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EXPERIMENTAL CONFIRMATION OF THE JAHN-TELLER DISTORTION OF CH_4^+

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MASTEREXPERIMENTAL CONFIRMATION OF THE JAHN-TELLER DISTORTION OF CH_4^+ *

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We report measured energy and angular distributions for H^+ and C^{n+} ($n = 2, 3, 4$) fragments resulting from the collisional dissociation of 200-keV/amu CH_m^+ ($m = 0-4$) in thin carbon targets. From the systematic trends of these "Coulomb explosion" spectra, one can obtain qualitative information on the structures of these species. In particular, the series displays a narrowing of the carbon angular and energy widths as protons are symmetrically added around a central carbon atom and provide a "focusing" effect. Because of the Jahn-Teller distortion, the carbon width in CH_4^+ is dramatically increased.

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The development of high-resolution techniques for studying the collisional dissociation of fast molecular-ion beams, coupled with an improved understanding of the physical processes involved in the interactions of the resulting clusters with matter, now opens up new possibilities for the investigation of molecular structures¹⁾. For diatomic molecules, such "Coulomb explosion" studies can determine bond lengths to an accuracy of about 0.01 \AA (ref. 2). Even more importantly, such measurements, applied to polyatomic molecular ions, show promise of supplying important new structural information that is presently unavailable. Very few polyatomic molecular-ion structures have been determined by traditional techniques (absorption or emission spectroscopy) because of severe difficulties confining the ions to a sufficient spatial plasma density. It is therefore of considerable interest to explore the extent to which these new techniques with high-energy beams may be employed to determine the geometrical structures of polyatomic molecular-ion projectiles.

For polyatomic molecular ions, particularly those having low symmetry and/or many atomic constituents, it is usually necessary to record spatial and temporal coincidences for two or more dissociation fragments to precisely determine the molecular structure. Singles measurements, however, can provide useful information. Such techniques have been employed to make the first experimental demonstration of the equilateral triangular shape of H_3^+ (ref. 3) and to show important qualitative differences of the linear CO_2^+ and N_2O^+ structures⁴⁾.

Because of their importance to astrochemistry, in addition to the basic quantum chemistry involved, there has been a great deal of interest in recent years in the structures of the series CH_n^+ . In this paper, we give a preliminary report on a series of singles measurements studying structural trends of this series. Further coincidence measurements will be published later⁵⁾.

The experimental apparatus used in these measurements has been described in detail elsewhere^{1,2,6}). We employed ion beams of C^+ , CH^+ , CH_2^+ , CH_3^+ and CH_4^+ at identical velocities of 0.194 MeV/amu (2.8 a.u.). After impinging on a 125 Å carbon foil, these ions are stripped of binding electrons and a Coulomb explosion ensues. As a result, the energies and angles of dissociation fragments observed downstream of the target are shifted proportionally to the excess center of mass velocity imparted to these particles. For the measurements reported here, this shift is typically ~5 keV. These shifts are easily resolved in the energy spectra of the light proton fragments, however, energy straggling in the solid target washes out the structure in the heavy fragment spectrum. It is this heavy fragment, however, which is most sensitive to an asymmetric distribution of surrounding protons. The width, therefore, of the energy spectrum of the heavy fragment can be very informative.

We show in Fig. 1 the measured energy widths (FWHM) of outgoing C^{4+} ions which emerge after the incident beam strikes the target. The value of 6.1 keV for incident C^+ represents the contribution of energy straggling convoluted with both our beam energy spread and the resolving power of the electrostatic analyzer system. The highly asymmetric CH^+ ions adds a large contribution from "Coulomb explosion" which increases the measured width to 14.6 keV. For the more symmetric CH_2^+ ions, because of near cancellation of the impulses produced by each proton on the carbon ion, the Coulomb explosion is reduced and thus we measure a width of only 10.1 keV. If CH_2^+ were linear, the width would be just the C^+ straggling value of 6.1 keV. A similar effect is seen in the measurement of the carbon width for the dissociation of CH_3^+ .

Again, the width is increased over the minimum that one would obtain with a planar structure, however, it is smaller than either the CH^+ or CH_2^+ results. The data for CH_4^+ , however, shows a dramatic departure from this general trend. The measured width of 11.1 keV is larger than all but the CH^+ measurement. This indicates a highly asymmetric proton distribution around the carbon nucleus. A quite similar effect is seen in the angular widths of the carbon fragments.

The asymmetry of the CH_4^+ ion has been known for some time to be caused by the Jahn-Teller distortion which follows the removal of an electron from a bonding orbital of the symmetric CH_4 molecule⁷⁾. We believe that these data represent the first direct experimental observation of the distortion of this structure. This phenomenon has been of much theoretical interest and thus these experiments demonstrate the utility of Coulomb explosion measurements in determining molecular structures of ionic species.

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Figure Caption

Fig. 1. Comparison of energy widths of C^{4+} spectra for $CH_n^+ \rightarrow C^{4+}$.
The calculations are based on an effective charge of 3.5
and neglect wake forces.

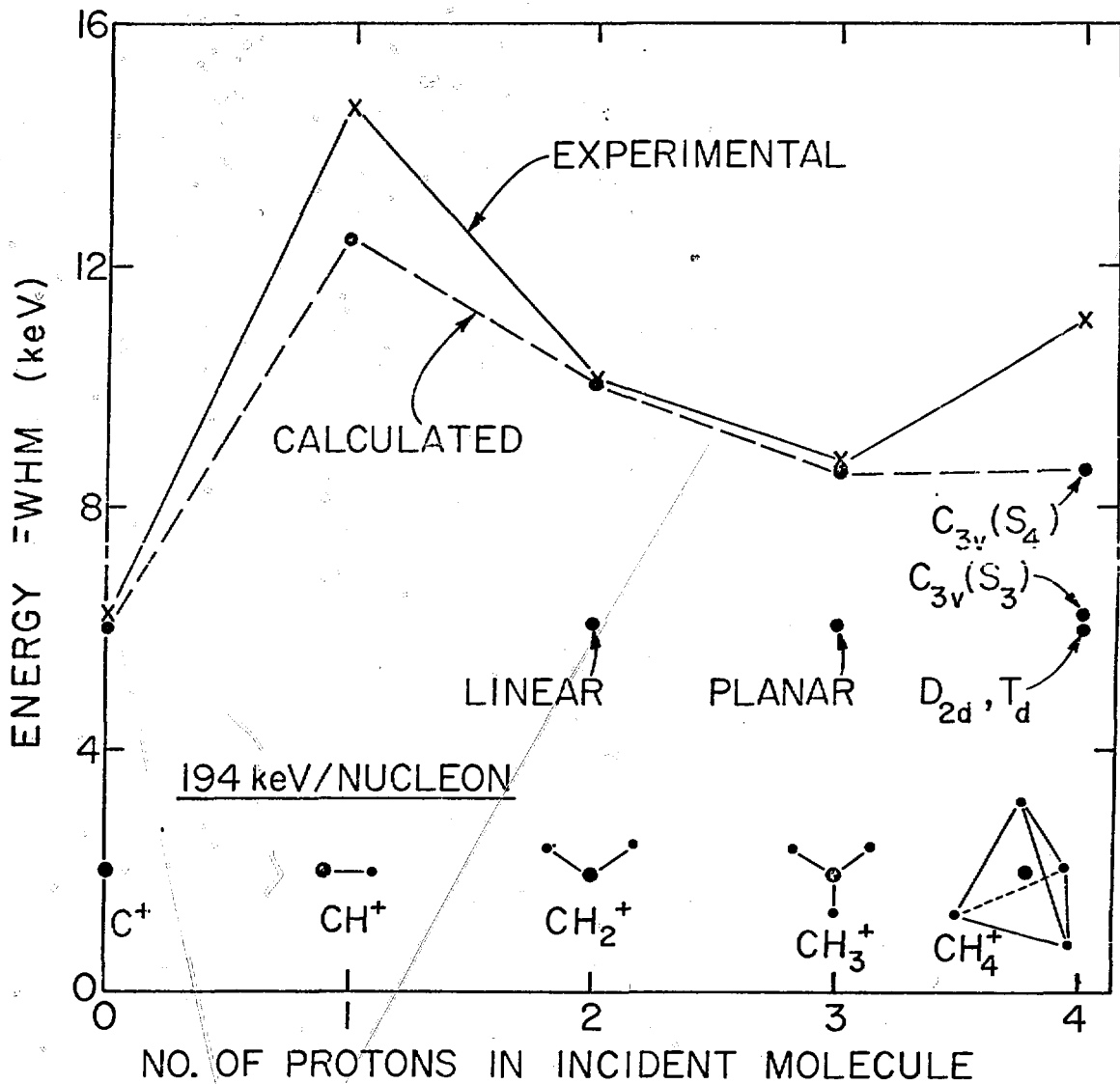


Fig. 1