

approximation. It would appear that theory and experiment are quite consistent for the 3s and 3d levels. For the 3p state, however, the theory consistently lies above the experiment by a factor of 2 or more; moreover, there is a significant difference between the energy dependence of theory and experiment.

X. CHARGE TRANSFER IN ARGON

In Fig. 3 are shown the cross sections for argon. Again a comparison may be made with work by Hughes *et al.*⁶; the 3s and 3d cross sections are consistent but again the 3p cross section of the present work lies above that measured by Hughes *et al.*

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For argon it is noted that the fraction of the $n = 3$ level population formed in the 3p state is somewhat higher than in the case of helium.

XI. CONCLUSION

Charge transfer into the 3s and 3d states on a helium target is in good agreement with the theoretical predictions by a Born approximation. The theoretical predictions for the 3p state, however, do exceed the measured values by a significant amount. It appears that the Born approximation is a satisfactory procedure for the calculation of these cross sections in the energy range of the present experiments.

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Formation of Fast Excited H Atoms. II. Charge-Transfer Neutralization of H⁺ on Molecular Gases*

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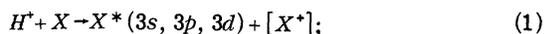
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An experimental study is made of the cross sections for forming fast hydrogen atoms in the 3s, 3p, and 3d states by charge-transfer neutralizations of H⁺ as it traverses molecular targets. The formation of excited hydrogen is detected by a quantitative measurement of collisionally induced Balmer- α emission; the contributions from the 3s, 3p, and 3d levels are separated by a method that utilizes the different lifetime of the excited states. Proton-impact energies range from 75 to 700 keV; targets include H₂, N₂, NO, O₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, and C₃H₈. Cross sections decrease rapidly with impact energy; the 3s cross section was always largest followed by the 3p and 3d. There was no convincing evidence for a general additive rule whereby cross sections could be assigned to the individual constituent atoms of the molecule and then used to predict cross sections for complex molecules.

I. INTRODUCTION

A study has been made of the cross sections for formation of fast excited hydrogen atoms in the 3s, 3p, and 3d states as a result of charge-transfer neutralization when protons traverse a molecular gas. The reaction equation may be written



here the square brackets indicate that the experi-

ments give no information on the state of excitation, ionization, or molecular association in which the post-collision target state is formed.

For the case of H₂ and N₂ targets a full study was made of the three cross sections over a wide range of energies. For targets of NO, O₂, CO, CO₂, C₂H₂, C₂H₄, C₂H₆, and C₃H₈ the data were restricted to measurements of the 3s state at three different impact energies only.

The techniques used in these measurements are

essentially the same as those in a preceding paper on charge transfer in atomic targets.¹ The preceding paper will hereafter be denoted as I.

II. EXPERIMENTAL METHOD

The method is identical to that published in I and will not be repeated here; the reader is referred to the earlier paper for full details.

Most target gases were obtained commercially and had a nominal impurity level of 1% or less. In the case of NO the commercially available gas was redistilled under vacuum to remove NO₂. Target pressures were all measured with a capacitance manometer; a device which is completely insensitive to the nature of the gas. All experiments were done under single-collision conditions; generally a target pressure of 5×10^{-4} Torr or less was used.

Particular care is necessary to eliminate the background signal caused by excitation of gas that has flowed out of the target cell and into the flight tube. This is most important when using H₂ and hydrocarbons because they will emit the Balmer- α line. The techniques for handling such backgrounds are discussed in I.

The accuracy of this data is assessed by the same arguments as were used in I. The possible systematic error in any cross-section measurement should not exceed $\pm 16.5\%$. Systematic errors in the energy dependence of cross sections should not exceed 3%. Random errors in the 3s-state measurement should not exceed $\pm 15\%$ for H₂ and $\pm 5\%$ for any of the other targets. The error limits in the case of nitrogen for the 3p level are -24 to $+19\%$ and for the 3d level -26 to $+21\%$; these figures include an estimate for the maximum error incurred due to neglect of polarization. For hydrogen the corresponding limits are much greater; this is due to the lower cross sections and the necessity for a large correction due to gas flowing from the cell into the observation region. For hydrogen the limits of accuracy are -34% to $+29\%$ for the 3p level and $\pm 100\%$ for the 3d.

III. RESULTS FOR H₂ AND N₂

In Figs. 1 and 2 are shown data for targets of H₂ and N₂. In both cases a comparison may be made with previous work by Hughes *et al.*²; these earlier data are at lower energies and involved a similar experimental technique to that of the present work. For both nitrogen and hydrogen there is excellent agreement between the two sets of data for the 3s state; this state exhibits the highest cross section and is therefore easiest to measure. There is also good agreement for the 3p and 3d states in nitrogen. In the case of hydrogen there is poor agreement between data for the 3p and 3d states; there is no obvious explanation for this discrepancy.

Edwards and Thomas³ have previously measured

the cross section for formation of H(3s) and H(3d) in a target of N₂; the absolute magnitudes of cross sections were assigned by normalization to previous cross-section data. The present technique is slightly different from that used by Edwards and Thomas; in particular it is not necessary to consider the effects of collisional destruction³ since the present work was carried out under single-collision conditions. The work discussed here supersedes that of Edwards and Thomas³ because it is more accurate and, moreover, is inherently absolute. It is noted that both sets of data are in fact in agreement within the quoted estimates of accuracy.

For both the H₂ and N₂ targets the formation of H(3s) predominates over formation of H(3p) and H(3d); in all cases the cross sections drop precipitously with increasing energy. At the highest energies in this work the cross section for formation of H(3s) with an H₂ target falls off with projectile energy E as $E^{-4.45}$, while with an N₂ target the cross section falls off as $E^{-4.05}$. It is not claimed that these represent the asymptotic high-energy dependence of the cross sections; asymptotic behavior will probably occur only at higher energies. It has been shown theoretically, that in the asymptotic region capture into the ns states should decrease as E^{-6} or more rapidly.⁴

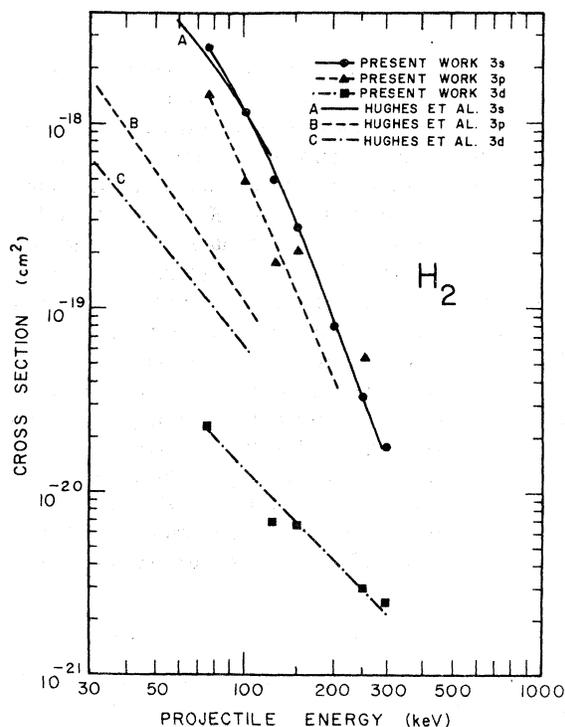


FIG. 1. Cross sections for the formation of H(3s), H(3p), and H(3d) atoms by charge transfer in hydrogen. Present measurements are shown along with those by Hughes *et al.* (Ref. 2).

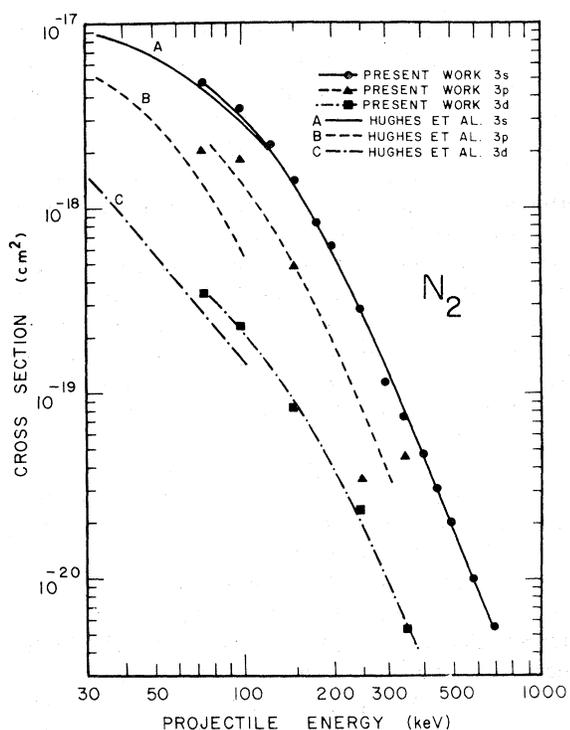


FIG. 2. Cross sections for the formation of H(3s), H(3p), and H(3d) atoms by charge transfer in nitrogen. Present measurements are shown along with those by Hughes *et al.* (Ref. 2).

It is interesting to compare the experimental cross sections for charge transfer in H₂ with the theoretical predictions of charge transfer in atomic hydrogen. It is sometimes convenient to regard an H₂ molecule as two independent H atoms; thus the theoretical predictions for H should be multiplied by 2 to arrive at an estimate for H₂. Such a comparison is shown in Fig. 3, using the Born-approximation calculations of Bates and Dalgarno.⁵ For the 3s-state formation the agreement between the experimentally and the theoretically generated curve is within experimental error. For the 3p and 3d curves the agreement is not so good; in view of the poor accuracy of the 3p- and 3d-state data the discrepancy may not be significant. It has been suggested by Tuan and Gerjuoy⁶ that this simple scaling of theory to experiment is not legitimate; in view of this, the observed agreement may be fortuitous.

IV. RESULTS FOR OTHER TARGETS

The work on H₂ and N₂ targets described above is a detailed study of cross sections for formation of three states over a range of impact energies. The work with other targets is more restricted in scope; it includes study of the 3s-state formation only at three different energies. The data for these

TABLE I. Cross sections for formation of H(3s) by H⁺ neutralization in various gases.

Target	Cross sections (10 ⁻²⁰ cm ²)		
	Energy (keV)		
	75	150	250
H ₂	254	27.3	3.32
CH ₄	624	147	17.2
C ₂ H ₄	768	...	26.1
C ₂ H ₆	874	235	27.7
C ₃ H ₈	1121	306	34.3
N ₂	452	138	27.9
O ₂	408	161	40.1
NO	456	148	34.8
CO	431	127	28.6
CO ₂	549	204	44.7

cases are displayed in Table I.

Toburen⁷ and Dague⁸ have successfully interpreted total capture for H⁺ projectiles impacting on a variety of different gases in terms of a simple additive rule. This rule assumes that at high-impact velocities the projectile sees the molecular target as an assemblage of separate atoms; thus molecular forces are assumed to be unimportant in the charge-

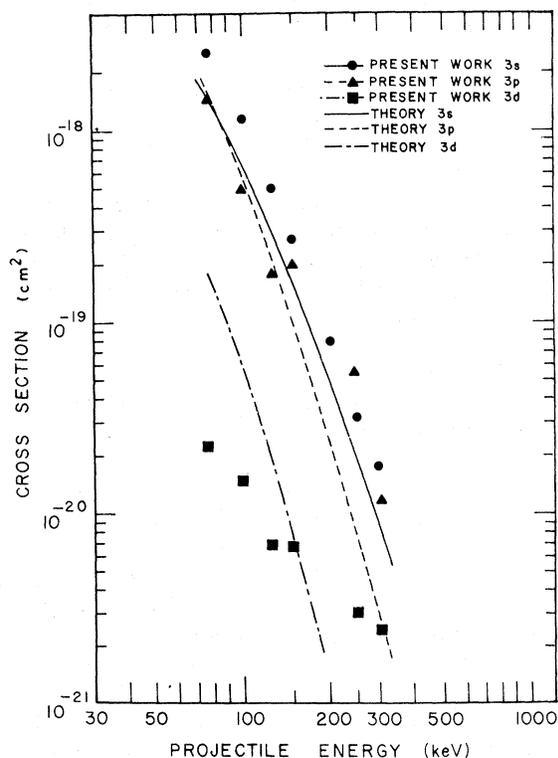


FIG. 3. Present measurements of the cross sections for formation of H(3s), H(3p), and H(3d) by charge transfer of protons in H₂ compared with theoretical predictions for charge transfer in H (Ref. 5). The theory has been multiplied by a factor of 2.

TABLE II. Derived values of atomic cross sections.

Target atom	Scheme of derivation	Cross sections (10^{-20} cm ²)		
		Energy (keV)		
		75	150	250
H	$\frac{1}{2}Q(\text{H}_2)$	127	13.7	1.7
N	$\frac{1}{2}Q(\text{N}_2)$	226	69	13.9
O	$\frac{1}{2}Q(\text{O}_2)$	204	80.5	20.0

transfer process. For this simple additive rule, the cross section for the molecular targets, $A_n B_m$, is taken to be

$$Q(A_n B_m) = nQ(A) + mQ(B). \quad (2)$$

Here $Q(A)$ and $Q(B)$ are effective cross sections for the constituent atoms A and B .

Attempts were made to use this additive rule on the data shown in Table I. In Table II are shown derived cross sections for N, O, and H obtained from N_2 , O_2 , and H_2 molecular cross sections by use of the additive rule; the scheme used for derivation is shown in each case. One may add together the derived cross sections for N and O, and compare them with the measured cross section for NO shown in Table I; the agreement is excellent. The additive rule becomes less convincing when one compares estimates of the effective cross section for carbon as derived from cross-section measurements with hydrocarbons and oxides of carbon. At 250 keV the average of the effective cross sections for carbon is 8.2×10^{-20} cm² with a spread of $\pm 30\%$. At lower energies the spread is even greater. It is also noted that within the hydrocarbons the derived cross section for carbon decreases systematically with increasing complexity of the target. The only conclusion that can be made is that around an impact energy of 250 keV the additive rule may be used to deduce effective cross sections to an

accuracy of about $\pm 30\%$. At lower energies the uncertainty becomes larger. These conclusions are quite consistent with the work of Toburen *et al.*,⁷ where the effective cross sections of carbon for total charge transfer into all states, as derived from measurements with hydrocarbons, exhibited a spread of $\pm 50\%$.

V. FRACTIONAL POPULATION OF THE EXCITED STATE

It is interesting to consider what fraction of the neutral atoms formed by charge transfer are in the excited state. We take the present data on the formation of H(3s) and divide by the total cross section for the formation of all neutrals as measured by Toburen *et al.* In fact Toburen *et al.*⁷ do not measure the cross section at exactly the same energies as were used in the present work, and it was necessary to interpolate between the existing data points; this procedure will obviously reduce the accuracy. For the hydrocarbon targets the H(3s) formation accounts for approximately 5.5% of all neutrals; for H_2 the fraction is about 5%. The fractional content in nitrogen and the oxides of carbon was about 4%. It follows therefore that the highest-excited-state component is found with hydrocarbon targets.

VI. CONCLUSIONS

The theoretical calculation of charge transfer in atomic hydrogen, scaled by a factor of 2, are consistent with the experimental measurements in molecular hydrogen. An additive rule for estimating cross sections for complex molecules does appear to give approximate predictions within an accuracy of $\pm 30\%$ for impact energies about 250 keV. However, the poor success of the additive rule does suggest that for the energies of this experiment one cannot properly consider the molecule as an assemblage of separate atoms.

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