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WHAT CAN COULOMB EXPLOSIONS TEACH US ABOUT CLUSTERS?

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INTRODUCTION

In recent years, there has been a considerable interest in the study of gas-phase atomic clusters. Among the motivations for this work is the fact that such clusters provide a bridge between molecular and condensed matter physics, and thus provide an opportunity to study the structural and electronic rearrangements involved in this transition. Small carbon cluster ions are particularly interesting because of their importance in many chemical processes such as catalysis and combustion and there has been a long history of work with these ions. While there now exists a substantial body of work on the subject¹, all of the experimental structural information to date is indirect. Typically, such experiments probe gross features by studying changes in stability with increasing size through measurements of relative abundances, ionization potentials, chemical activity, or fragmentation energies. Recently, more sophisticated spectroscopic techniques have provided some information on electronic states and further offered hopes of probing the nuclear vibrational motions within such systems.² Nevertheless, some of the most important findings (such as shell structure) still remain controversial because of the incomplete nature of the body of data. As has been reported at this Workshop, Coulomb explosion experiments have recently provided detailed images of the structures of several small molecules. It has thus been tempting to ask: can such methods be applied to clusters? We have explored this issue by studying the molecule C_3^+ .

Although C_3^+ is considered to be the fundamental building block of the larger carbon clusters³, the geometry of this molecule is unknown. Several authors have reported results of ab initio calculations in which the optimized geometry of the ion is deduced, assuming a linear configuration⁴, in agreement with the structure of the neutral C_3 mole-

cule.⁵ We report here the results of a series of measurements exploiting the Coulomb Explosion Method (CEM) to study the geometric structure of the C_3^+ ion. Our results indicate a cyclic structure for this ion. For comparison, measurements were also made of the carbon geometries of small hydrocarbon cations of the form $C_3H_n^+$ ($n=1-4$). Ring structures, of varying rigidities, are observed for all of these except $C_3H_4^+$ which exhibits a linear geometry. We also present results for doubly-charged species.

EXPERIMENT

The CEM is a technique which provides direct information on the nuclear densities within a molecule by imaging individual molecules. The technique, which has been described in detail elsewhere⁶, involves the foil-induced dissociation of a fast (MeV) beam of molecules. Through their mutual Coulomb repulsion, the resulting highly-charged atomic ions convert their Coulomb energy (which can be several hundred electron volts) into kinetic energy of relative motion. For a molecule containing N atoms, measurements of the $3N$ velocity components after the explosion provides information on the $3N$ spatial components within the original molecule.⁷⁻⁸

In the experiments reported here, the molecular ions were formed by bombardment of allene (C_3H_4) gas, at a pressure of ~ 50 mTorr, by $\sim 9-35$ eV electrons. For each molecular species that we studied, the electron bombarding energy was adjusted to lie just above (~ 0.5 eV) the measured threshold for production of the ion of interest. The ions were then accelerated by the Argonne 4.5-MV Dynamitron accelerator to an energy of 4.5 MeV, magnetically mass-analyzed, and then, after an ~ 8 - μ sec flight time, dissociated in a thin (~ 30 -Angstrom) Formvar film. The resulting carbon fragment ions were charge-state analyzed by deflection in a uniform electric field. After a flight path of ~ 6 meters, the ions were detected, in triple coincidence, by the MUPPATS detector system.⁹ Depending on the original spatial orientation of the molecule before the explosion, the ions can be separated by up to several centimeters on the detector surface and several tens of nanoseconds temporally. For each molecule, this system records the x - and y -coordinates where each fragment ion impinges on the surface of the detector (with 160 - μ m position resolution) as well as the relative time-of-arrival of each ion (600-psec time resolution). From this information, we deduce the 3 components of the velocity (relative to the molecular center-of-mass) of each fragment ion and therefore record 9 parameters per molecule. Because of their differing deflections in the electrostatic field after the target, the various charge states of carbon ions are dispersed across the detector surface. After correction for this deflection, we deduce the three body-fixed coordinates v_a , v_b , and v_c , representing the lengths of the three relative velocity vectors for the carbon ions after dissociation. For clusters, the problem of relating these velocities to the original bond lengths, is a difficult computational task because of the many-body nature of the interaction potential.

However, by comparing the distributions of these velocity coordinates for several molecules, we can explore comparative geometries quite easily. We discuss here only the symmetry features observed in the coordinate system defined by these velocities, herein described as "V-space". To further simplify the analysis, we will restrict our attention here to molecules in which all three carbon dissociation fragments emerge as C^{2+} ions and thus, aside from the differing final velocities acquired due to structural features, these fragments are all equivalent. For the protonated ions ($C_3H_n^+$) we neglect the effect of the protons on the V-space geometries. For molecules such as these, with symmetric proton geometries, the net momentum carried by the protons is small, as evidenced by our experimental data, and can be neglected for qualitative comparisons of the carbon geometries. A more comprehensive analysis of the complete spatial geometry of C_3^+ is currently in progress and will be reported elsewhere.¹⁰

DISCUSSION

To compare the carbon geometries of these molecules in V-space, we first construct the ordered sides $v_a \leq v_b \leq v_c$. Consider the quantity

$$R_s = \frac{v_b + v_a}{v_c} \quad (1).$$

This quantity is limited to the range $1 \leq R_s \leq 2$, corresponding to the extremes of linear ($R_s=1$) and equilateral ($R_s=2$) geometries. Figure 1 shows the distribution in this quantity derived from the V-space data for C_3^+ . While it is not possible to deduce the spatial geometries of these molecules directly from the V-space data without further complex analysis, comparisons of such distributions for different structures provide a very rapid and simple means of recognizing similarities in the stereochemistries of such molecules.

There are several molecules in the series $C_3H_n^+$ ($n=1-4$) for which there exist previous experimental and theoretical information concerning the probable geometries. The structure of $C_3H_4^+$ produced via electron impact ionization on allene has been studied by laser photodissociation¹¹ and photoion-photoelectron coincidence investigations.¹²⁻¹⁴ These results suggest that although the protons can rearrange to form different structural isomers, the carbon chain remains linear. The experimental evidence for the linear structure is further supported by ab initio calculations by Frenking and Schwarz.¹⁵ Similarly, there have also been studies of $C_3H_3^+$ produced by electron impact on allene (and also propyne). ICR experiments¹⁶⁻¹⁷ have proposed that both cyclic and linear isomers are produced. The branching ratio for producing the two isomers is about 2:1 (cyclic:linear) for impact on propyne and assumed to be similar for the case of allene. The ab initio calculations of Radom, et al.¹⁸ predict the cyclic species to be the more stable by at least 60 kcal/mole.

Fig. 1: Measured distributions for the ratio R_s , as described in text, for the carbon fragment ions (all C^{2+}) resulting from the dissociation of 4.5-MeV C_3^+ , $C_3H_3^+$, and $C_3H_4^+$. The ordinate represents the actual number of molecules for the case of C_3^+ . The data for $C_3H_4^+$ are normalized to yield the same integral as the C_3^+ data while the distribution for $C_3H_3^+$ has been arbitrarily scaled. Error bars represent the effect of sampling statistics only. The lines are drawn to guide the eye.

For comparison, Fig. 1 also shows the R_s -distribution obtained for $C_3H_4^+$ by considering only the carbon geometry. Here we find the R_s -distribution shifted toward unity, implying a more linear geometry. This observation is consistent with the results described above for this ion and the known structure of the neutral allene species. Additionally, we have studied the same distribution for $C_3H_3^+$. As can be seen from Fig. 1, this distribution is more ring-like, again consistent with previous results, and quite similar to the distribution we obtain for C_3^+ . If we assume that the distributions found for C_3^+ and $C_3H_4^+$ represent those of cyclic and linear structures respectively, then the $C_3H_3^+$ data can be best-fit by combining these in the proportions 0.71 ± 0.03 cyclic and 0.29 ± 0.03 linear. This is in good agreement with the 2:1 ratio extracted from the ICR experiments.

Additional data were also collected for the doubly-charged species $C_3H_3^{++}$. Figure 2 shows a comparison of the bond-length ratio, R_s , for this molecule and the singly-charged species. Here, the data seem to indicate that the double-charged molecule is extremely floppy with a more uniform spread between linear and cyclic geometries. It should be noted that this finding is in contrast to the blurring effects of experimental resolution (e.g. detector resolution, multiple scattering in the stripper foil, etc.) which all decrease with the increased beam energy used in our study of the doubly-charged ion.

Fig. 2: Measured distributions for the ratio R_s , as described in text, for the carbon fragment ions (all C^{2+}) resulting from the dissociation of 4.5-MeV $C_3H_3^+$, and 9.0-MeV $C_3H_3^{++}$. The data have been arbitrarily scaled. Error bars represent the effect of sampling statistics only. The lines are drawn to guide the eye.

The C_3^+ distribution, which is peaked near $R_s=2$, implies a geometry in which the two smallest sides are equal to the largest side, characteristic of a ring structure. We must stress that quantitative conclusions about the spatial geometries cannot be drawn from these simple distributions in V-space and in particular the shifts of these distributions away from $R_s=2$ does not necessarily imply non-equilaterality in the original structures. Nevertheless, these comparisons do provide strong evidence that the geometry of the C_3^+ ion is more like the carbon geometry within the cyclic $C_3H_3^+$ than that within the linear $C_3H_4^+$ molecule. While it is conceivable that these results could be due to the observation of highly-excited vibrational motions resulting in distorted geometries, the clear lack of any linear geometries ($R_s=1$) in the C_3^+ data ensemble makes this a very remote possibility. Furthermore, the good agreement we find between our electron ionization thresholds, and those reported by the other authors¹⁹, strongly suggests that we are indeed observing the ground state structures of these molecules. Additionally, experiments with C_3^+ ions prepared in a duoplasmatron source fed with CH_4 yielded identical results. More extensive exploration of the potential surface seems to indicate that the C_3^+ molecule is indeed bent²⁰, in agreement with these observations. Further analysis of our data, incorporating a mapping to spatial configuration space, is underway and should provide more detailed information on these structures.

Because of the strong coupling of their vibrational modes, and the intrinsically complicated many-body nature of polyatomic vibrations in general, molecular clusters represent a particularly difficult challenge to conventional experimental techniques.²¹ We believe that the data

presented here demonstrate an important new approach to the study of such molecules.

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