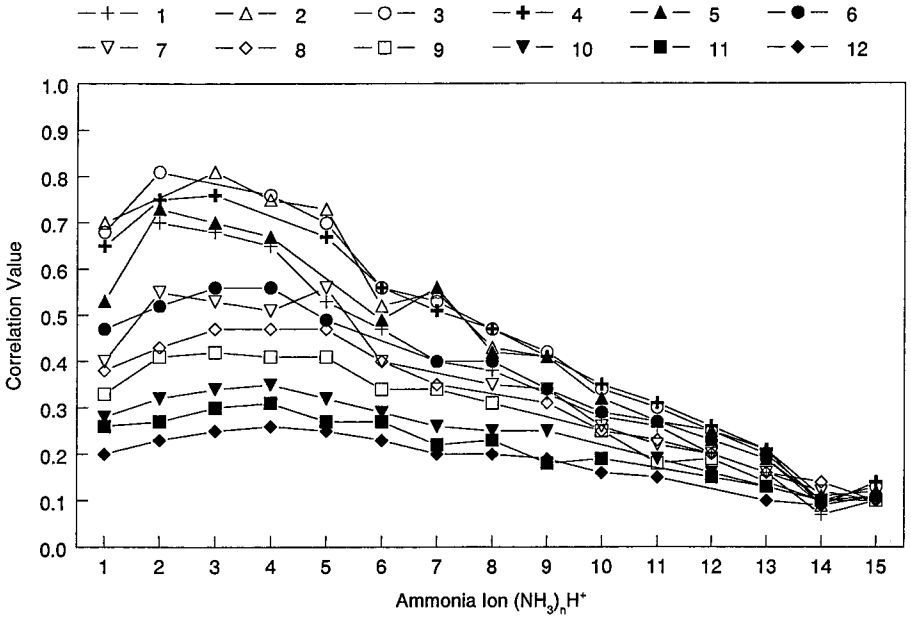

Figure 4. Clusters compared with other clusters using the correlation coefficient which removes intensity dependence. Larger singly charged clusters are seen to occur less frequently with similar order singly charged species. A preference of all singly charged clusters occurring with smaller size singly charged clusters is evident. Self-correlations are omitted to prevent skewing of the points.

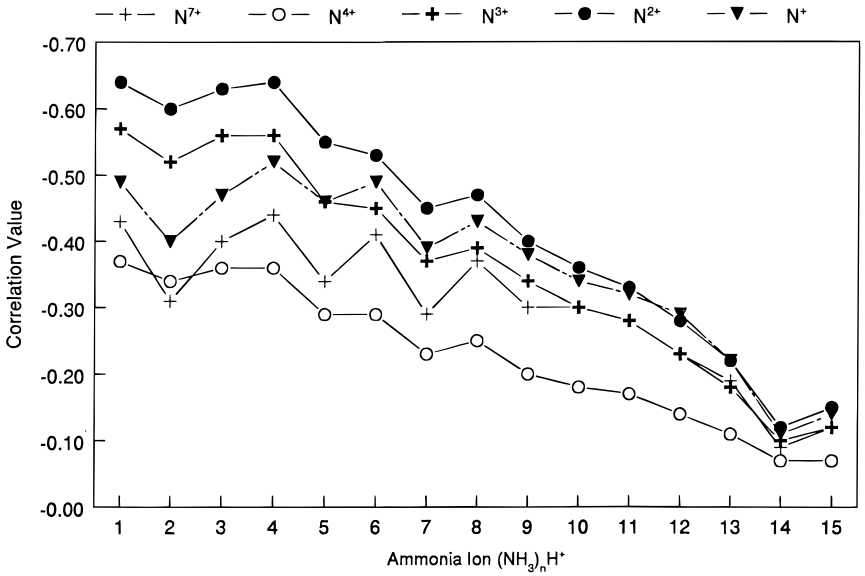

Figure 5. Multicharged nitrogen correlation with clusters. Using the correlation coefficient, the multicharged particles are compared with singly charged cluster species without the influence of intensity. Evident is the higher anticorrelation of multicharged species with smaller size clusters. Although some uncertainties still exist, the peak of mass-to-charge (m/z) 2 in the time-of-flight spectrum was assigned as N^{7+} because of the similarities exhibited in this plot with the other multicharged nitrogen atoms.

studies in which kinetic energy measurements pointed to unsymmetric charge distributions giving rise to split peaks arising from the Coulomb explosion of protonated species.[43] Except for a few cases, most high charge states show no correlations with singly charged species.

Importantly, the anticorrelation observed between CEPs and larger singly charged clusters presents a valuable concept of investigating a competitive ionization process. Indeed, the anticovariance map shows the operative nature of competitive channels in agreement with the model presented in Figure 1.

Taken together, the findings support the model due to Wei et al.[49] that attributes the production of protonated clusters which undergo Coulomb explosion versus the production of CEPs to a cascading of charge transfer reactions which occur at times short compared to the motion of the nuclei. Finally, the positive covariance seen between the CEPs and small ammonia cluster ions and the anticovariance found for the CEPs with the larger clusters further support the ignition model[45,47,54] as an important mechanism responsible for the initiation events of multicharge atom formation in clusters, which predicts only a weak dependence on cluster size. Our study and another which appeared in literature[55] after we had prepared the original version of this manuscript for publication show the power of covariance mapping in studying fragmentation processes in both neutral and ionized molecular clusters.

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