$C_{3,4,5}^-$ and $NCO^{+,-}$ Molecular Ion Structure Determination by Coulomb Explosion

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INTRODUCTION

The purpose of these experiments is to acquire structural information about molecules through their Coulomb explosion in thin carbon foils. The data presented here relate to the structure of C_3^- , C_4^- , C_5^- , NCO^- , and NCO^+ molecular ions where the resulting multiple charged ions from the Coulomb explosion were detected in polycarbonate sheets. A preliminary analysis of the C_3^- and NCO^- molecular structure data has been made and is presented here; however, the C_4^- , C_5^- , and NCO^+ molecular data has not yet been analyzed. Portions of these data were previously reported elsewhere.¹ In the future, it is planned to employ electronic multidimensional detectors with computer storage and analysis to improve the present study and extend it to heavier and more complex molecules as large as C_{12}^- .

EXPERIMENTAL PROCEDURE

The injector MP tandem, which is the first accelerator of the Brookhaven National Laboratory three-stage Van de Graaff facility, is equipped with a sputter ion source² in the high voltage terminal that provides negative ions for three-stage acceleration. This source produces carbon molecular ions ranging from C_2^- to C_{12}^- as illustrated in Fig. 1 which shows the mass spectrum from the ion source when it is being operated with a carbon cone. The data shown were taken with an external source similar to that used in the high voltage terminal and the negative carbon molecular ions were identified by accelerating them through the tandem accelerator and measuring the magnetic rigidity of the resulting positive carbon ions. Similarly, the CNO^- ions were produced by sputtering from a cone made of potassium cyanate KOCN. The CNO^+ ions were produced by charge exchange of the CNO^- ions with a small amount of stripper gas (N_2).

In this experiment, the terminal ion source was used to provide the C_N^- and CNO^- molecular ions which were then accelerated and magnetically analyzed for proper mass identification followed by supercollimation as shown in Fig. 2. The two adjustable apertures are followed by a permanent magnet and adjustable steering magnet that provide a 5° deflection of the negative ions with the same mass product as the 90° analyzing magnet. This final bend removes all of the ions that have been slit- or gas-scattered because they are then either neutral or positive and consequently removed from the negative beam. Horizontal and vertical cleanup slits adjusted to be close to but not touching the supercollimated beam ensure an extremely clean microbeam with sharp edges of a size varying from 0.05 to 1.0 mm diameter, depending on the selected aperture settings. After the beam is steered through the various apertures it is decreased in intensity to a few thousand ions per second as monitored

by a solid state detector. Final steering adjustments are then made to ensure that the beam is going through the center of a $1\mu\text{g}/\text{cm}^2$ carbon stripping foil which is mounted on a 3 mm diameter foil holder.

Once the final steering correction has been made, the intensity is decreased to approximately 2-5 counts/second by decreasing the aperture sizes further and closing down the object slit of the 90° analyzing magnet with all quadrupoles in the beam transport turned off to aid in the attenuation and to increase the optical quality of the beam.

The polycarbonate plastic sheets³ are $0.37 \times 3 \times 5$ cm in dimension and mounted as shown schematically in Fig. 2. The holder is rotated back and forth and raised and lowered manually. The holder is stepped vertically 2 mm before each rotary scan and a uniform exposure of $10\text{-}20$ events/ cm^2 would result if the beam current were absolutely stable. Unfortunately, beam current fluctuations cause frequent event clustering. However, many single events are observed. After exposure, the plates are developed by a combined chemical and electrical etching technique³ and a typical exposed plate is shown in Fig. 3. A number of data in each exposure are artifacts of various kinds and can be eliminated by observation through a microscope with a magnification of 100x.

Figures 4, 5, and 6 show examples of isolated three, four, and five carbon events corresponding respectively to C_3^- , C_4^- , and C_5^- ions of 4.67, 3.50, and 2.80 MeV. Fig. 7 shows examples of isolated 3 ion events corresponding to CNO^- ions of 4.00 MeV. The jagged edge spots are characteristic of heavy ion events with this etching technique. A few events show all three atoms of the C_3^- molecule anonymously closely spaced as shown in the lower right hand example of Fig. 4. These events could be due to molecular disassociation by collisions with residual gas molecules in the transport

system followed by subsequent stripping in the carbon foil with very little or no Coulomb explosion effect. Such events illustrate the excellent spatial resolution of this detection method which is smaller than the diameter of the spots.

The energy of the carbon atoms in the C_5^- exposure is 560 keV; the lowest energy so far recorded by this method. The detection efficiency appears to be close to 100% even at this low energy.

DISCUSSION

Originally, 34 C_3^- events were identified unambiguously and recorded. A rigorous analysis has to take into account, in addition to the molecular parameters, the charge distribution of the carbon ions (somewhat different from atomic carbon⁴), multiple scattering and the projection statistics. A simplified procedure, only allowing for the charge state distribution, was adopted for the first few C_3^- events that were analyzed in an attempt to extract some basic structure information from the data.

The eight largest triangles, having at least one side larger than 11 mrad, were selected for this analysis and are shown in Fig. 6. It was considered likely that the largest side of these triangles is either in the projection plane or at a small angle to it. This conclusion is also supported by the fact that the length of the largest side corresponds to a Coulomb explosion of C_3^- ions with an internuclear spacing of about 1 Å. If the largest side were at a large angle to the projection plane, the internuclear separation would be unreasonably small. If the long leg of the triangle is coplanar as assumed, then the events shown in Fig. 6 are projections obtained by rotating the original triangle around the largest side. The eight triangles are then found to be consistent with random projections of a Coulomb exploded equilateral triangle taking into account the possible different charge states, but they are not necessarily equilateral triangles. Fig. 9 shows as an ex-

ample of the relation of the apex angle of an isosceles triangle molecular structure of equal mass and charge particles before and after a Coulomb explosion. Although the equilateral triangle structure transforms into itself, there is also a large range of initial isosceles triangles which generate final apex angles close to 60° . It is found in this way that the apex angle of the C_3^- molecules can be as large as 140° and the present data are also compatible with a soft or "floppy" rod structure where the carbon atoms vibrate around an aligned configuration with a bending amplitude of at least $\pm 40^\circ$.

After this initial set of measurements and their subsequent analysis, the measurements were considerably extended for the $C_{3,4,5}^-$ molecules and NCO^+ and NCO^- molecules as well. A total of 81 C_3^- , 21 C_4^- , 12 C_5^- , 33 NCO^+ , and 86 NCO^- events were identified and analyzed. For each of the three-atom molecules, approximately a third of each group was selected by taking the ones having the longest single side. This selection represents molecules that have entered the stripping foil presumably with the longest leg of the triangle approximately parallel to the plane of the stripping foil. The original computer program which included the charge state distribution, but not the projection statistics, was extended to include the projection statistics of a random oriented molecule passing through the stripping foil. The program was then modified to select the largest triangles in the same manner in which they were selected from the analyzed data.

The distribution of the lengths of the longest sides of all triangles for the three molecular systems is shown in Fig. 10. Although the observed triangles for C_3^- and NCO^- as shown in Figs. 4 and 7, respectively, appear to have quite different distributions in terms of being acute or obtuse triangles, the distribution of the length of the longest side would appear to be very similar for all three cases studied. The mean predicted by the analysis

agrees very well in each case and actually varies only slightly from that measured for both the triangle and soft rod assumption for the C_3^- case.

In distinct contrast, a distribution of the ratio of the height of the triangle to the length of the longest leg, in Fig. 11, shows a striking difference between the NCO^- and NCO^+ and C_3^- distributions. The NCO^- distribution is peaked at a very small D/l ratio, corresponding to about .1 and implying that most of events correspond to very obtuse triangles. On the other hand, the C_3^- distribution is very broad and peaked at a ratio of approximately .4, which corresponds to a triangle with one included angle of approximately 100° . Since the NCO^- distribution is so sharply peaked, the theoretical calculation was made for an initial angle 170° , 175° , and 176° as shown, and with these limited statistics data, it would appear that the distribution fits inbetween 175° and 176° for the mean obtuse angle of the triangle. Theoretical predictions for the mean of the NCO distribution and equilateral triangle distribution and the C_3^- distribution for both the ground and the first excited state "floppy" rod are also indicated. These preliminary calculations are all completely classical; however, they will be extended to an exact quantum mechanical description in the future.

With these statistics, we can conclude from the fit of the D/l ratio that the NCO^- molecule is mainly a rigid rod similar to the NCO neutral molecule.⁵ The NCO^+ molecule appears to be less rigid in terms of the spread of the D/l ratios and its higher mean, while the C_3^- distribution infers a triangular structure; however, a mixture of both the ground and first excited states of a floppy rod-like structure cannot be excluded.⁵ The theoretical calculations provide relatively smooth curves which were converted to coarse histograms to match the limited statistics; however, their shapes varied considerably with different assumptions for the structure of the molecules.

This means that if much better statistics were available, a better selection could be made between the different structure possibilities for the different systems.

Electronic detection systems are currently under investigation to find a system suitable for the simultaneous detection of these molecular components so that the XY coordinates and relative intensities of each component of the explosion can be digitally recorded for subsequent display and analysis. One such system, based on the use of charge coupled devices, has been described recently.⁶ For molecules with different atomic components like NCO^- , the energy of each component will differ according to the different masses, which means that in principle each component can be completely identified and consequently greatly enhance the analysis capability. Also, with large statistics, it will be possible to select events where one of the three or more elements of a given explosion lies exactly along the beam line direction. This means that the Coulomb explosion had to occur in such a way that the only momentum transferred to the one particle on the beam line location was either in the direction or opposite to that of the original molecule. Presumably, such events would be quite rare, but can easily be selected from a large collection of good statistics data and would provide more insight to the initial molecular structure.

An image intensifier optically coupled to a thin scintillator and read out by a TV digital scanning system is presently under evaluation as a possible solution to the electronic detection problem.

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FIGURE CAPTIONS

- Fig. 1 Mass spectrum of negative ions produced by a cesium sputter ion source operated with a carbon cone. The numbers indicate the molecular mass of multiple carbon ions which were positively identified.
- Fig. 2 Schematic layout of the experimental arrangement for super collimation of the accelerated negative molecular ions and the mechanical arrangement for exposing polycarbonate plastic sheets to the Coulomb exploded ions. (See text for details).
- Fig. 3 Etched polycarbonate foil after exposure to stripped 4.67 MeV C_3^- ions.
- Fig. 4 Further magnification of selected C_3^- molecular explosion events at 4.67 MeV ion energy.
- Fig. 5 Selected C_4^- molecular explosion events at 3.50 MeV ion energy.
- Fig. 6 Selected C_5^- molecular explosion events at 2.80 MeV ion energy.
- Fig. 7 Selected NCO^- molecular explosion events at 4.00 MeV ion energy.
- Fig. 8 Plots of largest observed C_3^- triangles.
- Fig. 9 Initial and final apex angles of isosceles triangles of three particles of equal mass and charge experiencing a Coulomb explosion.
- Fig. 10 Distribution of the longest side (ℓ) of all triangular events (see text).
- Fig. 11 Distribution of the ratio of the height (d) to the length of the longest side (ℓ) of selected triangular events (see text).

Fig 1.

Fig 2

Fig 3

3 mrad
0.2 mm

Fig 4

$\longleftrightarrow$ 6 mrad
0.2 mm

Fig 5

20 mrad
0.5 mm

Fig 7

$\longleftrightarrow$
20 mrad
0.5 nm

Fig 6

Fig 8

Fig 9.

Fig 11