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Collisions of Electrons with Hydrogen Atoms. I. Ionization

WADE L. FITE AND R. T. BRACKMANN
John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California

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The cross section for ionization of the hydrogen atom on electron impact has been measured as a function of electron energy. A modulated beam of atoms and molecules in varying proportions, taken from a furnace, is crossed by a dc electron beam, and the positive ions formed are taken into a mass spectrometer. By using such modulation techniques, the ions formed by ionization of the beam are distinguished from the much larger number of ions formed by collisions of electrons with the residual gas in the vacuum chamber. From the study of the mass-spectrometer peak strengths as a function of temperature with constant gas flow, the ratio of the cross sections for ionization of the atom and the molecule is directly determined. The absolute atomic cross sections, determined by multiplying this ratio by the known molecular cross sections, are cross-checked by taking relative cross sections for the atom. Complete agreement with the first Born approximation is found only above about 250 ev. Deviations of experiment from theory at lower energies are as predicted qualitatively by theory.

I. INTRODUCTION

THE customary theoretical formulation of atomic scattering problems of the type where an elementary particle collides with an atomic system and where all the forces are known usually admits two sources of error in their solution. First, whenever the target atomic system consists of more than two bodies, its wave functions are not known and the problem cannot even be formulated exactly. Second, assuming that these wave functions are known, the scattering problem is still too difficult to solve exactly, for the quantum-mechanical treatment leaves an infinite set of coupled equations.

A number of methods have been developed to obtain approximate solutions to this infinite set of equations. Generally, however, the validity of any approximation method is known but qualitatively. Comparison of a theoretically predicted cross section with an experimental result has not been very helpful in determining the validity of an approximation method, because the experiments usually involve target atomic systems for which the wave functions are not known.

Clearly, by allowing the target system to contain only two bodies it should be possible to compare theory with experiment and known that any discrepancy between prediction and result must arise because of the intrinsic deficiencies of the scattering approximation used in the theory. Thus, the approximation methods themselves would be under direct scrutiny. To better analyze these methods, a program of experiments on the collision properties of the free hydrogen atom is being carried on at General Atomic, the results of which also bear directly on the understanding of controlled thermonuclear devices.

The present paper, which is the first of a series to be published, discusses the total cross section for ionization of the hydrogen atom on electron impact. Because of the computational difficulties involved in any ionization calculation, this cross section has been predicted over the entire energy range using, to date, only the first Born approximation. The measurement described here therefore gives information only on this simplest of all quantum-mechanical scattering approximations.

II. EXPERIMENTAL APPROACH

It is well known that hydrogen molecules can be thermally dissociated in a low-pressure furnace and that such furnaces may be used as sources for beams of neutral particles, an arbitrarily large fraction of which will be hydrogen atoms. Clearly, beams from such sources can be used in scattering experiments, in crossed-beam configurations.

In the study of the interaction between hydrogen atoms in a beam and electrons (or any second participant which interacts with molecules as well as with atoms) a basic difficulty must be overcome. Furnaces and other atom sources producing large fractions of atoms operate at rather low pressures. By the time a collimated beam of particles is drawn from the source and taken far enough away for an experiment to be conveniently conducted, the density of particles in the beam may be of the order of 10^9 particles per cm^3. This must be compared with a density of molecules in the residual gas in the vacuum chamber of about 4×10^{10} molecules per cm^3 (for a vacuum of 10^{-6} mm Hg). Since in the scattering of electrons any signal is proportional to the number density of scattering centers, a beam experiment on scattering requires isolating a signal of 1 part in about 40. Because of the rather violent slow fluctuations and drifts in pressure in ordinary vacuum systems, it is clear that looking for a signal of 1 part in 40 with dc techniques promises little but difficulty. Indeed, this appears to be a fundamental reason why electron scattering experiments using beams of free hydrogen atoms have been deferred for so long.

Clearly, an ac experiment is suggested. If the atom beam is modulated by a mechanical chopper and the electron beam is run dc, the desired signal can be

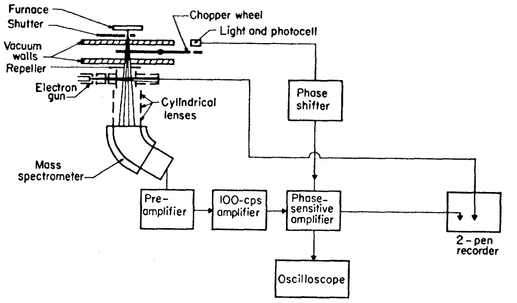


FIG. 1. Schematic diagram of ionization experiment.

identified by its having a specific frequency and phase. The signal arising from the interaction of electrons with molecules of the background gas will be a dc signal plus, of course, a certain amount of noise at the modualtion frequency. Most of the unwanted signal can be removed by a blocking condenser. Actually, the situation is somewhat more complicated than this and will be discussed later in this paper.

In studying the ionization process, we used the ac currents, at the beam modulation frequency, of positive ions after mass analysis. Figure 1 shows a block diagram of the experimental arrangement.

A. Source of Atoms

In the present experiments, the source of atoms was a furnace. The type of furnace most used was tubular, about 3 in. long and $\frac{3}{16}$ in. in diameter. The furnaces were constructed by rolling 0.001-in.-thick tungsten foil into tubes, with about 6 layers of foil making up the tube walls. The beam issued from an aperture in the side of the furnace and proceeded perpendicular to the furnace axis. Tungsten wadding was placed at each end of the furnace so that no gas could go from a cold surface (near the furnace mounting) to the aperture region without suffering many collisions with hot tungsten. The furnace was mounted between copper bus bars, one of which conducted gas to one end of the furnace. The other end of the furnace was blanked off.

Furnace temperature was normally measured with an optical pyrometer, but on those occasions when studies were made at furnace temperatures of less than 1200°K, thermocouples attached to the furnace were used. These thermocouples had to be detached, however, when the furnace was heated to above about 1800°K, as they would alloy with the furnace material, which led, usually, to burnout of the furnace. The usual temperatures measured, therefore, were room temperature and temperatures in the optical-pyrometer range.

In using the pyrometer, the furnace was observed through a window at the back of the vacuum system. The view was upstream against the neutral beam, through the slits, and into the furnace aperture. Measuring the temperature by comparing the brightness of the aperture with that of the filament in the pyrometer eliminated the need to correct for emissivity of the furnace material—the furnace itself was an ideal *Hohlraum*.

A correction had to be made, however, for the fact that the viewer was looking at the furnace aperture through the chopper wheel. Measurements of the temperature with the chopper wheel both running and stationary showed that the moving chopper wheel head a transparency of 0.51 ± 0.02, as was expected, and that this transparency was completely independent of temperature to within the limits indicated.

B. Beam Shape

In the design of a beam apparatus for the study of electron collisions, it should be noted that any signal derived is proportional to both the density of atoms in the neutral beam and the path length of the electrons as they cross the beam. The latter consideration suggests that the beam be made thick; the former, that the collision region be as close to the neutral-beam source as possible, in order to minimize the effect of geometrical spread of the beam with distance from the source. Thus, for collision work the neutral beam should be short and stubby, rather than long and thin as in conventional molecular-beam equipment. In the apparatus described here, the beam was about 4 cm long and at the collision region had a cross section of about 4 mm×6 mm.

C. Vacuum System

The neutral beam was not made appreciably shorter because two vacuum walls, bounding differentially pumped vacuum chambers, were interposed between the furnace and the collision region. This arrangement resulted from signal-to-noise considerations. It has already been remarked that the basic approach in these experiments is to modulate the neutral beam and run the electron beam dc. In this manner the desired signal is identified by its ac characteristics, while the dc signal arising from interaction of the electron beam with the residual gas in the vacuum chamber can be blocked by a condenser. Actually, the background interactions still compete with the desired signal as noise at the chopping frequency. Of course, shot noise arising from statistical variations in the interaction of the electrons with the background gas will always be present. Of much greater importance, however, is the effect of background pressure fluctuations, caused by irregular pumping by the diffusion pumps. Since the background interaction signal is proportional to the background density and, therefore, to the background pressure, even small changes of pressure can be quite serious because of Fourier components at the modulation frequency.

The major device to minimize pressure fluctuations was a three-stage, differentially pumped vacuum system. The first-stage chamber, containing the furnace, was pumped by a 6-in. diffusion pump, the high pumping speed of which quickly removed that gas issuing from the furnace aperture which was not part of the beam. This stage normally operated at a pressure of the order of 10^{-5} mm Hg. The second-stage chamber, containing the chopper wheel, was pumped by a 2-in. pump and normally operated at from 3×10^{-6} to 1×10^{-5} mm Hg. The first stage served as the forepump for the second stage. The third stage, in which the experiment took place, used a 2-in. pump identical to that of the second stage, and the forepump for the third stage was the second stage. The third stage normally operated at from 7×10^{-7} to 1×10^{-5} mm Hg, depending on how long the system had pumped since being opened to the air, on beam strength, etc. The beam passed from the first to the third chambers through slits in the vacuum-chamber walls. (It will be noted that 10^{-5} mm Hg is quite a high pressure for atomic-beam work. It is an intrinsic advantage of modulated-atomic-beam work that extremely good vacuums are generally not required.) This three-stage pumping system reduced pressure fluctuations in the third chamber due to irregular pumping because (1) the pressure difference between the high- and low-pressure sides of the third pump was small and (2) the third pump prevented irregular pumping in the early stages from producing serious effects in the third chamber.

Pressure fluctuations also influenced selection of the modulation frequency and the size and pumping speed of the high-vacuum chamber. With a volume of about 20 liters in the third chamber and a pumping speed of about 20 liters/sec, the pressure time constant in this chamber was about 1 sec. With a modulation frequency of 100 cps, pressure fluctuations at the modulation frequency were rather well integrated by the vacuum chamber.

Before leaving the subject of the vacuum system, two features of any modulated-beam experiment must be considered. Both are concerned with completely coherent signals not arising from interactions of electrons with the neutral beam and which therefore must be subtracted from the ac signal obtained.

The first results from having a differentially pumped vacuum system in which the pressures in the various chambers are not equal. Consequently, there will be a net flow of gas from a vacuum chamber of higher pressure to one of lower pressure through the slits which pass the beam. A fraction of this flow will coincide spatially with the beam. This fraction, of course, will be modulated by the chopper wheel and will be indistinguishable from the beam. With molecular beams this is usually not serious because the bulk of this gas flowing between vacuum chambers will be of the same species as the gas flowing from the beam source. With an atomic beam, however, one must subtract that part of the signal arising from the gas flow between vacuum chambers because it will be almost entirely molecular. In the present case, a dc shutter, operated by a solenoid, was placed before the furnace aperture so as to block the direct beam but not interfere with the background-gas flow. The desired signal was obtained by subtracting the signals obtained with the shutter open from those with the shutter closed. By having three vacuum chambers, this gas-flow signal was kept quite small, never constituting more than a few percent of the total modulated signals.

The second coherent modulation effect arises from the fact that when any neutral beam is admitted to a vacuum chamber, the pressure in the chamber increases because of the finite pumping speed of the vacuum pumps. (For usual beam apparatus this pressure gives an increase in the density of molecules over the entire vacuum chamber of about ten times the density of particles in the beam, if time is allowed for the steady state to be achieved. When an atomic beam enters the vacuum chamber, this background-gas increase is almost entirely molecular, because of the recombination of the atoms at the surfaces of the vacuum chamber. Thus, confusion between atoms and molecules appears unavoidable in any dc experiment on electron collisions with atoms.)

When modulation of the neutral beam at a suitable frequency is introduced, the tendency of the background-gas pressure to coherently follow the beam density changes exists but is not important. In this case, the vacuum chamber acts analogously to a large electrical condenser, or even more analogously to a muffler on an automobile. The vacuum pump and vacuum chamber are insensitive to pressure changes; as long as the period of chopping of the neutral beam is very small compared with the time constant of the vacuum system [i.e., the time for the pressure in the chamber to change by $(e-1)/e$ the amount that it would change in an infinite time], the amplitude of background-gas density oscillations will be small compared with the density changes in the beam as it is turned on and off at the modulation frequency. (In the case of the present apparatus, which had a time constant of about 1 sec, a modulation frequency of 100 cps was adequate.) Also, because the pressure in the vacuum chamber continues to rise as long as the beam is in its "on" half-cycle (assuming that this time interval is small compared with the vacuum-system time constant), and reaches its maximum at the moment the beam is turned to its "off" half-cycle, the phase of coherent background-gas-density oscillations at the modulation frequency will be 90° behind the signal associated with the atomic beam. Thus, phase-sensitive detection can completely eliminate any signals arising from interaction of the dc electrons with the background gas. Of course, since an amplifier tuned to the modulation frequency is employed in the detection circuits, only the background-pressure oscillations at the modulation frequency are of any concern.

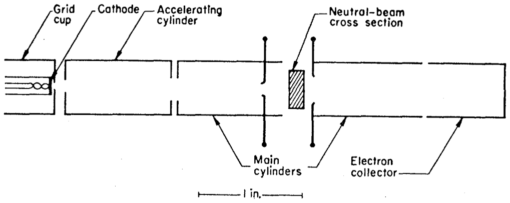


FIG. 2. Typical electron gun—schematic diagram.

D. Electron Gun

The source of electrons for the ionization experiment was constructed from cathode-ray-tube electron-gun components. Figure 2 illustrates schematically the type of gun most often used, which consisted of either an oxide-coated or a tungsten cathode; an aperture grid, usually 0.10 in. in diameter; an accelerating cylinder; two main cylinders, one on either side of the collision region; and an electron collector. The electron collector was maintained at a positive voltage with respect to the main cylinders, to prevent the escape of secondary electrons. The electron energy was determined by the potential difference between the main cylinders and the cathode, and calibration was made using the known ionization thresholds of H_1, H_2, and helium. In addition to the focusing provided by the electrostatic lenses, the electron beam was collimated as the electrons passed through the aperture in the first main cylinder. An aperture also appears in the second main cylinder, because for relative-cross-section measurements (see Sec. III), it was necessary to ensure that all electrons arriving at the electron collector had passed through the neutral-particle beam. The second aperture was slightly smaller than the height of the neutral beam. Current was measured both to the second main cylinder and to the electron collector. The focus was then adjusted to eliminate current to the second main cylinder. Under these conditions there was good assurance that all electrons were passing through the neutral beam and that all ions formed came from electrons whose current was being measured at the electron collector.

E. Mass Spectrometer

In the present experiments, the signals used were the 100-cps ac positive-ion currents which arose when the modulated neutral beam intersected the dc electron beam. It was desirable to mass-analyze these ions for two reasons. The first is that when relative cross sections for ionization of the atom were being taken, the signal-to-noise ratio could be greatly improved by preventing the dc molecular ions from reaching the ion detector. The second reason stems from the fact that the absolute cross section for ionization was determinable (see Sec. III) by comparing the numbers of molecular and atomic ions formed when the electron beam crossed a beam containing both atoms and molecules, i.e., by comparing the mass-spectrometer peak strengths.

The mass spectrometer used most in the present experiments was a 30°-deflection magnetic-sector instrument with a radius of curvature of 4 cm. It was inserted into the vacuum system. The ion energy was fixed, usually at 45 ev, and mass analysis was made by sweeping the magnet current.

The electron gun and mass spectrometer operated as follows: The main cylinders of the gun (and therefore the interaction-region potential) were 45 v positive with respect to ground, and the electron energy was varied by varying the potential of the cathode. The first cylinder of the lens system of the mass spectrometer was maintained slightly below 45 v and a repeller, on the opposite side of the interaction region from the mass-spectrometer lens system, was maintained at a potential slightly above 45 v. This weak field caused the ions to drift down to the second cylinder in the lens, which was very near to ground. Primary focusing was done at the lens between the first and second cylinders. The third cylinder was at ground, as were the body of the magnet and the ion collector. The collector was a simple brass cup, behind a slit, to which was attached a preamplifier, to be described below. The neutral beam entered through an aperture in the repeller, crossed the electron beam, and proceeded down the cylinders of the mass-spectrometer lens together with the ions. This geometry gave the atoms no surfaces on which to recombine into molecules in the vicinity of the electron beam.

Since only electrostatic fields were used in the auxiliary optics of the mass spectrometer, the only initial conditions affecting the ion's orbit as it entered the spectrometer were its energy and direction of motion; the orbit is independent of the mass of the ion. Since the neutral beam is directed, then if little velocity is imparted to the atom or molecule when it is ionized by electron collisions, the collection efficiency of the mass spectrometer is independent of mass for neutral beams arriving at the same temperatures. Certain indirect evidence, to be presented below, suggests that this is the case.

F. Circuitry

The circuitry required in this experiment was all designed to obtain good signal-to-noise ratio, and consists of (1) a preamplifier, to reduce the impedance at the ion collector; (2) a narrow band-pass amplifier; (3) a phase-sensitive detector and rectification stage; and (4) a dc recording potentiometer.

1. Preamplifier

The basic physical measurable in the ionization experiment was positive-ion current. Typical amplitudes of this ac current were about 10^{-12} amp. To provide a voltage signal, this current was passed through a 10-kilomegohm resistor. The thermal noise of this resistor, and other electrical noise, gave signal-to-noise figures of the order of 100 to 1. The function of the preamplifier was to transform this high impedance to a lower value, so that the voltage signal could be fed into the amplifiers.

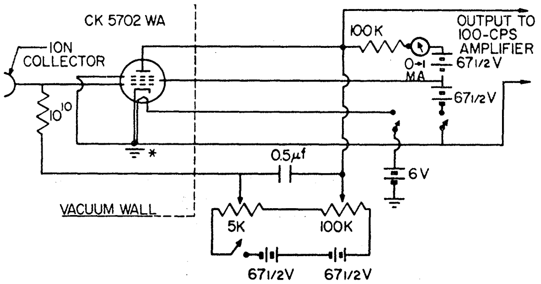
The circuit used for the preamplifier, the voltage of which was supplied entirely from batteries, is illustrated in Fig. 3. A single CK 5702 WA subminiature pentode was used in a plate-follower circuit. This tube was mounted inside the vacuum system on the mass spectrometer at the site of the collection of positive ions.

In applying a plate-follower impedance changer to this type of experiment, one slightly unusual feature must be employed. Positive ions formed by the electrons striking the background gas in the vacuum produce a dc ion current which changes with vacuum-pressure drifts and which, when passing the large resistor, greatly changes the grid bias on the preamplifier tube. Since such changes can affect the behavior of the tube, it is necessary to provide for keeping the grid bias constant throughout an experiment.

This is done by providing a variable dc potential between the plate of the preamplifier tube and the top of the large resistor. Assurance that the conditions are constant throughout an experiment is made possible by adjusting this variable potential so that a prescribed dc plate current is drawn at all times. The prescribed current is determined for any particular preamplifier tube by measuring the grid current as a function of grid voltage and selecting a value of grid voltage negative to that at which the extremum of the grid-current-*versus*-grid-voltage curve lies. The plate current corresponding to this bias is taken as the prescribed plate current. This preamplifier offers high input and low output impedances, stable plate current, and flexible control of operating conditions.

2. *Amplifier*

The major function of the amplifier is to increase the voltage signal by several hundred to several thousand times and to filter out those frequencies not in the immediate neighborhood of the chopper frequency. Actually, the narrow effective bandwidth of the entire electronic system was governed only by the time constant used in integrating the dc output signal after rectification. The narrow bandpass in the early stage of the amplifier merely reduced noise and oscillation which would otherwise have blocked the electronics by overloading the electron tubes in the later stages.



*ENTIRE SYSTEM GROUNDED AT ONLY ONE POINT INSIDE VACUUM SYSTEM

FIG. 3. Preamplifier.

3. *Phase-sensitive Detector*

The phasing signal was derived from a cadmium selenide photocell (Clairex CL-3) which was actuated by light reflected from the individual teeth of the chopper wheel. A unit consisting of a flashlight bulb and the photocell placed side-by-side was fixed in the second vacuum chamber just behind the plane of the chopper wheel. This unit noted the passing of each tooth. With such an arrangement the phasing signal was locked to the chopper wheel, and it was necessary to allow phasing of this reference signal to compensate for phase shifts of the ion signal as it passed through the main amplifier. Electronic phase shifting was used.

The phase-sensitive detector-integrator utilized a single tube with push-pull output to convert the ac ion signal to full-wave rectified dc and to lower the impedance to that of the recorder into which the signal was ultimately fed. This rectified signal was fed onto the two outer terminals of a dc-ac chopper, which was actuated by the phasing signal coming from the phase shifter. The signals from the central terminal of the dc-ac chopper were fed into *RC* integrating circuits connected in parallel with the recorder input.

An oscilloscope was used to ensure proper phase of the reference signal.

III. MEASUREMENT OF THE IONIZATION CROSS SECTION

A. Relative Cross-Section Measurements

The number of ions produced per second when an electron beam crosses a gas of fixed number density of neutral particles is proportional both to the cross section for ionization at the particular electron energy and to the electron current. Cross sections at two electron energies can be compared by comparing the ion-signal strengths divided by the respective electron currents at the two energies. For the comparison to be valid, of course, all the electrons whose current is being measured must pass similarly through the gas being ionized. For this reason, the electron gun in the present experiments had an aperture in the second of the two main cylinders (see Fig. 4); focusing the electron gun so that the current was received at the second main cylinder ensured that all measured electron current passed through a limited portion of the neutral beam. The ion-signal strengths used in the relative cross-section measurements were those received at the collector of the mass spectrometer.

To test the apparatus for the measurement of relative cross sections for ionization, these measurements were made on standard gases such as H_2. Confirmation of the results of other investigators on naturally occurring gases indicated that the experimental methods were sound.

In taking relative measurements for the ionization cross section of atomic hydrogen, the mass spectrometer was tuned on the proton peak and the neutral beam was adjusted to contain more than about 50% atoms. Atomic ions arising through dissociative ionization of the remaining molecules in the beam, even for such low dissociation fractions, necessitated corrections of less than 2% of the signal.

Such relative measurements are actually all that is required. The first Born approximation becomes valid at sufficiently high energies of the incident electrons (i.e., several hundred ev), and these relative-cross-section curves can be normalized to the Born approximation values at these energies. However, to cross-check this method of obtaining absolute cross sections by calibrating experimental results at high energies to Born approximation predictions, a different type of measurement was made which yielded absolute values.

B. Theory of Absolute Cross-Section Measurements

To determine experimentally the absolute cross section for ionization of the hydrogen atom, we first evaluated the ratio of atomic to molecular cross sections at any given electron energy and then used existing knowledge of the absolute molecular ionization cross section[1] to obtain the atomic cross section.

Assuming a single atomic species in the beam, the cross section Q for ionization at a given electron energy is given by $S=QL(I/\bar{c})$, where S is the ion current per unit electron current crossing the atom beam, L the path length of electrons through the atoms, I the beam intensity (particles per second per unit area normal to the beam's direction), and $\bar{c}$ the mean speed of beam particles. Calling N the total number of particles per second leaving the furnace through the beam aperture, irrespective of their direction, the beam density for effusive flow is given by $I=GN$, where G is a geometrical factor. Thus, the ion current per unit electron current is given by $S=QLGN\times 1/\bar{c}$.

If the gas comes to equilibrium in the furnace, the mean speed is given from kinetic theory by $\bar{c}=(8kT/\pi m)^{\frac{1}{2}}$, where m is the mass of the atomic species, k is Boltzmann's constant, and T is the absolute temperature. Substituting,

$$S=BQ(m/T)^{\frac{1}{2}} \quad B=LGN(\pi/8k)^{\frac{1}{2}}. \tag{1}$$

[Experimentally, gas was fed to the furnace from a reservoir in which the gas pressure was about 1 atmos. The gas crossed a needle valve as it flowed to the furnace, and then left the furnace through the beam aperture. On the furnace side of the needle valve the pressure was always less than 100μ Hg. Thus, with a fixed needle-valve setting the flow of gas to the furnace was independent of the furnace temperature and pressure. The furnace itself was mounted in such a way that at any furnace temperature at least 98% of the gas escaped through the aperture in which the beam was formed. Consequently, it is correct to a high degree of approximation to treat N as a constant independent of temperature. Since G, basically the fraction of particles leaving the furnace which pass through the beam-collimating slits, should be independent of temperature, B is a constant and S should depend on furnace temperature only through the inverse square root of T. Intuitively, one may interpret the temperature dependence in Eq. (1) by saying that the hotter the furnace, the faster the beam particles go, and the less time the electrons have in which to hit and ionize the neutral particles.]

If we now expand this agrument to consider not a single immutable atomic species (such as an inert gas) but a gas capable of thermal dissociation in the furnace, we have the experimental case with hydrogen. If we call D the fraction of molecules which are dissociated in the furnace and N the total number of molecules entering the furnace, the molecular ion signal per unit electron current, S_2, is given, from Eq. (1), by

$$S_2=BQ_2(m_2/T)^{\frac{1}{2}}(1-D), \tag{2}$$

where Q_2 and m_2 are the cross section and the mass of the molecule, respectively. The atomic ion current per unit electron current is given by $S_1=BQ_1(m_1/T)^{\frac{1}{2}}\times 2D$, the factor of 2 occurring because each molecule dissociates into two atoms. Dividing the equations, and taking into consideration that $m_2=2m_1$, we obtain

$$Q_1/Q_2=[(1-D)/\sqrt{2}D]S_1/S_2. \tag{3}$$

While this form of the equation is simple and convenient,* it requires determination of the degree of dissociation at the time the molecular and atomic ion signals are taken. This can be obtained as follows. For temperatures below which dissociation occurs (~1500°K), from Eq. (2)

$$S_2T^{\frac{1}{2}}=C=\text{const.} \tag{4}$$

We now define S_0 as the molecular signal at *any* temperature which would have been found had no dissociation occurred. That is,

$$S_0=CT^{-\frac{1}{2}}, \tag{5}$$

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[1] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

* *Note added in proof.*—This derivation neglects the contribution to the mass 1 signal on the mass spectrometer arising from dissociative ionization of the molecules remaining in the beam. The very low probability of dissociative ionization in electron collisions with hydrogen molecules justifies its neglect and also justifies, to within our experimental uncertainty, taking the total ionization cross section as measured by Tate and Smith to be equal to the cross section for forming the molecular ion in electron-molecule collisions. The subject of dissociative ionization probabilities of diatomic molecules will be discussed in a future paper.

for all temperatures, with C evaluated for temperatures at which $D=0$ in Eq. (4). Clearly, then, the degree of dissociation is given from

$$1-D=S_2/S_0. \tag{6}$$

It will be found convenient to substitute Eq. (6) into Eq. (3), giving

$$Q_1/Q_2=(1/\sqrt{2})[S_1/(S_0-S_2)]. \tag{7}$$

C. Measurement of Absolute Cross Sections

It is clear from Eq. (7) that three quantities will be sufficient for determining the ratio of atomic to molecular ionization cross sections, and two of these, S_1 and S_2, are directly measured on the mass spectrometer. The third quantity, S_0, the molecular signal which would have been observed had not the hydrogen molecule dissociated, must be obtained by extrapolation. It was expected that this could be obtained from Eq. (5), in which the constant, C, was evaluated from Eq. (4).

The major difficulty, however, was finding the conditions under which Eq. (4) was valid, i.e., where $S_2T^{\frac{1}{2}}$ was indeed equal to a constant for fixed gas flow over the temperature range below which any dissociation occurred. It is convenient to define a function of temperature, $C(T)$, by $C(T)=S_2T^{\frac{1}{2}}$. It was found that under most experimental conditions $C(T)$ increased with temperature, more or less linearly, at rise rates of up to 1.5% per hundred degrees Kelvin. With the mass spectrometer already described, $C(T)$ never decreased with temperature, while on many occasions it took a constant value as was expected. The major effort in this experiment was devoted to finding the causes of the observed behavior and the experimental conditions which led to acceptable results. In these rather extensive experiments, nondissociating simulant gases, e.g., helium, argon, and nitrogen, as well as hydrogen, were used to study the function $C(T)$ up to 3000°K.

The observed behavior of $C(T)$ is understood on the basis of two phenomena. The first is the change of mass-spectrometer collection efficiency with the energy of the neutral particle which becomes ionized. The second is the scattering of particles out of the beam by the gas cloud immediately before the furnace aperture.

Regarding the first phenomenon, it will be recalled that the axis of the mass-spectrometer entry system lay in the neutral beam. As the furnace temperature was increased, the initial momentum of the neutral particle, which was changed but little in the ionizing collision, tended to carry the ion into the mass spectrometer more efficiently. It was found, for example, that increasing the collection fields of the mass spectrometer, so as to weaken the effect of initial momentum, always reduced the rise rate of $C(T)$. A more dramatic demonstration of the effect of the particle's initial energy was made with a second mass spectrometer. This instrument was similar to the first, except that the ions were drawn away at an angle of about 70° from the initial direction of the neutral beam, so that increased energy of the neutral beam would tend to carry the ions past the mass spectrometer and decrease collection efficiency with increasing temperature, thus leading to a function $C(T)$ which monotonically decreased. This behavior was observed in the second instrument; $C(T)$ always behaved oppositely to that using the first mass spectrometer.

The strong variation of $C(T)$ with the collection efficiency of the mass spectrometer also suggests that the location of the mass spectrometer in the vacuum system might be quite critical, and this was observed to be the case. As long as the mass spectrometer was not moved, the functions $C(T)$ were found to be quite reproducible; however, after removing and replacing the spectrometer, the character of $C(T)$ would change, although it would again be reproducible in the new position.

It thus became standard procedure to use a simulant gas (usually argon) to determine the collection efficiency of the mass spectrometer as a function of temperature for any mass-spectrometer position, and to use these results to correct the hydrogen data.

The second important phenomenon, scattering of the beam by gas before the furnace aperture, was studied by varying the pressure in the furnace, keeping all other parameters fixed, and observing the functions $C(T)$. It was found in these experiments that $C(T)$ did not change until the gas flow through the furnace system was increased to where the room-temperature furnace pressure was about 10 μ Hg. Above this pressure, temperature increases appeared to reduce the number of particles scattered out of the neutral beam. Consequently, major reliance was placed upon results obtained with the room-temperature furnace pressure below 10 μ Hg.

Two experiments served to indicate that the gas was coming into translational equilibrium with the furnace, and therefore that nonequilibrium of the gas was not a difficulty in the experiment. The first was a study of $C(T)$ for hydrogen up to dissociation temperatures, with all quantities fixed except the size of the furnace aperture, the variation of which changed the mean number of collisions a particle would have with the hot walls of the furnace before leaving and entering the beam. Varying the size of the aperture with fixed furnace volume, so that the mean number of particle collisions with the walls varied from about 130 to several thousand, showed no significant effect upon $C(T)$. Assuming that equilibrium was achieved with several thousand collisions, the same result with the smaller number of collisions implies that the average thermal accommodation coefficient of molecular hydrogen on tungsten exceeds 0.04.

The second experiment was designed to study the function $C(T)$ without those complications resulting from temperature-dependent efficiency of the detection device that occur with ionization and mass-spectrometric detection. Basically, a signal derived from something other than the heavy particle which was originally in the neutral beam is required. The signal chosen was that arising from low-energy (i.e., less than 10-ev) electrons scattered elastically from the particles in the neutral beam. In this case, the current of electrons arriving at what was normally the repeller on the mass spectrometer was measured. With hydrogen (up to dissociation temperatures), argon, and nitrogen, it was found that $ST^{\frac{1}{2}}$, where S is now the scattered electron signal, showed no significant deviations from constancy when the room-temperature furnace pressure was less than about 100 μ Hg which was a good indication that equilibrium between the furnace and the gas was being reached. Above 100 μ Hg pressure, an increase of $ST^{\frac{1}{2}}$ indicated significant gas scattering of the beam. In the case of helium, poor signal-to-noise ratio in these experiments prevented similar conclusions. (Using hydrogen and carrying the temperature up to where almost pure beams of atoms were produced allowed a determination of the cross section for elastic scattering of electrons from hydrogen atoms. Indeed, these elastic scattering measurements closely parallel that of Bederson, Malamud, and Hammer,[2] although our results are much smaller. This will be discussed in a later paper.[3])

A third set of observations was made on the equilibrium of hydrogen with the furnace. In cases in the ionization experiment where the function $C(T)$ was constant, the degree of dissociation as determined by Eqs. (5) and (6) was measured as a function of furnace temperature and estimated pressure. The closeness of the results to those predicted from statistical mechanics gave reassurance of gas-furnace equilibrium.

In summary, it is believed that:

1. Thermal equilibrium was achieved for argon and nitrogen in all furnaces and at all temperatures, and for hydrogen at least up to temperatures at which dissociation occurs. Helium may not be in complete thermal equilibrium.
2. The major cause of $C(T)$ not being a constant is ascribable to the variations in collection efficiency of the mass spectrometer, due to the effect of temperature-dependent momentum of the particles in the neutral beam.
3. Placement of the mass spectrometer was quite critical in determining the form of $C(T)$.
4. Gas scattering of the neutral beam was not important at the low furnace pressures normally used in the atomic-hydrogen-ionization experiment (i.e., less than 30 μ Hg).
5. Argon simulated molecular hydrogen quite well in all experiments made.

For the evaluation of absolute cross sections, the function $C(T)=S_2T^{\frac{1}{2}}$ was significant because of the need to evaluate S_0, the molecular signal which would have been found at high temperatures had the hydrogen not dissociated, as was indicated in detail in Sec. III-B. If $C(T)$ were always a constant for all gases, the assumption that it was also a constant for hydrogen, dissociated to an arbitrary degree, would be a reasonable extrapolation. The studies described immediately above indicated that such a simple approach was not always applicable.

Particularly significant results from these studies are, however, that (1) in all experiments performed, molecular hydrogen and argon appeared to behave similarly, even to the extent of giving functions $C(T)$ of the same form for any given mass-spectrometer placement with comparable gas pressures; and (2) argon appeared to come into complete thermal equilibrium with the furnace. This allowed the next most simple extrapolation for obtaining S_0 to be tried. It was assumed that the functions $C(T)$ for molecular hydrogen and for argon are proportional at temperatures in excess of about 1200°K for any given mass-spectrometer placement. In this case, S_0 would be proportional to the argon signal at the same temperature. Alternatively, it is convenient to redefine S_0 by

$$S_0=C(T)/T^{\frac{1}{2}}, \tag{8}$$

where the shape of $C(T)$ above dissociation temperature will be determined from argon data. This approach may be thought of as using argon to determine the mass-spectrometer collection efficiency and then applying these results to the hypothetical molecular-hydrogen signal. Of course, using argon in this way is entirely satisfactory only if the momenta of both argon and hydrogen atoms and molecules are not changed in the ionizing collision. The mass of hydrogen is such that if large fractions of the momenta of the incident and liberated electrons were transferred to the remaining ion, very substantial sideways deviations in direction could occur, while the direction of motion of the argon would change negligibly in an ionizing collision because of its large mass. Although, to the authors' knowledge, no detailed studies have been carried out on the transfer of momentum to the proton in an ionizing collision between an electron and a hydrogen atom, certain features of the Born approximation calculations strongly suggest that appreciable momentum transfer does not occur.[4] Further, indirect evidence gathered in this experiment indicates that the difference in momen-

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[2] Bederson, Malamud, and Hammer, Bull. Am. Phys. Soc. Ser. II, **2**, 172 (1957).

[3] Brackmann, Fite, and Neynaber, this issue [Phys. Rev. **112**, 1157 (1958)].

[4] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, pp. 232–236.

tum between the atom and the ion is not important for the present purposes.

While other *a priori* objections may be raised against this procedure, it satisfies two necessary conditions of the entire experiment. First, it gives a satisfactory constancy of the ratio of atomic to molecular cross sections at various temperatures within a given run. Second, the values obtained from separate runs agree, for a given electron energy, even though the functions $C(T)$ for the two runs differ widely. (A third advantage of this procedure is that the values given at high electron energies, where it is expected that the Born approximation calculations will be correct, agree with the Born approximation values.)

To illustrate the first and second points, it is of interest to consider two sets of data which are extreme in the sense that the $C(T)$'s differ widely. These data are for an electron energy of 200 ev. In the first set, the $C(T)$ for argon was shown to be constant to within experimental accuracy for all temperatures above 1200°K and the constancy of $C(T)$ for hydrogen is assumed. The hydrogen data, with pertinent calculations, are given in Table I. (In this table the third significant figure is in doubt.)

TABLE I. First set of sample data.[a]

T(°K)	S_2	S_1	$C(T)$	S_0	D(%)	Q_1/Q_2
1250	65.0	0	230	...	0	...
1395	62.5	0	234	...	0	...
1590	57.0	0	228	...	0	...
2005	39.7	9.5	...	51.3	22	0.60
2200	23.0	22.5	...	48.9	53	0.62
2355	10.0	31.5	...	47.3	79	0.61
2530	3.5	36.0	...	45.7	92	0.61

[a] The temperature, T, and the molecular and atomic ion signals, S_2 and S_1, respectively, were directly measured. $C(T)=S_2T^{\frac{1}{2}}$. Values of S_0 were determined from Eq. (8), with the value of the constant $C(T)$ taken as 230, and D and Q_1/Q_2 were determined from Eqs. (6) and (7), respectively.

In the second set of data, conditions were such that $C(T)$ for argon strongly increased with temperature, and the points fitted quite well a straight line of the form $C(T)=C_{12}[1+0.0128(T-12.0)]$, where C_{12} is the value of $C(T)$ at 1200°K and T is measured in hundreds of degrees Kelvin. In the corresponding run with hydrogen, the experimental temperature nearest 1200°K was 1235°K, at which C had the value 868. Assuming the straight line given above describes the hydrogen case, it is straightforward to calculate that the value of C at 1200°K would have been 864. Table II describes the results of this run.

Clearly, the value of Q_1/Q_2 at 1815°K is wrong. It will be recalled that the difference between S_2 and S_0 enters into this calculation, the difference in this case being little more than 1% of the value of either. Neither value is known to this accuracy.

These two sets of sample data are extreme in a second sense. The first set was taken at a room-temperature furnace pressure of about 12 μ Hg, where gas scattering of the beam is believed to be unimportant. The pressure in the second set was about 5 times this and beam scattering probably occurred. The remarkable point is that, in spite of gas scattering of the beam, the hydrogen signals, when normalized to argon signals for comparable hydrogen and argon furnace pressures, still gave values for Q_1/Q_2 which were consistent within the run and agreed with the values obtained from other runs.

TABLE II. Second set of sample data.

T(°K)	S_2	S_1	C(exp)	C(calc)	S_0	D(%)	Q_1/Q_2
(1200)	...	...	...	864	...	...	...
1235	24.7	0	864	868	...	0	...
1445	23.4	0	890	890	...	0	...
1620	22.2	0	894	910	(22.6)	0	...
1815	21.5	0.9	...	931	21.8	1	2.1
2270	10.8	8.5	...	981	20.6	48	0.63
2580	2.4	15.3	...	1020	20.1	88	0.60
2820	0.7	16.6	...	1040	19.7	93	0.62

The data for all electron energies were handled as shown in the two preceding examples. The imposed requirements for acceptance of the results were that Q_1/Q_2 should (1) have the same values within any run, irrespective of temperature or degree of dissociation, and (2) have the same values between runs with different pressures and other operating conditions.

The final results of this experiment are summarized in Figs. 4 and 5. The solid line is the relative cross section normalized at 500 ev to the average value obtained from measurements of Q_1/Q_2. The probable error, based only on the statistical spread of the results and indicating the reproducibility of the results, is shown at the 500-ev point in Fig. 5. The other points on the curve are mean values of the absolute cross section as determined in this experiment.

While data were taken for the absolute cross section at energies lower than 40 ev, we feel that the relative cross-section curve is probably more accurate. Since below 40 ev the molecular curve is steep and actually crosses the atomic curve, the atomic cross-section values are more strongly dependent on exact knowledge

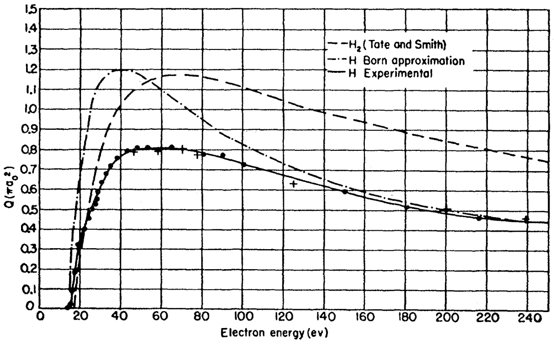

FIG. 4. Ionization cross-section curve for atomic and molecular hydrogen. Points are taken from relative cross sections normalized at 500. Crosses are absolute determinations.

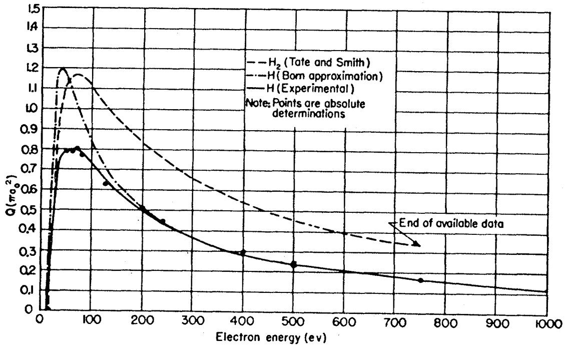

FIG. 5. Ionization cross-section curve for atomic and molecular hydrogen.

of the electron energy than are the relative-cross-section data, where differences of energy are measured quite easily and where the exact energy can be found by requiring that the threshold energy be at the known ionization potential of atomic hydrogen (13.6 ev).

Absolute cross sections were not determinable in this experiment above 750 ev, which is the highest energy used in the measurement of the molecular cross section by Tate and Smith. Thus, the portion of the curve above 750 ev is also obtained purely by relative-cross-section measurements.

Figures 4 and 5 show graphically the results of Tate and Smith for the molecular cross section, the calculated cross section using the exact Born approximation,[4] and the atomic cross section as determined in the present experiment.

Regarding uncertainties and errors in the results, the signal-to-noise ratio on the mass-spectrometer peaks normally ranged from 50 to 100, and electron current was known to be constant during any run to within 2% or less. The reproducibility of results within the experiment was generally about as indicated in Tables I and II, i.e., ±3%. The largest unknown in the experiment are, of course, the values of S_0, since they were obtained by an extrapolation the errors of which are impossible to ascertain. Also, in obtaining the absolute atomic cross section by multiplying the ratio obtained in these experiments by the molecular cross-section values of Tate and Smith, further uncertainty is introduced because probable errors in the molecular cross-section values are unspecified.

A further uncertainty arises through the assumptions that (1) transfer of momentum from the incident electron to the remaining ion, giving it a sideways velocity component, may be neglected, and (2) argon may be used to determine the collection efficiency of the mass spectrometer. The indirect evidence supporting these assumptions is as follows:

1. The agreement of the relative cross-section curves of H_2 with those of Tate and Smith indicates that if any sideways momentum transfer sufficiently strong to alter the mass-spectrometer collection efficiency occurs, it is not dependent on electron energy in the case of H_2.

2. If appreciable sideways momentum transfer occurs in ionizing the hydrogen molecule, $C(T)$ for hydrogen below dissociation temperatures should increase with temperature more rapidly than $C(T)$ for the heavy argon atom. Such a difference was not evident, suggesting that the H_2^+ ion does not pick up a sideways velocity component of an amount detectable with our equipment.

3. If appreciably more momentum were transferred to an atomic ion than to a molecular ion, Q_1/Q_2 would be expected to increase with temperature, and such a systematic increase was not discernible.

Of course, these observations pertain only to the mass spectrometers used in the present experiment, and it is not believed that they are particularly significant to the interesting question of momentum transfer in general.

The agreement with the Born approximation at energies where this approximation is expected to be valid suggests that this measurement is more accurate than we can legitimately claim solely on the basis of the experimental approach.

IV. DISCUSSION OF RESULTS

The results shown in Figs. 4 and 5 are self-evident. The first Born approximation agrees quite well with the experimental values above about 15 times the ionization potential and is higher than the experimental values at lower energies, as is predicted on the basis of the known limitations of the Born approximation. Unfortunately, at the present time there are no other theoretical predictions for the total cross section for ionization against which to compare the experimental results, except in the immediate vicinity of threshold.[5,6]

Also, as threshold is approached the cross section becomes so small that the single-modulation techniques employed here make the results insufficiently accurate for a comparison with theory to be meaningful. However, certain envisioned experimental modifications may make possible the study of the threshold in a future experiment.†

V. ACKNOWLEDGMENTS

The authors are deeply indebted to Dr. R. L. F. Boyd and Mr. G. W. Green of University College London. Not only was the first attempt at this measurement

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[5] G. H. Wannier, Phys. Rev. **90**, 817 (1953).

[6] S. Geltman, Phys. Rev. **102**, 171 (1956).

† *Note added in proof.*—Since submission of this paper, threshold measurements have been carried out with the result that the cross section increases linearly with excess electron energy for the first four ev above threshold. This linearity is as predicted by Geltman,[6] although the observed rate of increase (0.078±0.006 πa_0^2/ev) is greater than predicted (0.044 πa_0^2/ev). Presumably the discrepancy arises from Geltman's consideration of only S-wave contributions and it is expected that when the higher partial cross sections are calculated, the discrepancy between theory and experiment will diminish.

made by them in collaboration with one of the authors (W.L.F.), but they have continually provided us with results of their subsequent experiments. Their generosity has substantially advanced the progress of the measurements described here.

The first attempts at this experiment were made while one of the authors (W.L.F.), was a National Science Foundation Post-doctoral Fellow at University College London, in 1955.

The encouragement and helpful advice of Professor H. S. W. Massey and Dr. E. C. Creutz and Dr. Frederic de Hoffmann are deeply appreciated.

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Collisions of Electrons with Hydrogen Atoms. II. Excitation of Lyman-Alpha Radiation

WADE L. FITE AND R. T. BRACKMANN
John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California

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The cross section for excitation of Lyman-alpha radiation in electron-hydrogen atom collisions has been measured as a function of electron energy. The measurement is made by observing Lyman-alpha photons with an iodine-vapor-filled photon counter. A relative-cross-section curve is normalized to fit the Born approximation for high electron energies. The experiment utilizes a 100-cps-modulated atomic beam whose purity in hydrogen-atom content is determined by ionization and mass analysis. A dc electron beam crosses the modulated ground-state atomic beam. The photon counter, which looks at the interaction region, has its output passed through a tuned amplifier and phase-sensitive detection system. Although this treatment of the counter output as an ac current (in which the quantum of charge is that of a Geiger-Müller pulse) introduces some unique noise problems, it satisfactorily separates the photons which arise from the interaction under study from those which arise from other processes (e.g., electron collisions with the residual gas in the high-vacuum chamber).

Some implications of the measured excitation cross section upon scattering theory are discussed.

I. INTRODUCTION

IN the first paper of this series, the measurement of the total cross section for ionization of the hydrogen atom on electron impact was described.[1] The present paper discusses the excitation of the hydrogen atom to certain discrete states upon electron impact. The states of interest are those which lead to the emission of Lyman-alpha radiation, which occurs at 1216 A and corresponds to a transition from the $n=2$ to the $n=1$ state. Because of the differences in experimental procedures, this second experiment in General Atomic's program of research on the free hydrogen atom is presented in a separate paper, although objectives of the experiment are essentially the same as those of the ionization-cross-section measurements, namely, to ascertain the validity of scattering approximations and to measure atomic cross sections of interest in controlled thermonuclear research.

In the present measurements a relative-cross-section curve was taken directly. Absolute values were obtained by normalizing the relative measurements to Born approximation values at high energies.

II. EXPERIMENTAL APPROACH

The experimental arrangement was as shown in Fig. 1. The atomic beam flowed from a tungsten furnace in the first of three differentially pumped vacuum chambers. It was modulated at 100 cps by a mechanical chopper wheel located in the second vacuum chamber. The modulated atomic beam then entered the third vacuum chamber, in which the experiment was carried out.[2]

In the third vacuum chamber, a single electron gun, constructed of cathode-ray-tube gun components, provided electrons for both ionization monitoring of

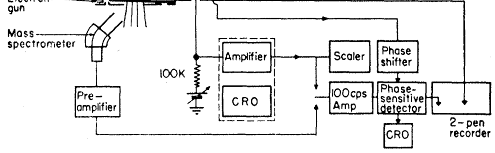

FIG. 1. Schematic diagram of experiment.

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[1] W. L. Fite and R. T. Brackmann, preceding paper [Phys. Rev. 112, 1141 (1958)].

[2] For further details of the beam apparatus and general experimental procedures, see reference 1 and W. L. Fite, General Atomic Report GA-267, December 20, 1957 (unpublished).