ing of the H(2s) atom on the basis of these results. Electron capture into autoionizing states is a likely explanation for the small H^- measurements. Electron capture into autoionizing states could not be detected in either our apparatus or the apparatus of Gilbody *et al.* The results of Donnally *et al.*[10] support the concept of electron capture into autoionizing states. If electron capture is as important as we suggest, then approximately 90% of the capture events result in autoionizing states of H^-.

The discrepancy between the experimental quenching cross sections of Krotkov *et al.*[11] and their calculation can at least be partially explained by the exclusion of the electron-capture process in the calculation. The discrepancy between their experimental quenching measurements and the quenching measurements of Gilbody *et al.*[3] precludes further quantitative comparison at this time.

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Angular Distribution of Metastable Hydrogen Formed by Dissociation of H_2^+

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A study has been made of H_2^+ dissociation by impact on targets of He, Ar, H_2, and N_2. Cross sections were measured for the angular distributions of metastable hydrogen, protons, and neutral hydrogen atoms resulting from dissociation. Projectile energies are in the range 4–12 keV; the angular range of the measurements extended from 0.5° to 5.0°. The angular distributions of metastables are consistent with their formation through excitation of the H_2^+ projectile into the $2s\sigma_g$ and $3p\sigma_u$ repulsive states of H_2^+. In all cases the dissociation cross section appears to be strongly peaked towards small angles between the internuclear axis of the molecule and the direction of the H_2^+ projectile; in the case of H(2s) formed by dissociation on He, the cross section appears to vary as approximately the square of the cosine of that angle. Angular distributions vary quite markedly from one target to another.

I. INTRODUCTION

A study has been made of the angular distribution of metastable hydrogen produced by the collisional dissociation of H_2^+. The reactions can be described by the following equation:

$$H_2^+ + X \rightarrow H(2s) + [H^+ + X] \quad . \tag{1}$$

The experiments provide no information on the states of excitation, ionization or molecular association of those postcollision products contained within the square brackets of Eq. (1). Measurements were made of the cross sections for the production of metastables as a function of scattering angle (0.5° to 5°); targets used in this work included He, Ar, H_2, and N_2. Projectile energies were from 4 to 12 keV.

Also studied was the distribution of scattered ions and of scattered neutral particles. The ion flux might include both elastically scattered projectiles and charged dissociation fragments. Similarly, the scattered neutral flux might include H and H_2 produced by the collision. No attempt was made to mass analyze these fluxes or to measure the relative importance of the various constituents. Consequently, these data do not repre-

sent cross sections for precisely defined processes. In some cases there is a possibility of using results from other experiments to clarify the situation and to identify the ion of neutral flux as being only of a single species.

II. EXPERIMENTAL METHOD

A previous publication[1] has fully described the apparatus and experimental methods. We will not repeat that material but only summarize the most important features.

The projectile ions were extracted from an rf discharge source and accelerated to the desired energy; the beam was then mass analyzed, finely collimated, and directed through the target gas. A pair of rectangular slits was used to select particles emerging from the collision region at some definite angle θ to the projectile beam direction. Behind these slits were located two detector systems; one monitors the metastable flux while the other monitors the flux of all neutral particles and the flux of all charged particles. The detectors and the slits were mounted on an arm that rotates about the center of the target cell; by rotating this arm one may monitor the scattered fluxes at various scattering angles θ.

The metastable detector is of conventional design[1,2] using an electric field to quench the metastable hydrogen and an open-ended multiplier to monitor the resulting Lyman-α photons. The variation of the Lyman-α intensity with projectile energy and with scattering angle gives directly the relative variation of cross section with these parameters. Absolute magnitude of the cross sections were not measured directly but were assigned by normalization to a previous measurement of a total charge-transfer cross section. For this purpose the detector was arranged to accept all scattered projectiles irrespective of scattering angle; in this way a total cross section for formation of metastables could be measured directly. Neutralization of protons to form metastables in an argon target $[H^+ + Ar \rightarrow H(2s) + Ar^+]$ was chosen as the reaction for normalization purposes. It was assumed[1] that the value of this cross section at 20-keV impact energy was 3.0×10^{-16} cm^2; This is the value given by Andreev *et al.*[3]

The detector of scattered ions and neutrals is fully described in a previous publication.[4] It has the general form of a Faraday cup: The construction permits the direct measurement of secondary electrons ejected from the cup base. Ion flux was measured directly as a current; neutral flux was measured by the emission of secondary electrons from the cup base. There remains the problem of determining the secondary electron emission coefficient for neutral-particle impact. In our previous publication[4] we have described how the secondary emission coefficient was determined for H^0 impact. For the present work on H_2^+ dissociation we assumed that the scattered neutrals were all H^0 and that the dissociated fragments had half the energy of the incident projectiles; thus for 10-keV H_2^+ impact, the neutral flux was measured using a secondary emission coefficient appropriate to 5 keV, H^0. These assumptions will be justified later in Sec VI.

It is well known that vibrational excitation of an H_2^+ may influence the dissociation process. Undoubtedly the H_2^+ ions used in this experiment did include a proportion in excited vibrational states. Tests were made to determine whether the operating conditions of the ion source influences the measured cross sections; no such dependences were found. This test may indicate only that the excited-state content of the ion beam is not a sensitive function of the ion source operating conditions. It should be noted that all previous experiments with which comparisons are made were also carried out with ion sources that produce unknown proportions of vibrationally excited molecular ions.

III. ACCURACY OF DATA

The limitations of accuracy are established through the same arguments that we have used previously.[2] The absolute values of cross sections for forming ions and for forming neutrals should not be in error by more than $\pm 8\%$; random errors for these data are, respectively, ± 6 and $\pm 8\%$. Maximum random errors in $H(2s)$ cross sections were $\pm 10\%$; relative value of cross sections at different energies should be accurate to within 10%.[4] We do not estimate accuracy limitations for the absolute values of the $H(2s)$ cross sections since these values were established by normalization. However, we note that the authors of the work to which we normalize[3] estimate their data to be accurate to within $\pm 20\%$; their data may be too low by as much as 15% due to the neglect of polarization in the field quenching detection technique.[1]

Error in the measurement of scattering angle did not exceed $\pm 0.034^\circ$ at any point. The energy of the primary projectiles was determined to within $\pm 3\%$.

We emphasize that the cross section measured in any differential scattering experiment is an average value over the range of scattering angles accepted by the detector. Thus there may be a systematic difference between the measured cross section and the true microscopic cross section. We do not attempt to unfold the true cross section from the measured data nor to estimate the resulting error. It is suggested that the most satisfactory method of comparing a theoretical prediction of cross section with this present data is to fold the theoretical values into the apparatus geom-

etry (given in Ref. 4) and thereby arrive at a predicted value of the experimentally measured quantity. This problem of resolution is, of course, inherent in any differential-scattering experiment.

IV. DATA

The case of H_2^+ impact on He was treated quite extensively; data were obtained at a number of energies between 4 and 12 keV. Figs. 1–3 show, respectively, the cross sections for forming ions, neutrals, and metastables. For H(2*s*) formation the cross sections remain fairly constant from 0.5° to about 1° or 2°; beyond that point the cross sections fall off rapidly with energy. For ions and neutrals the cross sections fall off quite rapidly with increasing angle; there is little evidence of the shoulder observed in data for H(2*s*) formation. Figure 4 repeats the data for H(2*s*) formation at an H_2^+ energy of 10 keV and compares it with the work of Jaecks *et al.*[5]; also shown are the cross sections for formation of all particles. Much of the data of Jaecks *et al.*[5] agree with the present work, within the accuracy limitations of both experiments. There is, however, a serious discrepancy at low angles where that last point of the work by Jaecks *et al.* is four times larger than the data of the present work. There is no obvious explanation for this serious discrepancy.

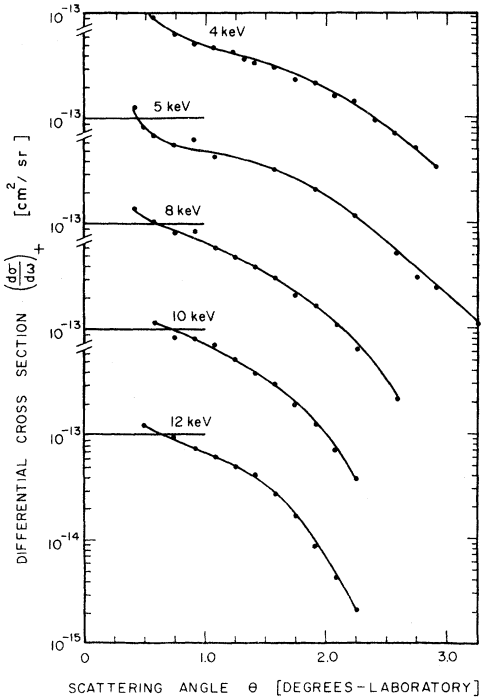

FIG. 1. Differential cross sections for the formation of ions induced by impact of H_2^+ on a target of He. Note the broken cross-section scale; the intersection of each horizontal line with a curve indicates a differential cross section of 10^{-13} cm²/sr.

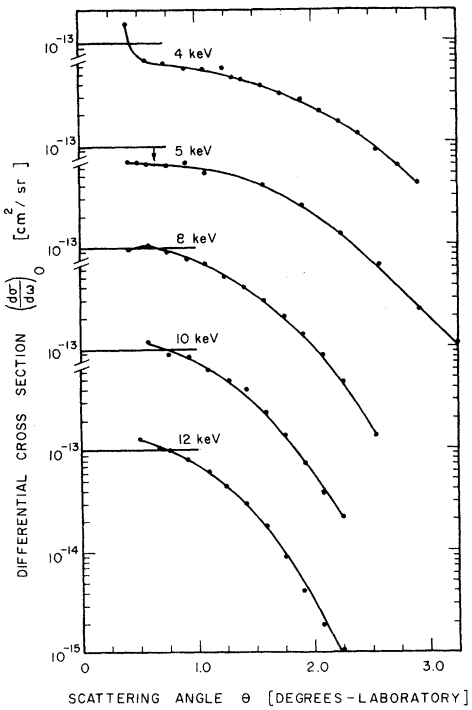

FIG. 2. Differential cross sections for the formation of neutral particles induced by impact of H_2^+ on a target of He. Note the broken cross-section scale; the intersection of each horizontal line with a curve indicates a differential cross section of 10^{-13} cm²/sr.

Figure 5 shows the data using an H_2 target at a single impact energy of 10 keV. In this case we know from the work of McClure[6] that the scattered ions and neutrals are entirely H^+ and H, respectively; there is no appreciable contribution from H_2^+ and H_2. Also included on Fig. 5 are some experimental results of McClure[6]; they are in good agreement with the present work.

In Fig. 6 are the data for the case of a nitrogen target at an impact energy of 10 keV. Figure 7 shows the same data for an argon target. In neither case is there previous data with which a comparison may be made.

V. H(2*s*) FORMATION—DISCUSSION

Dissociation of H_2^+ occurs through the formation of a repulsive state of a molecule. Energy is released as the two atoms separate and both atoms will acquire a velocity. In general the velocity of the separated atoms will have a component that is perpendicular to the original direction of the H_2^+ molecule; this velocity component will cause the fragments of dissociation, seen in the laboratory reference frame, to emerge from the collision event at some angle to the original direction of H_2^+ motion. Thus, even when there is no

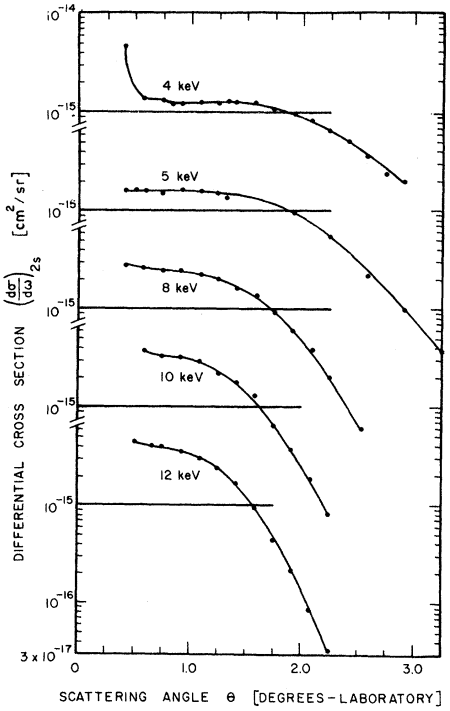

FIG. 3. Differential cross sections for the formation of metastable hydrogen atoms induced by impact of H_2^+ on a target of He. Note the broken cross-section scale; the intersection of each horizontal line with a curve indicates a differential cross section of 10^{-15} cm^2/sr.

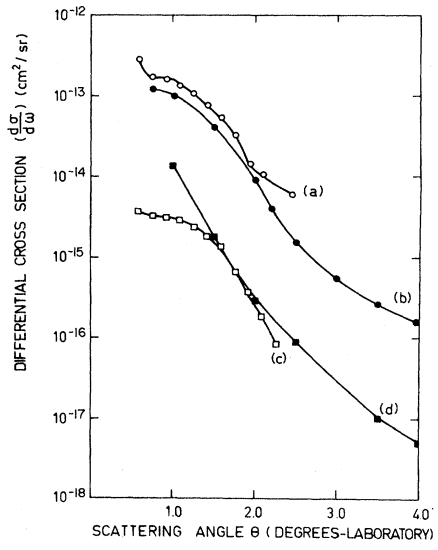

FIG. 4. Comparisons between the previous work of Jaecks *et al.* (Ref. 5) and the present results for dissociation of 10-keV H_2^+ on He. (a) Present work, sum of the cross sections for production of ions and neutrals. (b) Jaecks *et al.*, sum of cross sections for production of ions and neutrals. (c) Present work, cross section for production of metastables. (d) Jaecks *et al.*, cross section for production of metastables.

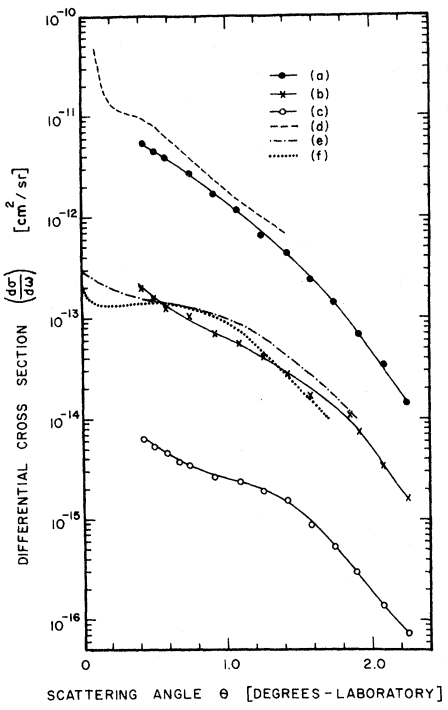

FIG. 5. Differential cross sections for the dissociation of 10-keV H_2^+ by impact on a target of H_2. (a) Present results for the production of neutral particles (multiplied by 10 for clarity), (b) present results for the production of ions, (c) present results for the production of H(2*s*), (d) McClure's (Ref. 6) experimental measurement of H formation (multiplied by 10 for clarity), (e) McClure's (Ref. 6) experimental measurement of H formation, (f) McClure's (Ref. 6) theoretical calculation of H formation.

scattering of the H_2^+ center of mass, one would still expect to observe an angular distribution of the fragments.

We may come to some understanding of these data by following a previous discussion of dissociation by McClure.[6] Let us suppose that the dissociation event takes place through a direct Frank–Condon transition to the repulsive state; it will be assumed that the internuclear axis does not rotate and that the center of mass of the H_2^+ ion is undeflected. Consider the situation in the center of mass frame of the H_2^+ molecule. In dissociation, the H_2^+ molecule releases an amount of energy Q giving a velocity $u=(Q/m)^{1/2}$ to each of the fragments; here m is the mass of the hydrogen atom. If the internuclear axis makes some angle Θ to the direction of the H_2^+ motion then that angle will be maintained as the molecule dissociates. The component of velocity perpendicular to the original direction of H_2^+ motion will be $u\sin\Theta$. Now the original velocity of the H_2^+ molecule v is very much greater than the velocity u. Thus the angle θ made by the trajectory of the fragment in the laboratory

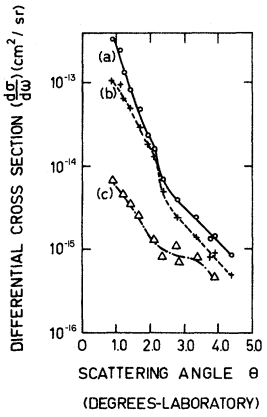

FIG. 6. Differential cross sections for the dissociation of 10-keV H_2^+ by impact on a target of N_2. (a) Production of neutrals, (b) production of ions, (c) production of metastable hydrogen.

frame, with respect to the original direction of the H_2^+ molecular ion, is given to a very good approximation by

$$\theta = u\ (\sin\Theta)/v \quad . \tag{2}$$

If E is the energy of the H_2^+ projectile (in electron volts) and Q is the energy released in dissociation (also in electron volts) one may rewrite Eq. (2) as

$$\theta = (Q/E)^{1/2} \sin\Theta . \tag{3}$$

One may also readily transform the differential cross section.[6] If $(d\sigma/d\omega)_{lab}$ is the cross section measured in the laboratory frame, then

$$\left(\frac{d\sigma}{d\omega}\right)_{lab} = \left(\frac{d\sigma}{d\omega}\right)_{c.m.} \frac{E}{Q} \frac{1}{\cos\theta} \quad . \tag{4}$$

A. Helium Target

One may readily transfer the cross sections measured as a function of angle into cross sections as a function of transverse velocity component; this is done by multiplying the angular scale by the original projectile velocity v. When doing this for

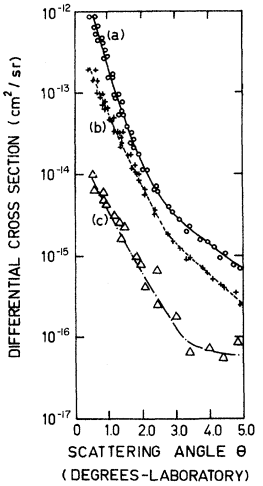

FIG. 7. Differential cross sections for the dissociation of 10-keV H_2^+ by impact on a target of Ar. (a) Production of neutrals, (b) production of ions, (c) production of metastable hydrogen.

$H(2s)$ formation induced by H_2^+ impact on He (Fig. 3), one finds that the distribution is essentially the same for all energies. These various distributions have been normalized together and the mean of the various distributions is shown in Fig. 8. Systematic divergences of distributions from this average curve are observed; the divergences are generally small and do not exceed 10%. The single exception to this is the smallest angle point at an energy of 4 keV; this point lies higher than all the other data (see Fig. 3) and may mark the onset of a different behavior at the very small transverse velocity component which lies outside the range of the present experiment. The similarity of the curves suggest very strongly that the mechanism leading to dissociation is invariant with energy within the range of this experiment.

One possible dissociation mechanism is a charge-transfer process leading to the formation of an excited H_2 molecule that in turn subsequently dissociates:

$$H_2^+ + X \rightarrow H_2^* + X^+ , \quad H_2^* \rightarrow H(2s) + H \quad . \tag{5}$$

Now, according to Sharp's[7] potential-energy curves, all the H_2^* states that terminate with formation of $H(2s)$ are, in fact, attractive. Thus, within the bounds of our initial assumptions, the process described by Eq. (2) cannot occur. The second possible mechanism is the direct excitation of H_2^+ to a repulsive state which then decays:

$$H_2^+ + X \rightarrow H_2^{+*} + X, \quad H_2^{+*} \rightarrow H(2s) + H^+ \quad . \tag{6}$$

According to Sharp[7] the repulsive $2s\ \sigma_g$ and $3p\ \sigma_u$ states of H_2^+ both terminate with the formation of

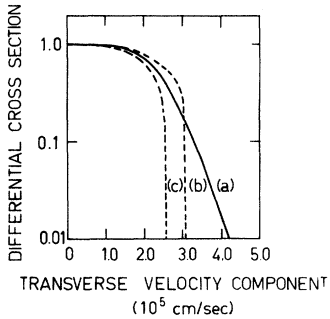

FIG. 8. Relative distribution of metastables as a function of transverse velocity component for H_2^+ impact on He. Curve (a) is a normalized distribution which fits all the data of Fig. 3. Curves (b) and (c) are predicted curves for a dissociation process whose cross section varies as $\cos^2\Theta$ (Θ is the angle between the H_2^+ internuclear axis and the H_2^+ direction of motion, measured in the H_2^+ frame of reference). Curve (b) is for a dissociation energy Q of 10.0 eV, appropriate to the formation of the $3\ p\sigma_u$ state of H_2^+. Curve (c) is for a dissociation energy Q of 7.2 eV, appropriate to the formation of the $2s\sigma_g$ state.

$H(2s)$. From this one concludes that $H(2s)$ formation proceeds via the excitation of the $2s\ \sigma_g$ and $3p\ \sigma_u$ states of H_2^+; formation of the excited H_2 should not lead to the ejection of H atoms in the $2s$ state.

On may determine the energy released in dissociation from the potential curves of Sharp.[7] Assuming a Frank–Condon transition at the equilibrium ground state internuclear separation of H_2^+ (1.05 Å) the energies for formation of the $2s\ \sigma_g$ and $3p\ \sigma_u$ states are, respectively, 7.2 and 10.0 eV.

From Eq. (2) it is clear that the transverse velocity component should not exceed a value of u; this occurs when θ is $\frac{1}{2}\pi$ and the internuclear axis is perpendicular to the direction of motion. The values of u expected for the dissociation of the H_2^+ via the $2s\ \sigma_g$ and $3p\ \sigma_u$ states are, respectively, 25.8×10^5 and 30.3×10^5 cm/sec. Most of the distribution lies within these maximum bounds; the small part of the distribution that lies outside the limits must indicate an error in the simplifying assumptions that have been made.

One may proceed further on these lines and attempt to deduce the angular distribution of fragments in the H_2^+ frame of reference. Three simple distribution for $(d\sigma/d\omega)_{\text{c.m.}}$ in Eq. (4), have been tried; an isotropic distribution, a $\sin^2\Theta$ distribution and a $\cos^2\Theta$ distribution. Both the isotropic and $\sin^2\Theta$ distributions must inevitably give a laboratory cross section that rises with increasing scattering angle; this is contrary to the experimental observations. The $\cos^2\theta$ distribution will give a falling cross section and is, therefore, in qualitative accord with the data. In Fig. 8, we show a predicted distribution of velocity components using the $\cos^2\Theta$ form of cross sections; the calculation if carried out separately for the $2s\ \sigma_g$ and $3p\ \sigma_u$ states. This very simple prediction is in good agreement with experiment at small scattering angles. At large angles the predictions and experiment disagree; however, we have already noted above that the large-angle data lying outside the predicted values of u is not expected on the basis of this simplified approach; thus, the discrepancy does not necessarily reflect an error in the assumed distribution.

From the above discussion one may conclude that formation of $H(2s)$ induced by H_2^+ impact on He proceeds via the formation of the $2s\ \sigma_g$ and $3p\ \sigma_u$ states of H_2^+; moreover, the cross section in the center-of-mass frame is strongly peaked towards small angles Θ and is approximately given by $\cos^2\Theta$. There is some theoretical justification for the assumption of a $\cos^2\theta$ distribution. Green and Peek[8] show that this will be the approximate distribution for excitation of the $2s\ \sigma_g$ state when the momentum transfer during the collision is generally parallel to the direction of H_2^+ motion.

Discrepancies between the predicted distribution of velocity components and the results of the above discussions are probably due to the considerable simplifying assumptions that have been made. One must clearly include a range of internuclear distributions and possibly a number of excited vibrational states of the H_2^+ molecule; this will obviously cause a distribution of energies Q and a consequential slight broadening of the predicted distribution.

B. H_2 Target

One may attempt to treat the data for an H_2 target in the same manner as the data for a helium target. When the distribution of transverse velocity components is determined, then there is some similarity to helium. Transferring the data of Fig. 5 to the same sort of graph as Fig. 8, one finds complete agreement between the He and H_2 target data at transverse velocities above 15×10^5 cm/sec; however, the distribution for an H_2 target rises rapidly towards lower velocities while the data for helium remains about constant. Thus, there is a significant difference between the dissociation in helium and in hydrogen.

C. N_2 and Ar Targets

The distributions for these cases are different from those of the He and H_2 targets discussed above. The distributions all fall off more rapidly and show little evidence of the shoulder exhibited for helium and hydrogen. The angular distribution is peaked more strongly towards small angles in the center-of-mass system than for the cases of helium and hydrogen. Within the angular range of 0.5° to 2.5° there is considerable similarity of the relative variations for Ar and N_2 targets. Differences between these two cases occur only at large angles.

The marked differences between the angular distributions for these four targets suggest that the dissociation mechanism is a strong function of the target.

VI. SCATTERED IONS AND NEUTRALS—DISCUSSION

In the measurements of ion and neutral fluxes the data may have included contributions from

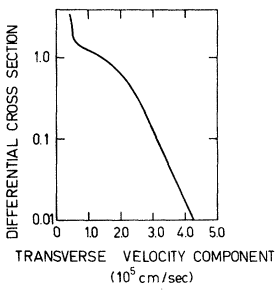

FIG. 9. Relative distribution of neutral atoms as a function of transverse velocity components for H_2^+ impact on He. This curve fits all the data of Fig. 2.

scattered H_2^+ and H_2. McClure[6] has shown that for an H_2 target the contribution from scattered molecules may be neglected at angles greater than 0.1°. Similarly, Fedorenko *et al.*[9] have shown that scattered molecules may also be neglected in the case of an argon target. It follows that in these two cases the measured ion and neutral fluxes are unambiguously H^+ and H, respectively. In our analysis of the data we have assumed that this result will also hold for the cases of helium and nitrogen targets.

A calculation of the angular distributions of H^+ induced by H_2^+ impact on H_2 has been made by McClure.[6] He assumes that dissociation occurs only through the formation of the $2p\,\sigma_u$ repulsive states of H_2^+. The results of that calculation have been shown in Fig. 5 and are in reasonable agreement with experiment.

We may attempt the same sort of analyses as were used above in the discussion of H(2*s*) formation; we will consider first the case of a helium target for which the data is most extensive. We can transfer the cross-section measurements into a distribution of transverse velocities simply by multiplying the laboratory scattering angle by the H_2^+ projectile velocity. The form of the distributions for neutral production is independent of projectile energy. Figure 9 shows a relative distribution of the neutral particles transverse velocity; with proper normalization factors this fits all the neutral-particle distributions that have been measured. In contrast the transverse velocity distribution of ions becomes broader as the projectile energy increases. Figure 10 shows relative values of the transverse velocity distributions for

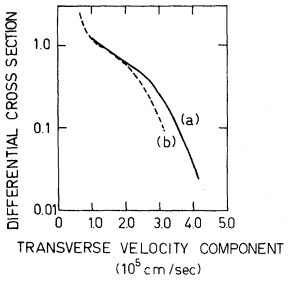

FIG. 10. Relative distribution of H^+ ions as a function of transverse velocity component. Curve (a) is for 12-keV H_2^+ impact on He; curve (b) is for 4-keV H_2^+ impact on He. The two curves are normalized together.

ions; the situation for projectile energies of 4 and 12 keV are shown on the figure while data for all other energies lie between these lines. These observations are similar to McClure's results for H_2^+ on H_2 where one also finds the neutral distribution to be independent of energy and the ion distribution to become broader with increasing energy.

We have not attempted to deduce an angular distribution in the H_2^+ center-of-mass frame. It is clear, however, that in each case the angular distribution must be strongly peaked in the forward direction (small angles Θ). The peaking is stronger than the $\cos^2\Theta$ distribution that was found to fit certain of the H(2*s*) production data (see Sec. V).

It is to be noted that the angular distributions are characteristic of the individual targets; we found this also to be true for H(2*s*) distributions.

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