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The interaction of titanium-carbon cluster fragments

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Abstract. Covariance and correlation coefficient mapping techniques are utilized to investigate the formation mechanism of titanium carbon clusters in a laser vaporization source, and also to elucidate the details of fragmentation of these clusters under excitation with an intense femtosecond laser pulse ($\sim 10^{15}$ W/cm^2 at 120 fs). This study, and a previous investigation of the Coulomb explosion of ammonia clusters, demonstrates the potential which covariance mapping has in discerning the details of cluster formation and fragmentation processes. Particular attention is paid to the titanium metallocarbohedrene (Met-Car), Ti_8C_{12}.

PACS. 36.40.Qv Stability and fragmentation of clusters – 78.47.+p Time-resolved optical spectroscopies and other ultrafast optical measurements in condensed matter

1 Introduction

Photoionization studies of clusters systems in molecular beams, from van der Waals to molecular, have often been complicated by fragmentation concurrent with ionization. For example, higher mass clusters may dissociate upon ionization and "feed-down" into lower mass clusters. When using non-resonant above threshold ionization schemes, it is typically difficult to discern whether the observed low mass clusters are formed by direct ionization, or are the result of the fragmentation of higher mass species. Unfortunately, most common experimental techniques employed to study the photoionization of cluster systems are unable to probe the possible initial fragmentation events. In addition, cluster formation or building processes are difficult to experimentally investigate and conclusions about building processes are typically inferred from trends or patterns observed in mass spectra.

In the past, exploration of cluster systems has successfully employed signal averaging to alleviate difficulties in low signal levels, fluctuating signal intensities, and background noise. However, Codling and his coworkers demonstrated the technique of utilizing every trace recorded, without averaging [1–8]. Moreover, they discovered that the fluctuations in signal intensities revealed the hidden interactions left unseen by signal averaging. Their method, covariance mapping, opened a new area of research. The technique requires large computational resources, extensive data processing and storage space, and has attracted only limited attention to date. Despite these difficulties, the method is extremely powerful and provides unique insight into the study of molecular clusters.

Recently, we have reported the use of a covariance technique to probe the Coulomb explosion process in ammonia clusters [9]. The ammonia clusters, which exhibit a dendramer like structure built upon covalent and hydrogen bonds, undergo Coulomb explosion when photoionized with a high intensity, femtosecond pulse. Both singly charged protonated cluster ions as well as nitrogen atoms in various charge states were observed in the ammonia system [9, 10]. The intensities of the singly charged clusters vary inversely with the intensities of the multicharged nitrogen atoms. Also, a change in the ratio of their relative abundance is seen when the laser focal point is varied. These observations are consistent with the following model:

$$(NH_3)_x + h\nu \rightarrow (NH_3)_x^{z+}$$

$$(NH_3)_x^{z+} \rightarrow (NH_3)_m H^+ + (NH_3)_n^{(z-1)+} + NH_2 \quad (1)$$

$$(NH_3)_x^{z+} \rightarrow NH_3^+ + NH_2^+ + NH^+ + N^{p+} + H^+ \quad (2)$$

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.

The purpose of the present paper is to investigate titanium carbon clusters subjected to intense pulsed radiation in the femtosecond time domain and to employ covariance mapping techniques to gain insight into the formation and dissociation processes present. In this investigation, we exploit the concept of covariance and correlation coefficient mapping to definitively establish the relationships between cluster species. Moreover, the value of the covariance and correlation coefficient subsurface maps is utilized to ex-

amine possible parallel reaction processes involved in this system.

2 Experimental

The equipment used in this study has been described in detail earlier [11]. In brief, a femtosecond pulse is created when a continuous-wave argon ion laser is focused 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 a series of three (2 mm/6 mm/12 mm) Bethune cell amplifiers. Pulse recompression is achieved using a grating pair. After amplification, the 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 a molecular cluster beam.

A 10 Hz Nd:YAG laser pulse, at 532 nm, is focused onto a rotating and translating titanium rod in the presence of methane gas creates titanium-carbon clusters in a laser vaporization source. A laser pulse ionizes the molecular packet at the center of TOF grids. The TOF grid geometry was optimized for resolution and the reflectron was operated in a hard reflection mode, which prevented the ions from penetrating the reflecting electric field and causing separation of the peaks. All species traverse a drift region of 2.1 m and are detected at a microchannel plate. The electrical impulses were read via a digital oscilloscope coupled to a personal computer.

3 Results and discussion

Covariance mapping compares the changes in one measurement with another measurement, via a shot-by-shot analysis. This analysis becomes statistically relevant when a large number of repetitive measurements (e.g. 10 000 times) are made. Covariance is defined as the deviation in two intensity measurements of two different species, just as the variance is the deviation in two intensity measurements of the same species. Thus the covariance analysis provides a measure of connection between two different species in a single process and can be used to gain insight into complicated dissociation processes.

To understand covariance mapping, one must first examine the cluster ionization event and the decay of the resultant ions. Understandably ions with long lifetimes, singly or multiply charged, remain intact while in the TOF 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 and the parent ions are not evident from the observed fragments.

Notwithstanding this plethora of possible processes, some semblance of order may be uncovered by using the technique of covariance mapping. Covariance mapping uses the subtle changes in the ion intensity to discern if ions are connected in their formation or reaction.

Mathematically, the covariance, $C(x, y)$ can be expressed by [1, 12, 13]:

$$C(x,y) = \frac{1}{N}\sum_{i=1}^{N} X_i(x)\cdot Y_i(y) - \left[\frac{1}{N}\sum_{i=1}^{N} X_i(x)\right]\left[\frac{1}{N}\sum_{i=1}^{N} Y_i(y)\right] \quad (3)$$

where $X_i(x)$ and $Y_i(y)$ represent the oscilloscope intensities at some trace position "i" for a particular ionization period or shot and, for specific species x and y.

Another closely related term to the covariance is the correlation coefficient, $\varrho(x, y)$. It is a "direct measure" of the changes in trace intensity [3, 12], and is defined as:

$$\varrho(x,y) = \frac{C(x,y)}{\sqrt{C(x,x)\cdot C(y,y)}} \qquad \text{where } |\varrho(x,y)| \le 1\,. \quad (4)$$

If $\varrho(x, y)$ equals 1, 0, or -1, the peaks of x and y are considered perfectly correlated, not correlated, or anti-correlated, respectively [12]. 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 $\varrho(x, y)$ 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 anti-correlated if one is seen to increase when the other decreases. And if a peak does not change when another peak increases or decreases they are, of course, uncorrelated. Correlated peaks suggest that the species originate from a parallel process or reaction, while anti-correlated species come from competitive processes.

3.1 Titanium-carbon clusters

To decrypt the multitude of processes in the titanium-carbon system, the covariance map and the anti-covariance map are utilized. Comparative analysis of the two maps identifies several products that are distinctly coupled. Figure 1 is the covariance map of the titanium-carbon system with covariances greater than 300, while Fig. 2 is the anti-covariance map of the titanium-carbon system with covariances less than -100.

Figure 1 also identifies a fragmentation channel for titanium-carbon clusters with one or two titanium atoms in the cation. For example, the coupling of $Ti_2C_2^+$ with TiC_4^+, TiC_2^+, TiC^+, Ti^+, and H^+ yields peak covariances of appreciable magnitude indicating a high degree of correlation.

Comparing Figs. 1 and 2 identifies an intense connection between the titanium-carbon clusters $Ti_xC_y^+$ where x is less than 2 and y is less than 4 with titanium-oxide cations. This coupling of titanium-oxide with $Ti_2C_4^+$,

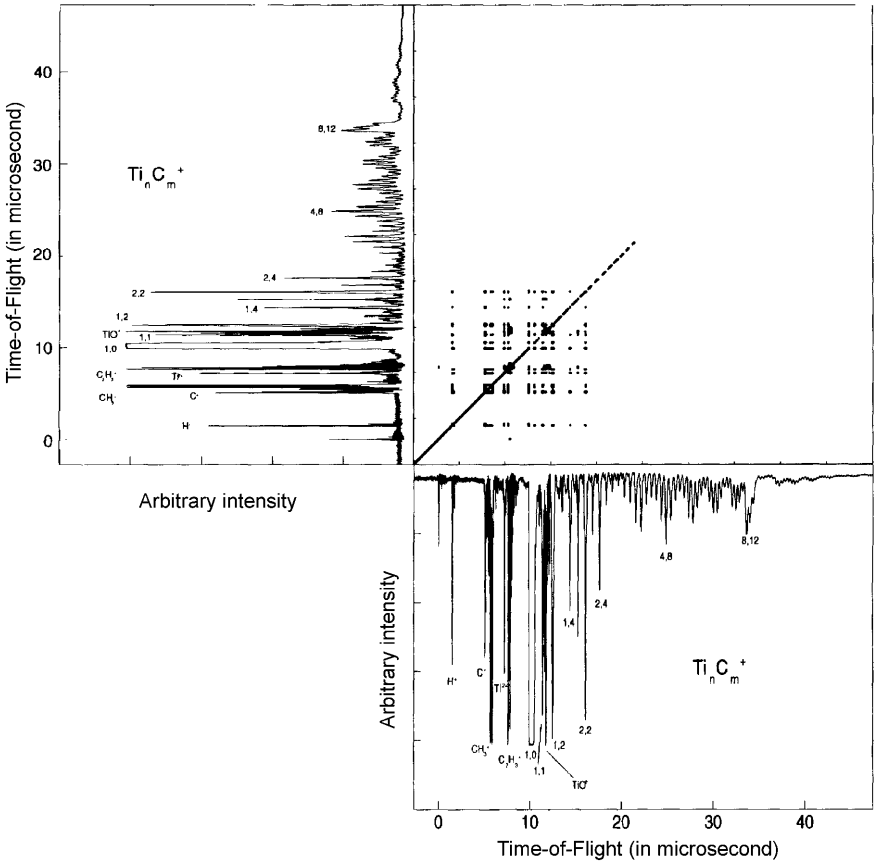

Fig. 1. Covariance map of titanium-carbon clusters. The covariance map is developed for covariances greater than 300. Strong interactions are visible for titanium-carbon ions with intense peaks in the time-of-flight spectra.

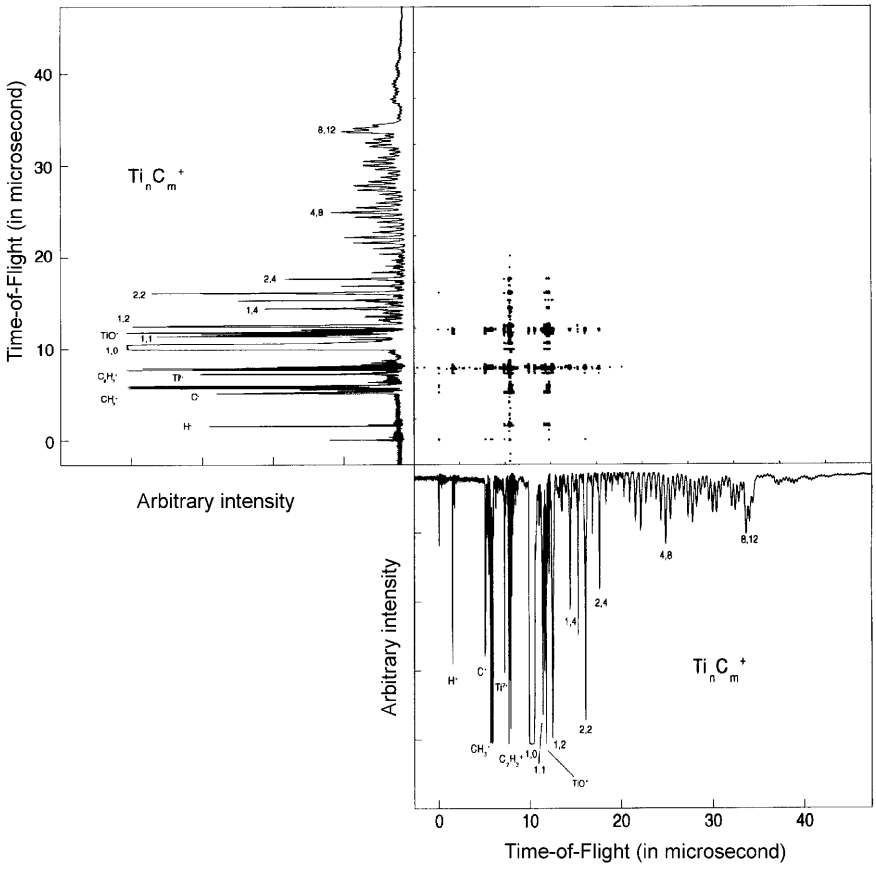

Fig. 2. Anti-covariance map of titanium-carbon clusters. This map is developed from covariances less than −100. Similarly, titanium-oxide clusters (m/z 64) are predominantly prevalent in this anti-covariance map.

$Ti_2C_2^+$, TiC_4^+, TiC_2^+, TiC^+, and Ti^+ yields peak covariances showing substantial anti-correlation. These quantitative results agree with previous qualitative observations; when an intense titanium-oxide peaks is present, it is difficult to produce larger titanium-carbon clusters and if the titanium-oxide peak is intense enough, the titanium Met-Car will not be produced.

Furthermore, the comparison of the two maps also shows a distinctive connection with the hydrocarbon clusters at mass-to-charge 27 and 28, $C_2H_3^+$ and $C_2H_4^+$ respectively. Peak covariances of $C_2H_3^+$ with $Ti_2C_2^+$, TiC_4^+, TiC_2^+, TiC^+, and Ti^+ yield values suggesting strong anti-correlation. Similar peak covariances of $C_2H_4^+$ with $Ti_2C_4^+$, $Ti_2C_2^+$, Ti_2C^+, TiC_4^+, TiC_3^+, TiC_2^+, TiC^+, and Ti^+ yield increasingly greater anti-correlation.

Figure 3 is the correlation coefficient map for titanium-carbon clusters with values between 0.2 and 1.0. Figure 4 is the anti-correlation coefficient map for titanium-carbon clusters with values less than -0.1 and greater than -1.0.

Figure 3 identifies several interactions seen earlier in Fig. 1. However the titanium-carbon clusters with four or more titanium atoms do not exhibit any interaction with protons as seen in the smaller clusters, but interact strongly with each other. The plethora of small fragments seen in the ammonia study [9] is not visible and implies that the titanium-carbon clusters are more strongly bound than the ammonia clusters, which is expected. Also, a comparatively low correlation is observed between the series of titanium-carbon clusters, which have nine titanium atoms, when compared with the other high mass clusters. This supports previous experimental results that show that the nine atom metal containing clusters undergo metastable dissociation to form eight atom metal containing clusters, ultimately forming a Met-Car.

Figure 4 reinforces the processes identified in the anti-covariance map only imparting the couplings through all clusters. Note the extremely strong coupling found between every titanium-carbon cluster and titanium yielding a near continuum in the larger clusters. Moreover Fig. 4 also identifies the anti-correlation of TiC_2^+ with C^+, CH_3^+, and CH_4^+. This observation is also consistent with previous work; the complete dehydrogenation of the starting hydrocarbon gas is critical in the production of high mass titanium-carbon clusters, specifically the Met-Car.

3.2 Comparison of ammonia and titanium-carbon clusters

Comparison of the ammonia and titanium-carbon systems reveals higher charged states indicative of Coulomb

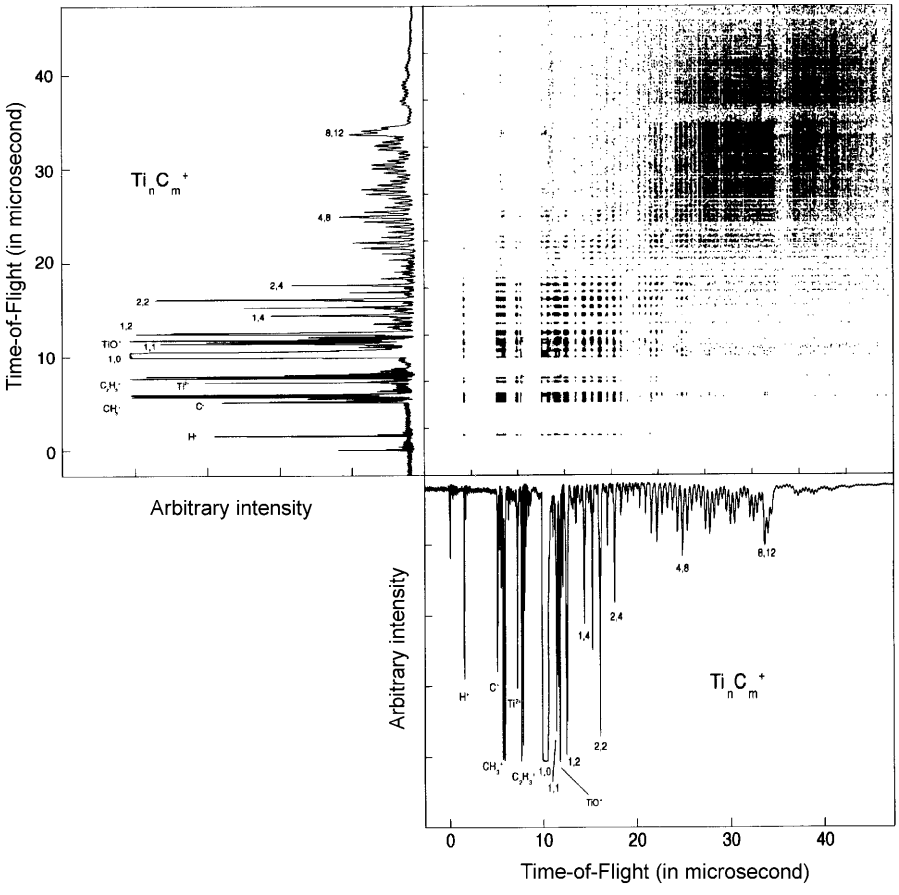

Fig. 3. Correlation coefficient map of titanium-carbon clusters. The correlation coefficient equals the covariance value divided by the square root of the product of the variances in the ion intensities. This value normalizes the covariance and yields a value between -1 and 1. Normalization permits comparison independent of the signal intensity. This map developed from the covariance map in Fig. 1 displays the correlation coefficient values greater than 0.2 and less than 1.0. Note the strong coupling between the larger clusters that were missing in the covariance map of Fig. 1.

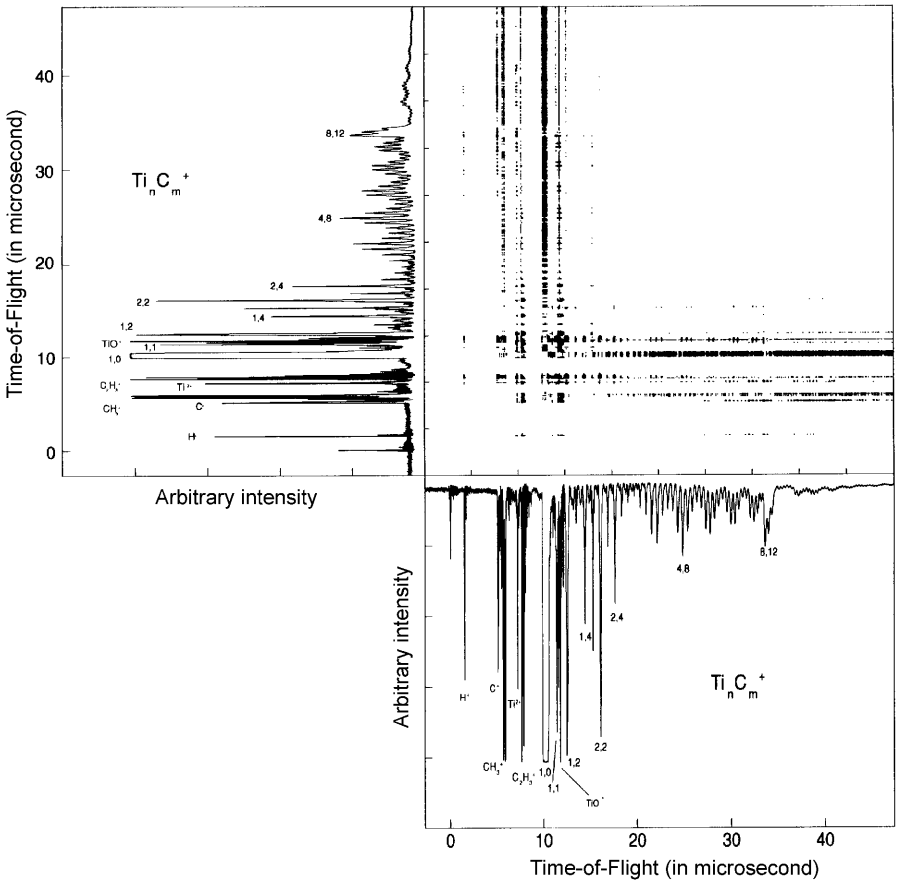

Fig. 4. Anti-correlation coefficient map of titanium-carbon clusters. This map displays the correlation coefficients less than -0.1 and greater than -1.0. Extremely strong coupling is seen between the titanium, titanium-oxide, and methane fragments (C^+, CH_3^+, and CH_4^+) cations and with the titanium-carbon clusters – especially the larger clusters.

explosion in the ammonia system alone. The titanium-carbon clusters are expected to be more strongly bound than the ammonia clusters. Although the rigid structure in the titanium-carbon clusters presents a higher electron density than ammonia clusters; Coulomb explosion is not observed, while ammonia clusters, with their van der Waals bonds, do undergo Coulomb explosion under similar experimental conditions. These finding suggest weaker bonded clusters are more susceptible to Coulomb explosion.

In both the ammonia system [9] and the titanium-carbon system, a notable change in the cluster and fragment distribution was evident upon translating the focal point of the laser beam. Similarly, changes were observed when changing the molecular beam parameters. These observations suggest that different fragmentation and formation channels may be dominant under different conditions. By selecting the focusing condition and the molecular beam conditions the connection between different processes can be explored. Further experiments are planned to investigate the effect of varying formation and ionization conditions.

In addition, it was recently observed in our laboratory, that under appropriate formation conditions, up to four intact methane molecules could cluster with a neutral Met-Car molecule. Exposing these clusters to intense femtosecond radiation, and employing covariance analysis techniques, is expected to provide information on the dehydrogenation process crucial in the formation of Met-Cars.

4 Conclusion

The findings presented herein provide insight into the formation and fragmentation of titanium carbon clusters. The titanium-carbon system demonstrates the advantages of using the comparative analysis of positive and negative covariance maps. This comparison establishes the presence of parallel reactions, which deplete the same progenitor and act as a competitor. Thus the mapping of the negative covariance values becomes crucial to discern the processes. Moreover, the titanium-carbon system demonstrates the need of utilizing the correlation coefficient maps to determine the low intensity details associated in the time-of-flight region.

In the Met-Car formation process, several previous experimental results are confirmed. The anti-correlation observed for titanium-oxide with several possible building blocks of higher mass clusters, including the Met-Car is observed. This agrees with the observation that oxide formation must be minimized to produce high mass titanium-carbon species, especially the Met-Car. Also, an anti-correlation is observed between the partially dehydrogenated methane species. This also agrees with

previous experimental results that show that Met-Car formation is favored when complete dehydrogenation is accomplished.

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