Experimental determination of the structure of H_3^+

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Three different measurements on the structure of the H_3^+ molecular ion are reported. The measurements all make use of a new technique—the foil-induced dissociation of a fast molecular-ion beam. It is shown that the structure is equilaterally triangular in shape. The most probable length of side of the triangle is determined by the three measurements to be 0.97 ± 0.03 Å, 0.95 ± 0.06 Å, and 1.2 ± 0.2 Å, respectively.

I. INTRODUCTION

The recent development of techniques for studying the dissociation of fast molecular-ion beams in thin foils[1-4] has opened up new possibilities for the investigation of molecular structure. Here we introduce the method through three experiments to study the structure of the H_3^+ molecular ion.

Many calculations have been carried out for H_3^+ and there is general agreement that the H_3^+ ion in its most stable form should have an equilateral triangular configuration,[5] although the collinear form is also thought to be stable but with a smaller binding energy. The calculated equilibrium value of the proton separation in the electronic ground state is $d_e = 0.87$ Å. To our knowledge, the experiments reported here represent the first experimental determination of the geometry of H_3^+.

II. PRINCIPLES OF THE TECHNIQUE

Consider a beam of well-collimated H_3^+ ions with energy in the MeV range incident on a very thin (~100 Å) carbon target. When one of these molecular ions enters the solid target, its two binding electrons are stripped off, usually within a few angstroms of the entrance surface. At these beam velocities, the resulting three protons are expected to remain essentially fully stripped during their passage through the target. The three protons form a cluster which in the c.m. system undergoes a "Coulomb explosion" as the initial potential energy is converted into kinetic energy. For the equilateral triangular form, this initial potential energy ($3e^2/d_0$, where d_0 is the length of side of the triangle at the instant of removal of the electrons) is large compared with the vibrational and rotational energies of the molecular ion. The time required for the Coulomb explosion to develop is typically a few femtoseconds (fsec). In fact, the time for the length of side of the triangular form to increase by a factor ξ is easily shown to be

$$t(\xi) = \tau\{[\xi(\xi-1)]^{1/2} + \ln[\xi^{1/2} + (\xi-1)^{1/2}]\}, \qquad (1)$$

where $\tau = 1.095\, d_0^{3/2}$ fsec (d_0 given in angstroms).

In times of the order of femtoseconds, the beam travels a few hundred angstroms. So, for carbon targets 100–200 Å thick, a significant portion of the Coulomb explosion occurs downstream in the vacuum outside the target. The initial configuration of the protons can be deduced from a measurement of the final (that is, for $t \gg 10^{-15}$ sec) velocity distributions of the dissociation fragments. (We postpone at this stage a discussion of possible complications caused by multiple scattering, energy loss, and "wake effects" due to induced polarization of the target electrons.[4])

The relatively high c.m. velocity not only results in the convenient simplification that the protons are fully stripped, but in addition it provides an "amplifying" effect for the small molecular potential energy. For example, in the energy spectrum for those protons emerging from the target in a direction parallel to the incident beam, one finds two peaks (see Sec. III) separated by several keV. These (keV) energy differences are easily measured with an accuracy that can only be achieved with difficulty for the eV energies characteristic of the c.m. system.

Studies of the velocity distributions for the emergent clusters of three protons can be performed in several hierarchies of correlations. We present here three experimental examples: (i) The measurement of the magnitude and direction of the velocities for individual protons (the Argonne experiment). (ii) The measurement of the angular distribution for spatially correlated pairs of protons (the Lyon experiment). (iii) The measurement of spatial correlations between all three protons of each cluster (the Rehovot experiment).

Each of these three experiments is sensitively dependent upon the structure parameters of the H_3^+ molecule. The experiments are described and their results compared and discussed in the following sections.

III. ARGONNE EXPERIMENT

The experimental arrangement is shown in Fig. 1. A magnetically analyzed H_3^+ molecular-ion beam from Argonne's 4-MV Dynamitron accelerator was collimated to have a maximum angular divergence of ±0.09 mrad at the target position. A set of "predeflector" plates permitted electrostatic deflection of the beam incident on the target. Similarly, a set of "postdeflectors" was used to deflect charged particles emerging from the target. Charged particles entering the electrostatic analyzer were energy analyzed with a relative resolution of 6×10^{-4}. The angular acceptance of the analyzer was ±0.11 mrad. Distributions in angle and energy were measured for particles emerging from the target by varying the voltages on the predeflector and/or the postdeflector in conjunction with that on the analyzer. The overall angular resolution was ±0.14 mrad (0.008 deg). Selection of the required charge state for particles leaving the target was facilitated by a suitable combination of pre- and postdeflection. The optimal combination also rejected spurious incident beams (e.g., predissociated fragments arising from interactions in residual gas upstream from the target). Precautions were taken to ensure that no carbon buildup occurred on the target foils.

Figure 2 shows the energy distribution for zero angular shift and the angular distribution for zero energy shift of protons arising from the bombardment of a 2.3-$\mu g/cm^2$ carbon foil by a 2.1-MeV H_3^+ beam. From the shape of these distributions one can immediately see that the collinear form must be extremely rare, since it would generate three peaks in both distributions. There would be a large central peak flanked by two smaller peaks, reduced in intensity by solid-angle effects. (This type of shape has been observed recently in the energy and angle distributions measured for nitrogen ions arising from the dissociation of 3.5-MeV N_2O^+ in carbon foils[6]; the ground state of N_2O^+ is known[7] to be collinear and has the structure N-N-O.) The slight bumps observed in the center of the distributions shown in Fig. 2 are in harmony with results[2] seen in the dissociation of diatomic beams (H_2^+, HeH^+, etc.) and are thought to arise from breakup modes which result in a

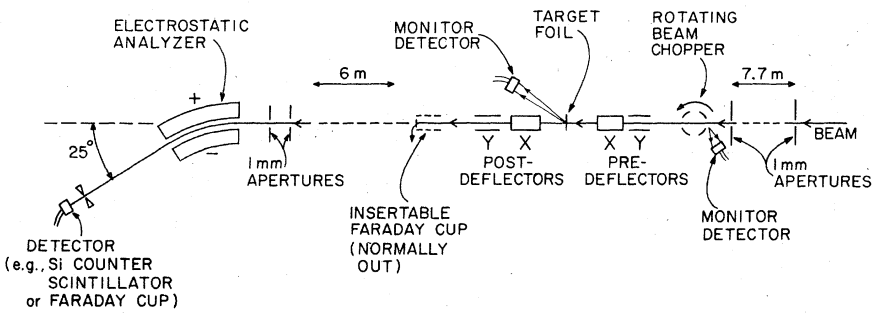


FIG. 1. Schematic of the experimental arrangement used at Argonne's 4-MV Dynamitron accelerator.

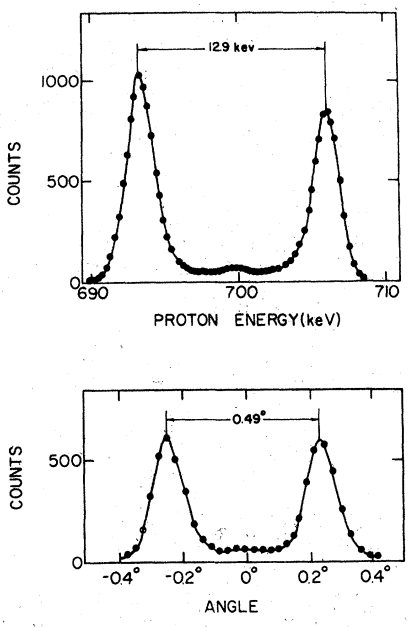


FIG. 2. Energy spectrum for zero angular shift (i.e., in beam direction) and angular distribution for zero energy shift (i.e., 700-keV protons) measured for protons arising from the dissociation of 2.1-MeV H_3^+ ions in a 2.3-$\mu g/cm^2$ carbon foil.

neutral projectile and a proton (in the present case, this would most probably be $H_3^+ \rightarrow H_2 + H^+$).

The observation of just two main peaks in each distribution in Fig. 2 is consistent with an equilateral triangular geometry for the incident H_3^+ ions. Any other equilibrium arrangement of the three protons in H_3^+ (even if permitted by symmetry rules) would result in more than two peaks. The asymmetry in population of the two peaks in the energy spectrum is now well understood[4] in terms of "wake effects" due to local polarization of the target electrons induced by the passage of the charged projectiles. These wake effects also cause a slight increase in the separation ΔE of the two peaks in the energy spectrum and a slight decrease in the separation $\Delta\theta$ of the two peaks in the angular distribution. In the absence of any wake effects and multiple scattering, and if there were no spread in the initial values of d_0, one would expect

$$\Delta E = 4Muv \tag{2}$$

and

$$\Delta\theta = 2u/v\,, \tag{3}$$

where M is the proton mass, v is the beam velocity and $u = (2e^2/Md_0)^{1/2}$. The introduction of a range of permissible initial values for d_0 causes the peaks to be separated by a little less than the values of ΔE and $\Delta\theta$ calculated from Eqs. (2) and (3). (This is because the most probable value of $1/d_0$ differs slightly from the reciprocal of the most probable value of d_0.)

We have estimated the influence of wake forces and multiple scattering on the values of ΔE and $\Delta\theta$ by using a computer calculation[4] of the dissociation of a hypothetical dinuclear cluster, viz., a proton (H^+) and a diproton ($^2He^{++}$), that in many respects resembles the situation for H_3^+. From this it was established that the wake forces reduce $\Delta\theta$ by less than 0.5% and increase ΔE by about 3% for the case corresponding to the data shown in Fig. 2.

After minor corrections for the effects just discussed, we deduce the most probable value of d_0 to be 0.97 ± 0.03 Å. The estimated error here is a composite that includes effects due to counting statistics and to limitations on our ability to estimate the influence of the wake potential and multiple scattering.

IV. LYON EXPERIMENT

At Lyon the dissociation of 2.2-MeV H_3^+ ions in thin carbon foils was studied. A movable tightly collimated silicon semiconductor counter was used downstream to detect the break-up fragments. The energy resolution of the detector was insufficient to permit observation of the energy groups resulting from the Coulomb-explosion component along the beam direction. The incident beam was monitored by the detector of protons forward scattered from the target into an annular Si detector.

The pulse-height distribution from the detector was composed of three peaks, corresponding to the approximate energies E, $2E$, and $3E$, $3E$ being the energy of the incident ions. The peak (E) was the most intensely populated, and its angular dependence gave the angular distribution for single protons issuing from the Coulomb explosions of the triproton clusters. The pulses corresponding to energies $2E$ and $3E$ arose from the detection of two and three protons, respectively, within a very short time (shorter than the time resolution of the detection system). We will not consider the pulses ($3E$) of which there were very few, scattered over all angles, but we will concentrate on the peak ($2E$). The pulses ($2E$) can originate from three sources: (i) Electronic pile-up due to the quasisimultaneous detection of two protons from two distinct molecules. In order to subtract this background properly, the pile-up rate was measured as a function of counting rate, and then care was taken to keep the counting rate at a moderate level throughout the experiment. (ii) The presence of H_2^+ molecules downstream from the target. It has been shown[3] that H_2^+ can be observed in beams

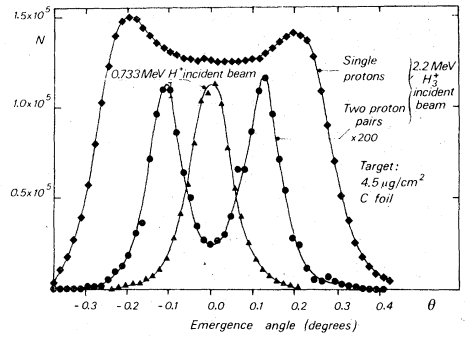


FIG. 3. Angular distributions (simultaneously recorded) of single protons and proton pairs, detected within an angular acceptance of $\pm 0.019°$, transmitted through a 4.5-μg/cm^2 carbon foil bombarded by 2.2-MeV H_3^+ molecular ions. The comparison of the angular widths, the angular distribution of protons transmitted through the same foil bombarded by protons with the same velocity is shown.

transmitted through thin amorphous or crystalline foils bombarded with H_2^+ or H_3^+ ions, the production process most likely being a recombination occurring at the exit surface of the foil. We will come back later to this question. (iii) A nonfortuitous coincidence in the detector of two free protons coming from the same incident H_3^+ molecule. This event is the one we want to observe in the present experiment. Such a coincidence signifies that the Coulomb explosion of the cluster has caused two protons to emerge along the same direction. Clearly, a study of the angular distribution of these events ($2E$) will provide precise information on the Coulomb explosion and thus on the configuration of the incident molecule.

Typical angular distributions for events (E) and

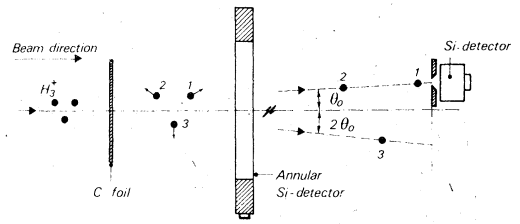


FIG. 4. Schematic description of the Lyon experiment showing, from left to right, an incident H_3^+ molecular ion with two protons aligned along the beam direction, the Coulomb explosion of the triproton cluster after emergence from a thin carbon foil, represented in the center-of-mass system (arrows), and in the laboratory system. Proton pairs are detected at angle θ_0, the third proton being deflected at angle $2\theta_0$. Protons forward scattered by the foil into the annular Si detector, located in the target chamber and aligned on the transmitted beam, are used to monitor the measurements.

($2E$) are shown in Fig. 3 for 2.2-MeV H_3^+ ions bombarding a 4.5-μg/cm^2 carbon foil. The pile-up contribution has been subtracted and was ~10% at a maxima of the angular distribution of events ($2E$). The acceptance angle of the detector was $\pm 0.018°$.

Before considering the physical meaning of the distribution of the events ($2E$), let us evaluate the contribution of the H_2^+ molecules to this distribution. From recent experiments,[3] we know that the production rate of H_2^+ at this energy and for this target thickness is around 10^{-4} (that is the number of H_2^+ molecules produced per incident H_3^+ molecule). The fraction of incident molecules that are able to produce two protons within the angular acceptance defined above is

$$\alpha = \frac{\int_0^{\theta_{\max}} n_2(\theta)\theta\, d\theta}{\int_0^{\theta_{\max}} n_1(\theta)\theta\, d\theta},$$

where θ is the angle of emergence and n_1 and n_2 the number of events (E) and ($2E$), respectively, at this angle θ. This ratio is easily calculated from the data to be 1.4×10^{-3}. If all the events ($2E$) were due to H_2^+ ions, the corresponding H_2^+ production rate would be 4.2×10^{-3} (the number of transmitted protons is three times the number of incident molecules). The H_2^+ contribution is seen to represent less than 3% of the events ($2E$) and is obviously small enough to be neglected. We may now assume that the angular distribution of events ($2E$) is in fact the distribution of free proton pairs. It consists of two well-resolved peaks that are symmetrical about 0° and separated by $2\theta_0 \sim 0.23°$.

Figure 4 shows the only incident geometry for a molecule able to produce an off-axis proton pair: first, the molecule must have a triangular configuration; second, it must enter the target with two protons aligned along the beam direction. The protons "1" and "2" are repelled by the proton "3" and transmitted along the same direction (not exactly the same, because of their mutual repulsion, giving them unequal velocities; but the difference is much smaller than the angular acceptance). It is clear that the signature of a collinear configuration would have been a peak ($3E$) centered at 0° [or rather a peak ($2E$) because of the destruction of the triple coincidence by multiple scattering in the target].

For the sake of comparison, we have shown in Fig. 3 the angular distribution for transmitted protons observed when the H_3^+ incident molecules are replaced by protons with the same velocity.

For a given equilateral triangular projectile that leads to the detection of an event ($2E$) at angle θ_0 (and, therefore, with the proton "3" emerging at angle $2\theta_0$) the interproton separation in the incident

molecule is given by

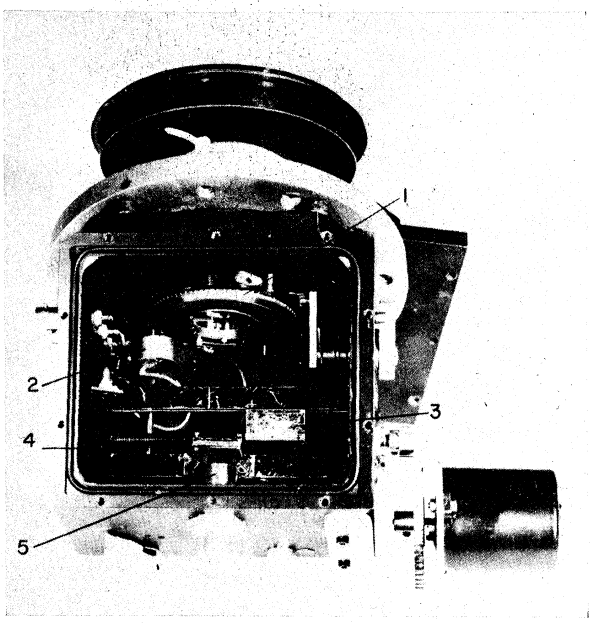
$$d_0 = \frac{e^2}{4E\theta_0^2} . \quad (4)$$

The measurements give the angular distributions of events ($2E$). These are mainly determined by the distribution of interproton distances in the incident projectiles and by multiple-scattering effects in the target. When comparing the multiple scattering suffered by aligned proton pairs and by isolated protons, one has to consider that there is certainly some degree of correlation in the impact parameters of the two protons in a pair with respect to each target atom (a total correlation should lead to identical multiple-scattering effects). The width of the peak ($2E$) also receives contributions from (i) the finite angular acceptance of the detector, (ii) the multiple scattering suffered by protons "3" as these protons determine the transverse deflection of the proton pairs, and (iii) the alignment effect of the wake force which favors the detection of proton pairs.

All these effects make a quantitative evaluation of the width of the peak ($2E$) very difficult. In order to calculate the most probable internuclear separation we assumed for the sake of simplicity that there were no correlation effects in the multiple scattering of the proton pairs. With this assumption we calculated the angular distributions corresponding to a zero-thickness target and, using the methods discussed in Sec. III, the mean value of the most-probable interproton separations d_0, calculated from four angular distributions corresponding to carbon foils of various thicknesses (from 2–4.4 $\mu g/cm^2$), is found to be 0.95 ± 0.06 Å. The error here includes the effects of counting statistics and uncertainties inherent in the analysis procedures outlined above.

V. REHOVOT EXPERIMENT

The experiment at Rehovot was set up to record complete planar projections of individual exploded H_3^+ ions. The three protons from each molecular Coulomb explosion were recorded on photographic emulsion in a camera shown in Fig. 5. Molecular H_3^+ ions of 2.2 MeV were produced from the Weizmann Institute 3-MV Van de Graaf accelerator. The ion beam was kept at a very low level—about 10 ions per second—by a set of apertures shown schematically in Fig. 6. This intensity was far too low for the conventional voltage stabilization which is linked to an error signal from a defining slit at the exit of the analysis magnet. Instead, the voltage of the accelerator was stabilized with the aid of a generating-voltmeter output, and the ion beam was passed through the analyzing magnet



1. SHUTTER AND DIAPHRAGM
2. RETRACTABLE FARADAY CUP
3. EMULSION CARRIAGE
4. FOIL HOLDER
5. SURFACE BARRIER DETECTOR

FIG. 5. Photograph of the ion camera. The ion beam is defined by a commercially available adjustable diaphragm and camera shutter. The shutter can be set either for single snapshot operation down to $\frac{1}{100}$ sec or for time exposure. The photographs of Fig. 7 were all taken in time exposures. The emulsion carriage is motor driven, and during exposures it is moved across the molecular beam. The stripping foil, made of carbon, is mounted in front of the exposed emulsion at a distance of 2.2 mm. The surface barrier detector is used for beam adjustment. It is exposed to the ion beam when the emulsion is retracted to one side.

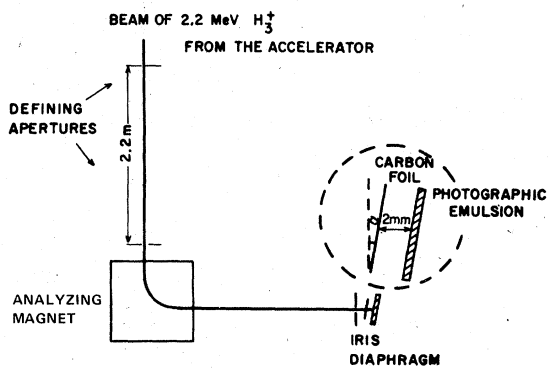


FIG. 6. Schematic layout of the beam definition systems. The opening of the defining apertures was usually kept very small—of the order of a few tens of microns—in order to reduce the ion beam to the low intensity required. The tilt angle α was either 30° or 60°.

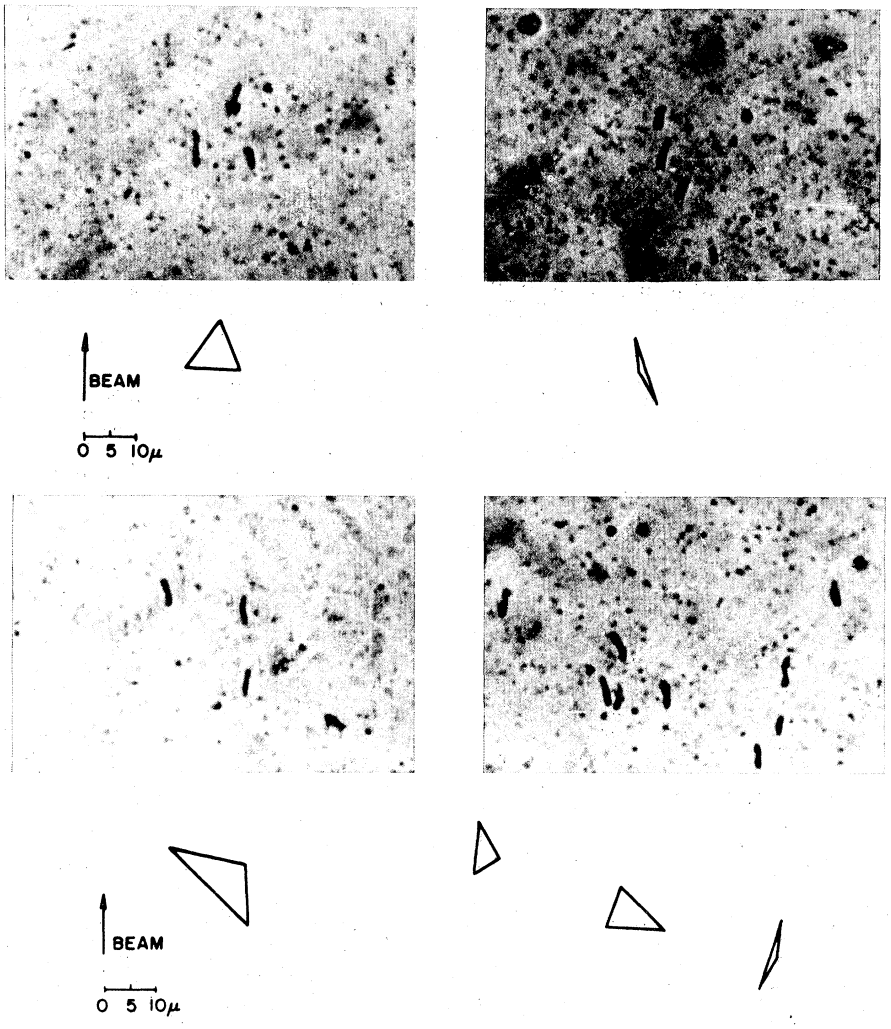


FIG. 7. Selected examples of exploded H_3^+ photographs taken with a 30° tilt (cf. Fig. 2). Underneath each photograph is a reconstructed normal projection of the exploded molecular ion.

without any further collimation until the defining diaphragm of the camera.

The beam was adjusted with the aid of a surface barrier detector situated behind the emulsion carriage. The ions were stripped in a carbon foil of 2–4 $\mu g/cm^2$ and the residual protons impinged on a strip of nuclear emulsion which was moved across the ion beam 2 mm behind the stripper foil.

Some typical photographs of exploded H_3^+ ions are shown in Fig. 7 together with reconstructed normal projections. Most of the photographs are triangular in shape. A few (on the order of 5%) collinear or near collinear configurations were observed but were quite consistent with a triangular projection. An analysis of 350 photographs was carried out under the assumption that all the observed shapes are projections of equilateral triangles. The distribution of the triangle sides derived in this way is shown in Fig. 8. The observations appear to be entirely in accord with the assumption of an equilateral triangular shape and, in fact, rule out any component of a different

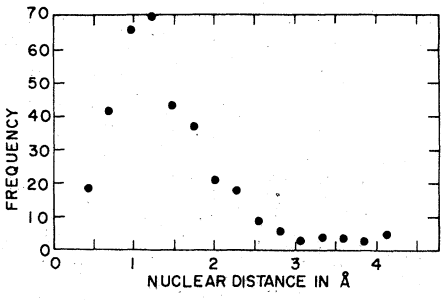


FIG. 8. The distribution of the lengths of the triangle sides derived from 350 photographs on the assumption of an equilateral triangular shape for all observed H_3^+ ions.

shape in all but a very small fraction of the ions. The most probable length of a side of the triangle was found to be 1.2 ± 0.2 Å, in reasonable agreement with the measurements presented above. The relatively large error in this particular measurement is due almost entirely to the uncertainty in the distance between the stripper foil and the photographic emulsion.

VI. SUMMARY

We have demonstrated here that the technique of stripping fast molecular ions in a foil and allowing them to Coulomb explode can serve as a valuable tool in the study of molecular structure. A variety of techniques has been displayed, emphasizing various features and aspects of the structure problem. The interaction of the molecular ions or their constituents with the solid they traverse can play an important role in determining the motion of the particles issuing from the stripper foil, but it is believed that these interactions are now sufficiently well understood for adequate control and interpretation of the Coulomb-explosion process. Measurements of this type can be particularly valuable in the study of many light molecular ions that are of great interest in theoretical chemistry and in astrophysics and that cannot be easily studied by more conventional methods. (It should be noted that the form of the molecular ion could be dependent upon its production mode. Different sources or the same source operated under varying conditions could produce molecular ions in differing states. In the present work, both duoplasmatron and radio-frequency sources gave the same result for the structure of H_3^+. This was true even when the source gas mixtures and the ion-source conditions were deliberately varied over a wide range.)

The H_3^+ molecule that was the object of these studies has now been shown to be predominantly of an equilateral triangular shape. The triangle side is slightly larger than predicted by current structure theories. This may be due to the incident molecular ions populating a small range of vibrationally excited states.

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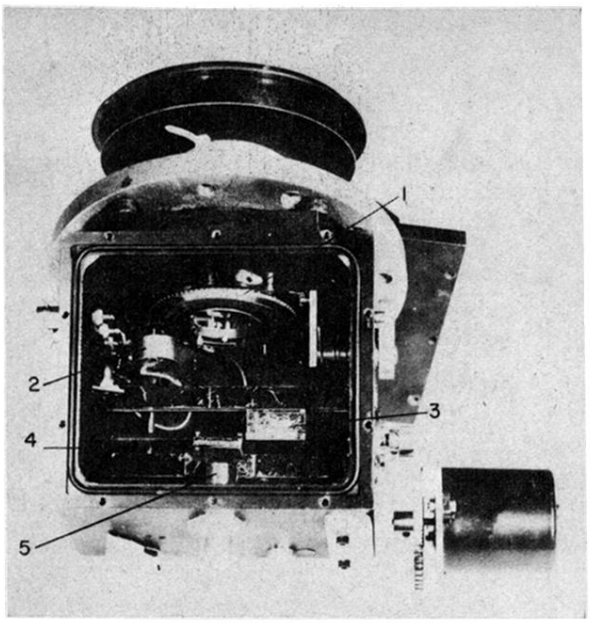

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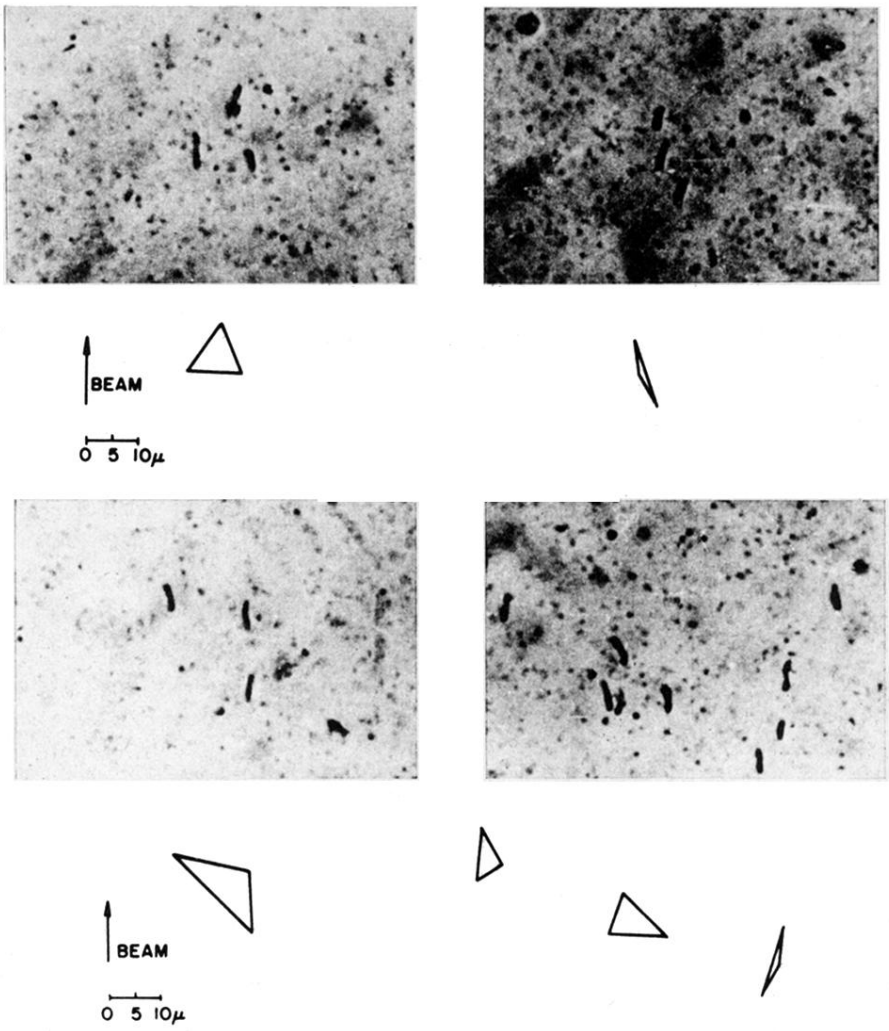

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