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A Multiparticle 3D Imaging Technique to Study the Structure of Molecular Ions

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ABSTRACT

When energetic molecular ions (E_{ion} = 0.1 - 0.5 MeV/amu) pass through thin solid targets a Coulomb explosion ensues due to the rapid (~10^{-17}s) stripping of the valence electrons. This process has been successfully used to derive stereochemical information on diatomic and on selected triatomic ions. In order to investigate more complex molecular ions as well as to obtain more accurate and detailed structure information, a large area, multiparticle, position- and time-sensitive detector has been developed to detect all atomic fragments in coincidence. The requirement of multiparticle detection independent of the relative particle positions leads to a rather complex data-readout and -reduction system containing ~650 analog-to-digital conversions per event. The system relies heavily on techniques developed for high energy physics experiments during recent years. The single event resolution of the apparatus with respect to bond-lengths and -angles has been studied by Monte Carlo simulations and is typically a few percent.

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MASTER

1. INTRODUCTION

As fast molecular ions (0.1-0.5 MeV/amu) pass through a thin foil, their valence electrons are stripped away. Thus, a molecular dissociation process (Coulomb explosion) is initiated. This process has been successfully used by several groups to investigate molecular structure [1, 2]. Since the stripping of outer-shell electrons takes place within a short time (10^{-17}s) compared to vibrational and rotational motions it allows one to make a "snap-shot" of the positions of the nuclei in the molecular ion. Different approaches have been used to perform those investigations: A complete, high resolution measurement of some of the dissociation fragments gave valuable information for diatomic and, in special cases, triatomic molecular ions [1] but failed to determine correlated variations in bond-lengths and -angles. On the other hand, two-dimensional imaging detectors allow the simultaneous measurement of the transverse velocity components of all fragments [2]. This provides direct information about certain aspects of the stereometry of the molecular ion (e.g. linear or triangular shapes) but fails in general to give an accurate determination of the structure.

Due to recent developments in detector technology, both techniques can be combined now with reasonable effort permitting the accurate determination of both the longitudinal and transverse momenta of all fragments thereby yielding complete information on the molecular ion structure, even for a single ion with "frozen" nuclear degrees of motion.

2. EXPERIMENTAL SET-UP

Figure 1 shows a schematic overview of the experimental set up which has been developed at Argonne for three dimensional imaging of molecular ions. A well collimated molecular-ion beam (typically a few 100 keV/amu) passes

through a thin (~100Å) carbon foil and undergoes a Coulomb explosion on a time scale of $\sim 10^{-14}$s (Fig. 2a). After a flight path d of ~6.5 m, the fragment atomic ions reach the MUltiParticle Position And Time Sensitive (MUPPATS-) detector where their positions x_i, y_i perpendicular to the beam axis and the times of arrival t_i are measured (Fig. 1). Since the velocities u_i of the fragments in the center-of-mass frame of the molecule are small (~1%) compared to the beam velocity v, the ions diverge on "explosion cones" with opening angles θ of the order of 10 mrad. The reconstruction of the CM-velocities from the measured times and positions is therefore given rather simply:

$$u_z^i/v = (t_{cm}-t_i)/t_{cm}, \qquad u_x^i/v = x_i/d, \qquad u_y^i = y_i/d \tag{1}$$

$$\text{or } u_{\parallel}^i/v = (E_i-E_o^i)/2E_o^i; \qquad u_{\perp}^i/v = \theta \text{ respectively,} \tag{2}$$

in which t_{cm} denotes the time-of-flight of the CM-system and E_{oi} the kinetic energies $m_i v^2/2$ of the fragments without Coulomb explosion. An example of the proton distribution after the Coulomb explosion of HeH^+ is shown in Fig. 2b. These data were taken using the high resolution electrostatic analyzer also shown in Fig. 1, detecting the proton only [1]. In order to obtain structural information for molecular ions the CM-velocities u_i must be transformed into relative velocities u_{ij} between the fragments. The u_{ij} are independent of the orientation of the molecule with respect to the beam axis. These quantities do not require knowledge of the absolute time-of-flight values of the fragments. The conversion of the u_{ij} into bond-lengths and -angles has been successfully carried out for a variety of molecular ions having a rather simple structure [1]. Although no analytical proof is known that the relative

velocities are uniquely correlated to the internuclear distances r_{ij} of the molecular ion, numerical calculations (performed for a few triatomic systems) gave a unique transformation from the u_{ij} to the r_{ij} [3].

For molecules containing heavier atoms (e.g. C, N, O) the transformation from the measured relative velocities after the Coulomb explosion to the initial internuclear separations of the molecular ion depends strongly on the charge state Q_i of the emerging ions. In order to obtain the charge state, the fragments can be deflected by a transverse electrostatic field directly behind the target (Fig. 1). The MUPPATS detector is large enough to detect the whole charge state distribution simultaneously. The incident beam can be predeflected in order to assure that all fragments are detected for a variety of experiments with a fixed detector position (Fig. 1). Whereas most parts of the apparatus shown in fig. 1 have been intensively used for several years, the MUPPATS-detector as well as the hardware electronics were completed only recently. In the following, the basic features of this new system are described.

3. THE MULTIPARTICLE POSITION-AND TIME-SENSITIVE (MUPPATS) DETECTOR

The heart of the system is a multiparticle, large area, gas detector. It allows the simultaneous measurement of the x, y positions and arrival times of up to ~10 ions simultaneously. In order to use the detector to derive stereochemical structures of molecular ions via the Coulomb explosion technique, the following properties are required:

- Simultaneous determination of the ion positions and times independent of where the ions actually strike the detector.
- The active area of the detector must be larger than the diameter of the "explosion cones" (up to 30 cm for low-velocity protons).

- A large dynamical range, i.e., the simultaneous detection of ions with different energy losses such as isotachic protons and Ne.
- Position resolution of better than 1 mm.
- Time resolution of better than 1 ns.
- Nearly 100% detection efficiency and essentially no background in order to allow the search for rare structures of e.g. highly excited molecular ions.
- High count rate capability of up to 10^6 events per second.
- Long lifetime of the detector.
- Low overall cost.

These requirements can be matched by a new generation of low pressure multi-wire-avalanche detectors which were recently developed by A. Breskin [4, 5]. Our detector consists of 5 wire planes where an anode at positive potential (~ + 350 V) is sandwiched between two cathodes (each 5 mm apart) at negative potential (~ -350 V) (Fig. 3). In addition, two pick-up cathodes at ground potential are arranged close to the anode (2 mm). The wire spacing amounts to 1 mm for the anode and 0.4 mm for the two cathodes. The pick-up cathodes consist of pairs of wires 0.4 mm apart, separated by 0.6 mm. All ~3000 wires are gold-plated rhenium-doped tungsten, 20μ in diameter. The active area of the wire planes forms a symmetric hexagon with a diagonal length of 34 cm. The wire-frames and a frame containing the window foil (stretched polypropylene of ~80 $\mu g/cm^2$ thickness) are sandwiched between an aluminum front- and back-plate. Thus, neither housing nor vacuum feed-throughs for the 870 signal lines are necessary. Isobutane at ~3 Torr pressure is supplied to the detector.

When an ion passes through the active volume, electron avalanches

(starting nearly simultaneously at both cathodes) develop towards the anode. The low pressure, together with the large electron drift velocity in isobutane results in short signal rise times (~4-5 ns) allowing a time resolution of some 100 ps. A position resolution of 1/10 of the wire spacing can be achieved by interpolating between neighboring wires according to the pulse height [4, 5]. The electron cloud around the anode also induces a signal on the pick-up cathodes which were introduced mainly to limit the radial spread of the field lines caused by the avalanche. Furthermore the effects of space charge due to the slowly moving gas ions are reduced by these cathodes and a field stabilization inside the detector is obtained allowing larger gains and a larger dynamical range of signals.*

4. DATA READOUT AND REDUCTION

Whereas low pressure multiwire detectors as described above have been used to detect single ions, the main feature of the MUPPATS-detector is its capability to detect several particles within the same event, independent of their relative positions. This requires a different and more complex data readout- and -reduction technique compared to the single particle version. One major problem is that two sets of orthogonal wires are not sufficient to determine the position of more than one particle. A set of N x- and y-coordinates can be combined in N^2 different ways resulting in a (N-1)(N)-fold ambiguity. This ambiguity is solved by taking the position information from three planes rotated by 120° with respect to each other (cf

*The interpretation of the role of the pick up cathodes given by the authors differs from that originally given by others [4, 5] who prefer to interpret this kind of detector as a two-stage detector. Because such detectors work best if the fields at both sides of the pick-up cathode are the same, we do not share this interpretation.

section 5, Fig. 4). Although this arrangement does not rigorously solve the general ambiguity problem, the additional information about the pulse height and arrival time of the ions allow the unique assignment of the position information from the three planes to the individual particles.

The main problem of the multiparticle aspect of the detector was the design of the electronic set-up for data-readout, -reduction and trigger decisions. The electronics is based on the latest generation of data readout modules developed for future experiments in high-energy physics [6, 7]. Compared to the use of conventional electronic modules (e.g. constant fraction discriminators, time-to-digital converters, etc.) which are commercially available in the form of NIM- and CAMAC-modules, the concept finally chosen has reduced the total cost for the electronics by nearly a factor of 10. Furthermore, due to the high degree of integration, the complete electronics (if not attached directly to the detector) fits into a single crate.

The readout electronics is shown schematically in Fig. 3. Two different schemes are used: signals from different wires of the pick-up cathodes are pipelined along a delay-line with 5-ns delay between neighboring pairs of wires. Therefore, within one event several pulses appear at both ends of the delay line, thus requiring proper pulse-shaping at the connection of each wire pair to the delay line (cf section 5). To reduce damping of the signal the delay line of each pick-up cathode is segmented into four subunits which are attached directly to the wire frames. Both ends of the delay line are connected to preamplifiers. Due to the large range of pulse heights and the problem of partially overlapping signals each pulse is analyzed by four leading edge discriminators working at different thresholds. The position in time of the leading and trailing edges of each train of logic signals is

recorded in a so called "pipeline time-to-digital converter" (TDC). The common stop signal is used for a simple trigger decision requiring that at least one particle is "seen" by each pick-up cathode (Fig. 3).

To maintain the good time resolution of the low pressure gas detectors a different readout scheme was chosen for the anode wires (Fig. 3): Each wire is connected separately to a fast preamplifier (τ_{rise} ~3 ns) which is directly attached to the wire frame. The analog signals are converted into logic pulses by leading-edge discriminators. Both the width of each logic pulse and its position in time are converted into a charge signal by a time-to-charge converter and analyzed by a charge-sensitive analog-to-digital converter (Q-ADC). The conversion of the time into a charge signal (based on [8]) is necessary because no TDC's with a time resolution of ~100 ps and reasonable cost per channel are available. The width of the logic pulse is a measure of the height of the analog signal. It is used to correct (by software) for the pulse-height dependent walk of the leading-edge discriminators, thus avoiding (rather expensive) constant-fraction discriminators.

Due to the ~650 analog-to-digital conversions per event, fast data-readout and -reduction are required. Both processes take advantage of the recently developed FASTBUS-standard which allows data transfer in about 1/10 of the time needed in case of the CAMAC-standard. Furthermore, FASTBUS-modules contain already built-in "intelligence" allowing data reduction parallel to the conversion process [7]. For example, the content of ADC-channels belonging to wires without any signal above threshold (~90% of all channels) are suppressed and not transferred to the computer. In addition, a multiplicity trigger (not shown in Fig. 3) based on multiplicity outputs contained in the ADC's and the TDC, allows a fast clear of all modules within ~500 ns if the event does not fulfill the required multiplicity condition.

5. FIRST TEST RESULTS

In order to test the readout concept and to optimize the detector parameters a small test detector (44 mm diameter) was developed. To limit the complexity of the data-readout and -reduction during the test phase a readout spacing of 2 instead of 1 mm was used at all electrodes.

Both the delay-line readout and the separate readout were successfully tested using molecular and atomic beams of H_2^+, HeH^+, O^+ and Ne^+. A typical event pattern obtained with a 1.5 MeV H_2^+ beam and separate wire readout is shown in Fig. 4. It indicates the ambiguity problem and its solution using three wire-planes which, in this case, were rotated with respect to each other by 45°. Wires giving a signal above threshold are shown as lines for a single event. Out of the four possible particle positions given by the crossings of x- and y-wires the anode wires (45°) separate clearly the two where the protons hit the detector. The time resolution obtained with separate wire readout amounted to 600 ps for a 1 MeV H_2^+ beam. It was limited by external noise. With improved shielding the noise could later be reduced by a factor ~4.

The main problem of pipelining several pulses using a delay line lies in proper pulse shaping. Signal over- or under-shoots with long time constants degrade the position information contained in the following pulses. In particular, the slow ionic component (~μs) following the fast (some ns) electron-induced signal must be suppressed. The signal at the end of a delay line is shown in Fig. 5. The pulses due to two particles 18 mm apart are clearly separated whereas at a distance of 12 mm the pulses start to overlap. An average minimum distance of 10 mm was obtained where two particles still could be separated. The position resolution was measured by analyzing directly a well collimated (~0.5 mm diameter) low intensity (~10^3/s)

proton beam. The measured resolution of 0.5 mm FWHM was basically given by the size of the beam spot.

6. MONTE CARLO SIMULATIONS

In order to optimize the use of information delivered by the MUPPATS-detector, Monte Carlo simulations for some tri-atomic molecular ions were performed. In particular we investigated

- the identification of ions according to their mass,
- consequences of multiple scattering, and
- the single event resolution with respect to the coincident determination of relative fragment velocities.

Besides the time and position information for all three particles, momentum conservation perpendicular to the beam axis was included in the analysis. Because the transverse velocity $u_\perp$ is small compared to the beam velocity momentum conservation can be expressed as follows:

$$\Sigma\, m_i x_i + K \Sigma\, Q_i = 0 \quad ; \quad \Sigma\, m_i\, y_i = 0 \quad , \tag{3}$$

where K contains the characteristic properties of the postdeflector, deflecting in the x-direction. Not taken into account was momentum conservation parallel to the beam axis which requires knowledge of the absolute flight times. A result similar to the one discussed below can be obtained for four-atom molecular ions if this information is taken into account. The accelerator provides for this purpose a pulsed beam with nanosecond pulse width.

Using Eq. 3 and the known total mass $\Sigma\, m_i = M_{tot}$ (4) of the molecule the masses of the atomic fragments can be calculated. For a target thickness of

~100Å and molecular beams of 0.2 MeV/amu the mass resolution is determined by multiple scattering in the target. The resolution obtained using measured multiple scattering distributions as input in the Monte Carlo simulations is better than one mass unit in the mass range of 1 to ~20 amu (e.g. 0.45 amu for protons and 0.7 amu for oxygen in case of 3.5-MeV H_2O^+ on a 2-$\mu g/cm^2$ carbon foil). Although the three equations (Eqs. 3 and 4) contain four unknowns the total charge can be derived in general by choosing it such that the calculated masses fit best to those contained in the molecule. If the transverse field is strong enough to separate the "explosion cones" belonging to neighboring charge states, the charges can be obtained independently of Eq. 3.

The fact that multiple scattering violates momentum conservation for the molecular fragments (Eq. 3) can be used to improve the resolution of the system. Events with a large multiple-scattering contribution can be discarded by requiring small deviations of the calculated masses (Eq. 3) from the known fragment masses. This is especially important because multiple scattering affects the Coulomb explosion process itself, leading to systematic errors in determining the molecular structure. An example is shown for oxygen ions "detected" after the Coulomb explosion of a 3.5-MeV H_2O^+ beam incident on a C-foil with 100Å thickness (Fig. 6). Figure 6a shows the original multiple scattering distribution used as an input for the Monte Carlo simulation whereas Fig. 6b gives the reconstructed distribution after requiring momentum conservation according to Eq. 3.

The resolution which can be obtained for the relative CM-velocities u_{ij} of the Coulomb-exploded molecular ion is shown in Fig. 7 for the case of a 3.5-MeV CH_2^+ "beam" incident on a 100Å thick carbon foil. Only moderate use of the reduction of multiple scattering by momentum conservation was made in this case. 20% of all events were found within the mass windows of $\Delta m = \pm 0.15$

amu for the protons and $\Delta m = \pm 0.1$ amu for the carbon ion. Results shown in Fig. 7 are for a reconstructed charge state of 4^+ for the carbon. The resolution of ~5% to ~6% is the single event resolution, the mean values can be obtained with a much higher accuracy. This finally leads to a resolution of $\Delta\Theta$ ~5° and $\Delta r/r$ ~10% for the bond-angle and -lengths, respectively.

7. OUTLOOK AND CONCLUSIONS

The experimental arrangement discussed above will be used to investigate the structure of 3- to 5-atom molecular ions, paying special attention to the correlated variations of bond-lengths and -angles of highly excited species. Due to the high density of states in those cases, classical spectroscopic methods either fail or are extremely difficult to apply [9]. Furthermore, we plan to analyze molecular fragments produced by laser-induced unimolecular reactions of beam ions or neutralized molecules.

Besides the field of molecular structures the MUPPATS-detector holds great promise for many other fields e.g. the study of nuclear reactions or atomic processes induced by energetic ion-atom collisions.

8. ACKNOWLEDGEMENTS

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REFERENCES

[1] D. S. Gemmell, Chem. Rev. 80 (1980) 301.

[2] G. Goldring, P. Thieberger, H. E. Wegner (p. 53); P. Thieberger, H. Wegner, R. D. Lee (p. 56); M. Alqranati, A. Faibis, R. Kaim, Z. Vager (p. 59) in "Molecular Ions, Molecular Structure and Interaction with Matter", B. Rosner, ed., Annals of the Israel Phys. Soc. 4 (1981).

[3] A. Faibis, Ph.D.-Thesis, Weizmann Inst. of Science (1983).

[4] A. Breskin, Nucl. Instr. Methods 196 (1982) 11.

[5] A. Breskin, F. Chechik, Z. Fraenkel, P. Jacobs, J. Tserruya, N. Zwang, Nucl. Inst. and Meth. 221 (1984) 363.

[6] R. S. Larson, Interfaces in Computing 1 (1982) 19.

[7] W. Farr, L. B. Levit, R. Rousch, JEEE Transactions on Nucl. Science NS-31, 1 (1984) 217.

[8] W. Farr and D. Habs, private communication.

[9] A. Carrington, R. A. Kennedy, J. Chem. Phys. 81 (1984) 91.

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the experimental arrangement at Argonne's 4.5-MV Dynamitron accelerator.

Fig. 2. Schematic view of the Coulomb explosion of HeH^+ (2a) and the observed ring pattern for H^+ (2b) [1].

Fig. 3. Arrangements of electrodes in the MUPPATS-detector and signal-readout and -processing scheme (see text).

Fig. 4. Detector-wires responding to a two proton event resulting from the Coulomb explosion of 1.5-MeV H_2^+ in a carbon foil (wire-readout spacing = 2mm).

Fig. 5. Signal forms measured at the output of a delay line for a 2-proton event due to the Coulomb explosion of 3-MeV H_2^+ in a carbon foil. Δx denotes the distance between the two protons perpendicular to the wires.

Fig. 6. Multiple-scattering distribution of oxygen ions after the Coulomb explosion of 3.5-MeV H_2O^+ in a 100Å thick carbon foil. a) the original distribution used in a Monte Carlo simulation. b) reconstructed distribution after selecting events for which the calculated masses (eq. 3) deviated less than 0.1 amu from the fragment masses.

Fig. 7. Spectra of relative ion velocities between C^{4+} and the two protons obtained by a Monte Carlo simulation of the Coulomb explosion of 3.5-MeV CH_2^+ incident on a 100Å carbon foil.

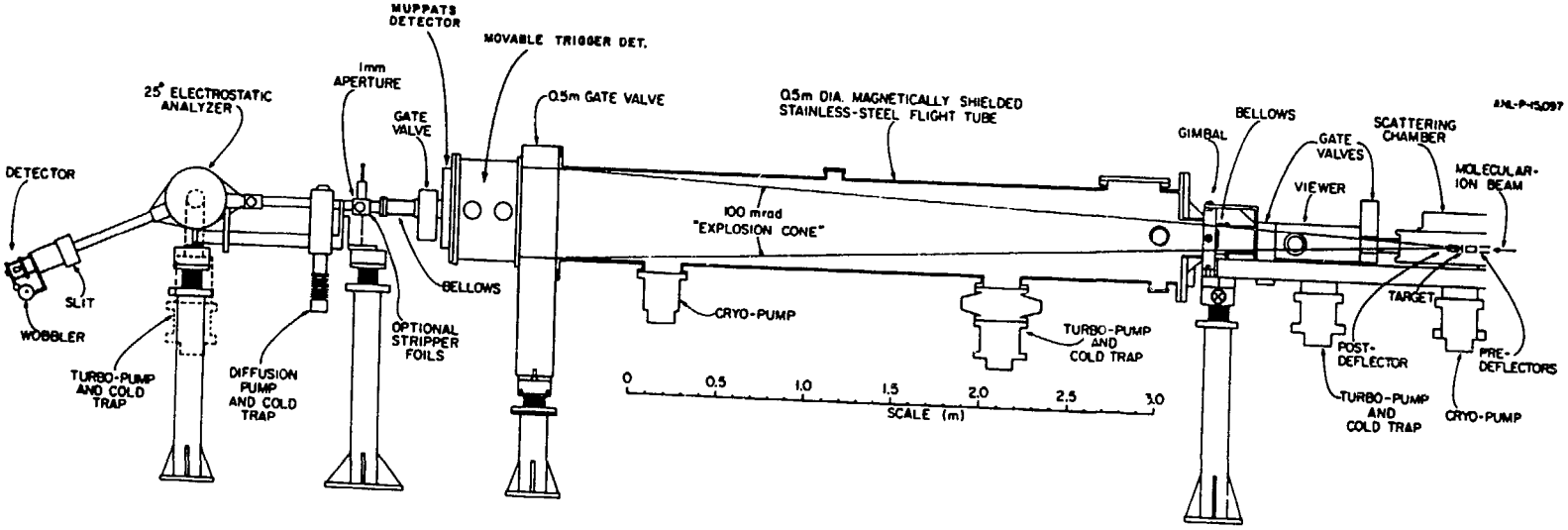

MUPPATS DETECTOR
MOVABLE TRIGGER DET.
1mm APERTURE
25° ELECTROSTATIC ANALYZER
GATE VALVE
0.5m GATE VALVE
0.5m DIA. MAGNETICALLY SHIELDED STAINLESS-STEEL FLIGHT TUBE
ANL-P-15,097
GIMBAL
BELLOWS
GATE VALVES
SCATTERING CHAMBER
MOLECULAR-ION BEAM
VIEWER
DETECTOR
100 mrad "EXPLOSION CONE"
SLIT
WOBBLER
BELLOWS
CRYO-PUMP
TURBO-PUMP AND COLD TRAP
TARGET
TURBO-PUMP AND COLD TRAP
DIFFUSION PUMP AND COLD TRAP
OPTIONAL STRIPPER FOILS
POST-DEFLECTOR
PRE-DEFLECTORS
TURBO-PUMP AND COLD TRAP
CRYO-PUMP
0
0.5
1.0
1.5
2.0
2.5
3.0
SCALE (m)

Fig. 1

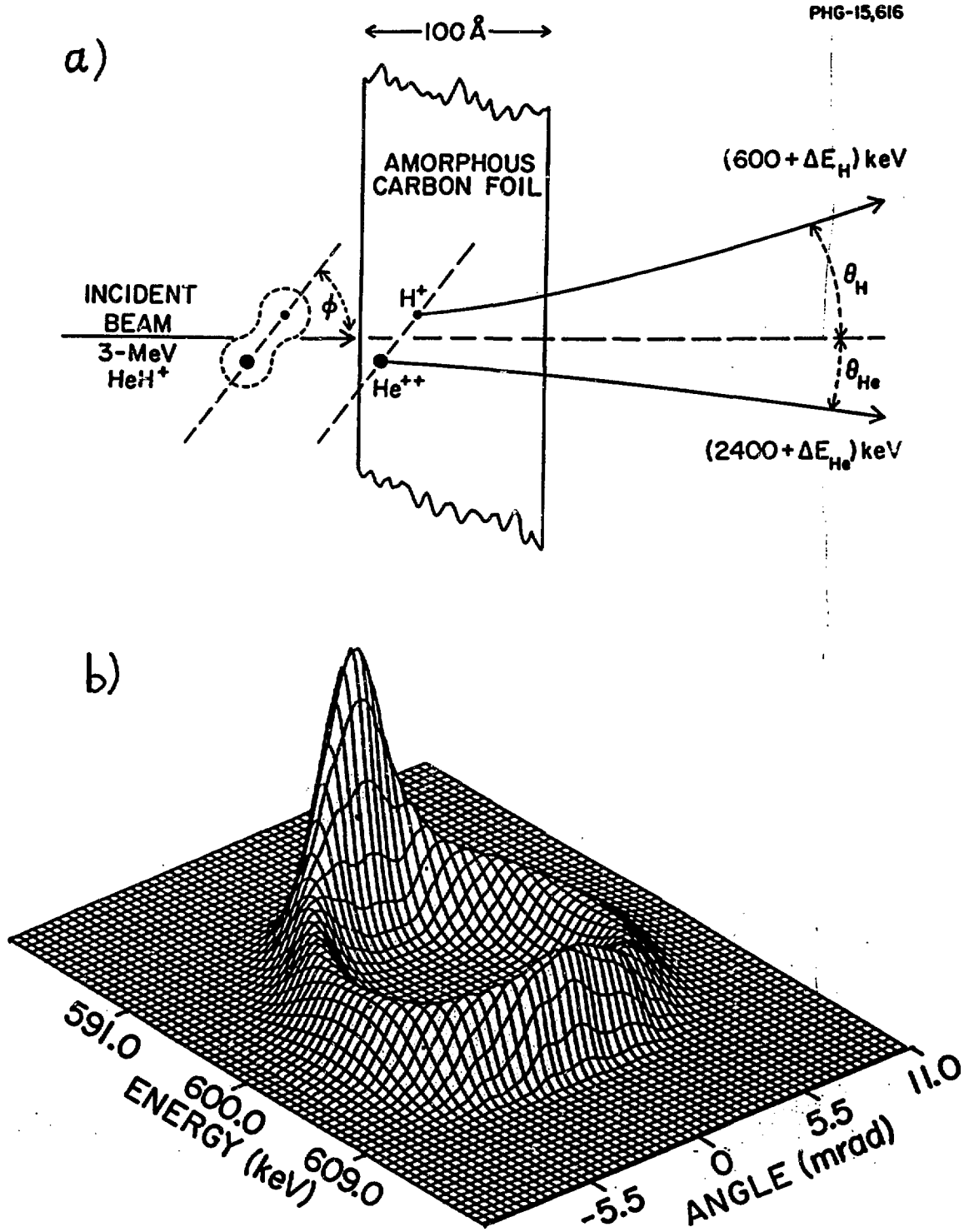
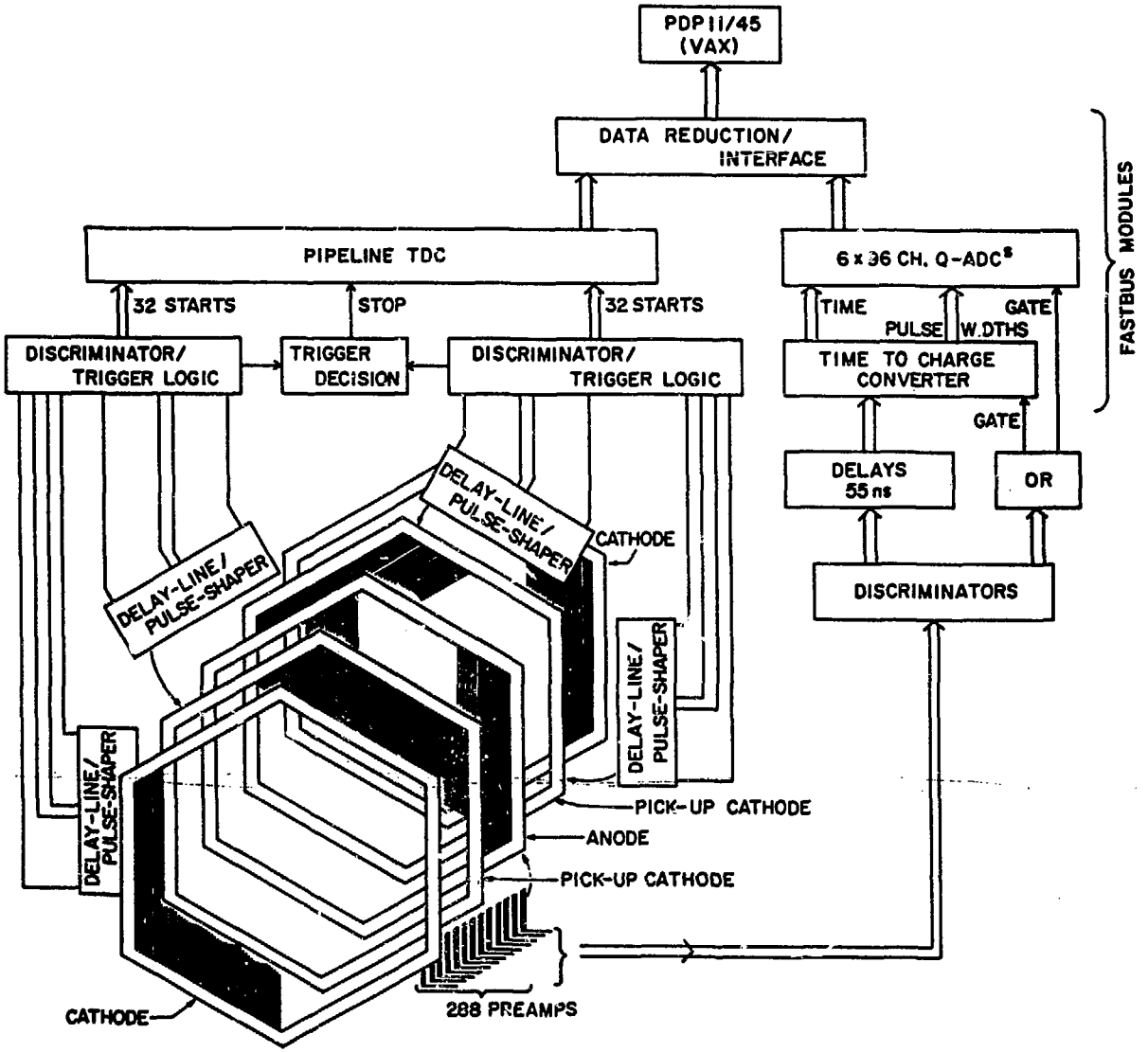

PHG-15,616
a)
100 Å
AMORPHOUS CARBON FOIL
(600 + ΔE_H) keV
INCIDENT BEAM
3-MeV HeH+
φ
H+
He++
θ_H
θ_He
(2400 + ΔE_He) keV
b)
591.0
600.0
609.0
ENERGY (keV)
-5.5
0
5.5
11.0
ANGLE (mrad)

Fig. 2


PDP11/45
(VAX)
DATA REDUCTION/
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FASTBUS MODULES
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STOP
32 STARTS
TIME
PULSE
W.DTHS
GATE
DISCRIMINATOR/
TRIGGER LOGIC
TRIGGER
DECISION
DISCRIMINATOR/
TRIGGER LOGIC
TIME TO CHARGE
CONVERTER
GATE
DELAYS
55 ns
OR
DISCRIMINATORS
DELAY-LINE/
PULSE-SHAPER
DELAY-LINE/
PULSE-SHAPER
CATHODE
DELAY-LINE/
PULSE-SHAPER
DELAY-LINE/
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PICK-UP CATHODE
ANODE
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CATHODE
288 PREAMPS

ANL-P-17,658

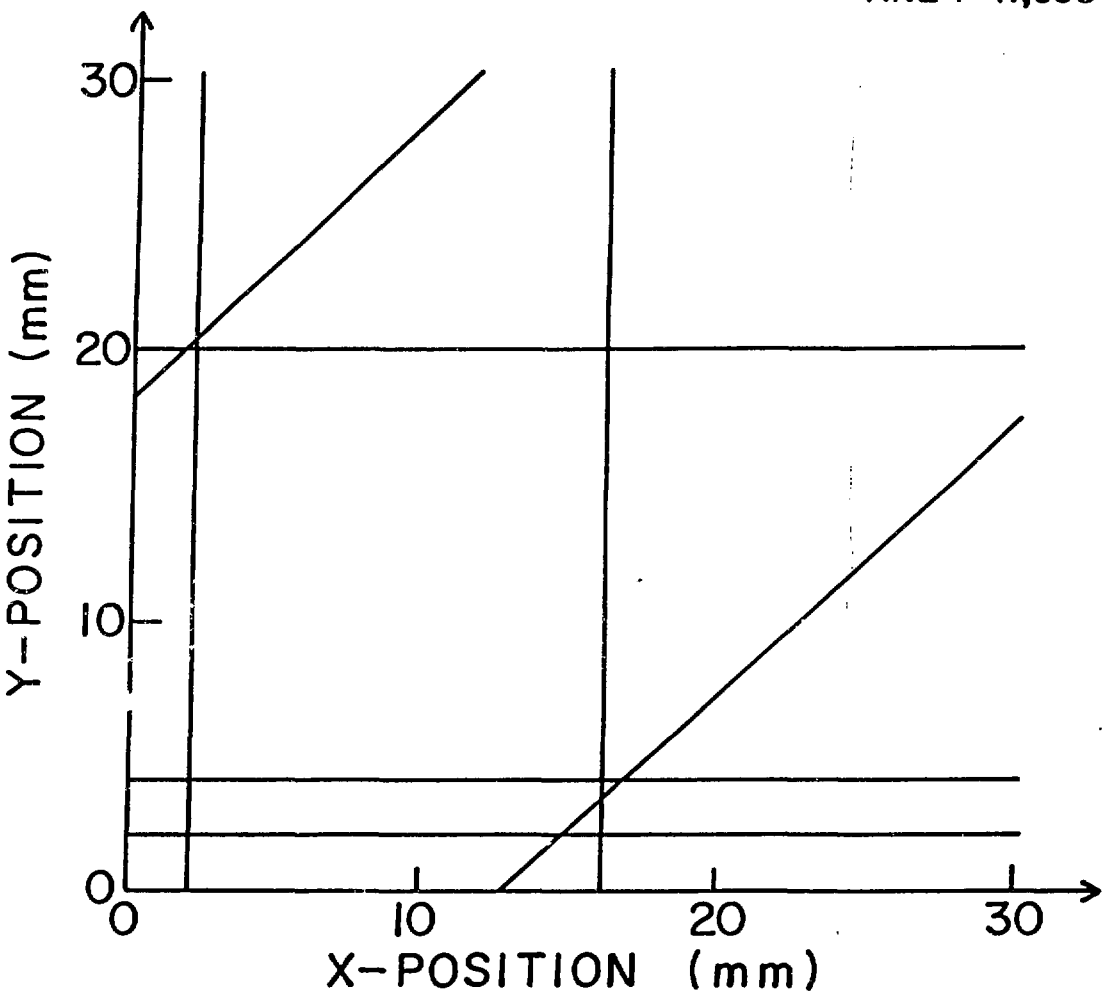

Fig. 4

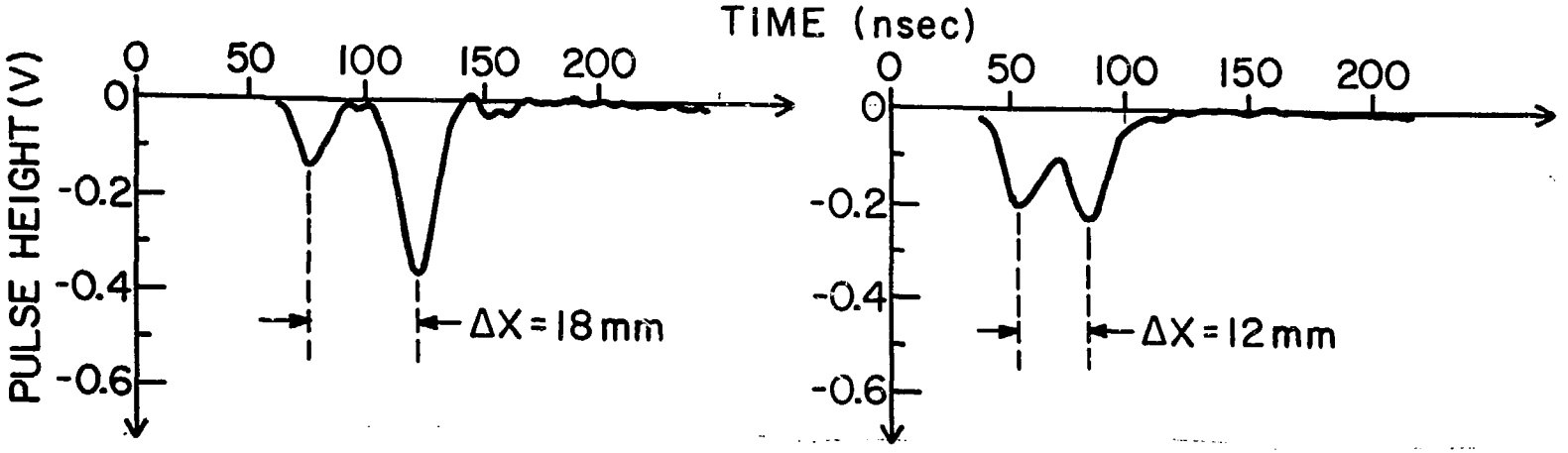
TIME (nsec)
PULSE HEIGHT (V)
0
50
100
150
200
0
-0.2
-0.4
-0.6
ΔX = 18 mm
ΔX = 12 mm

Fig. 5

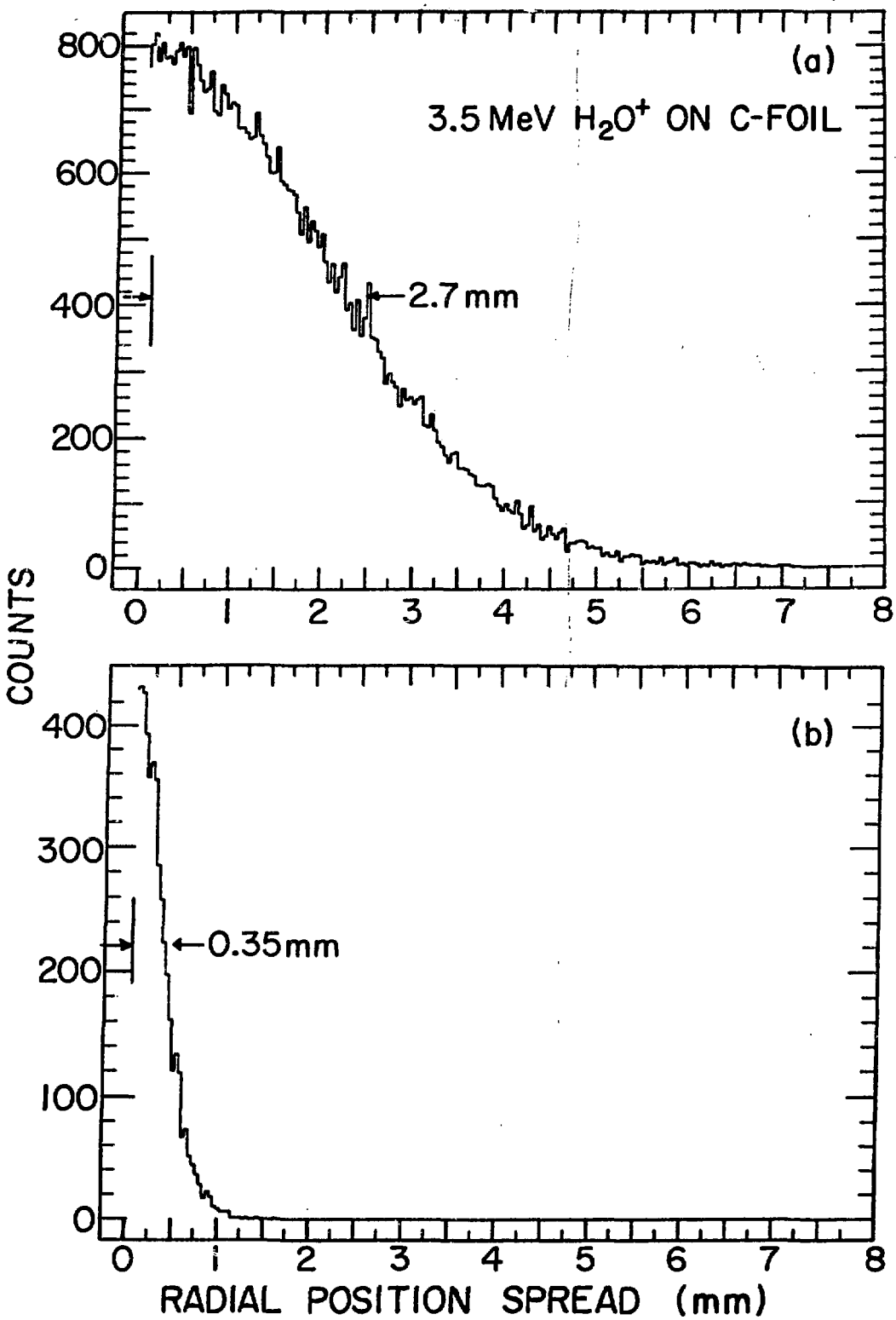
(a)
3.5 MeV H_2O^+ ON C-FOIL
2.7 mm
800
600
400
200
0
(b)
0.35mm
400
300
200
100
0
COUNTS
0 1 2 3 4 5 6 7 8
RADIAL POSITION SPREAD (mm)

Fig. 6

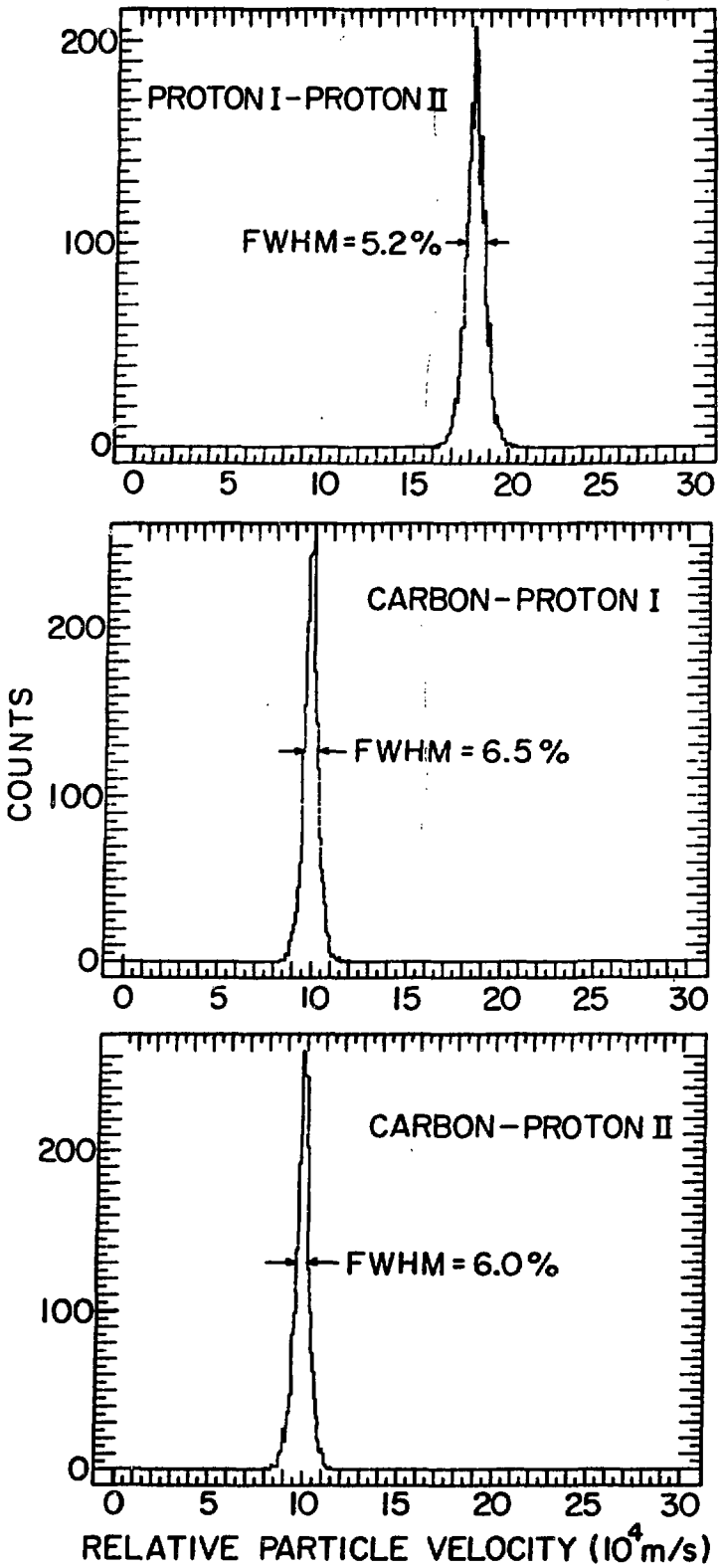
PROTON I - PROTON II
FWHM = 5.2%
CARBON - PROTON I
FWHM = 6.5%
CARBON - PROTON II
FWHM = 6.0%
COUNTS
0
100
200
0 5 10 15 20 25 30
RELATIVE PARTICLE VELOCITY (10^4 m/s)

Fig. 7