

Study of $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ Using Merging Beams*

R. H. NEYNABER AND S. M. TRUJILLO

Space Science Laboratory, General Dynamics/Convair, San Diego, California

(Received 19 October 1967)

A merging-beams technique was used to determine cross sections for the reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ as a function of interaction energy W . Cross-section measurements at W were accompanied by measurements at 1 eV so that we obtained ratios of cross sections, Q_W/Q_1 . These ratios were determined for $0.1 \text{ eV} \leq W \leq 10 \text{ eV}$. Some information about the reaction was also obtained for $W \leq 0.03 \text{ eV}$. An absolute cross section was determined for $W = 1 \text{ eV}$. Its estimated error is considerably larger than errors associated with the cross-section ratios. Gioumousis and Stevenson (GS) predict a linear dependence of the cross section on $W^{-1/2}$. On a Q_W/Q_1 versus $W^{-1/2}$ plot, a straight line can be fitted, within experimental error, to our values for $0.1 \text{ eV} \leq W \leq 1 \text{ eV}$. This line is in fair agreement with that predicted by GS. On either side of this range, however, our ratios fall below the $W^{-1/2}$ fit. Between 5 and 7 eV our results indicate that, within experimental error, Q_W/Q_1 vanishes. On the high-energy side, such a falloff could perhaps be explained by a spectator stripping model. Our cross-section ratios are in general agreement with those obtained from a tandem mass-spectrometer experiment by Giese and Maier, and in rather poor agreement with the results of a single-stage mass-spectrometer experiment by Reuben and Friedman. Lower W 's were obtained with the merging-beams technique than with the mass-spectrometer methods.

INTRODUCTION

THE merging-beams technique was developed to study two-body collisions at low energy, i.e., in a range from a few hundredths of an eV to 10 or 20 eV. With this method measurements have been made of symmetric-resonance charge transfer in H and D by Belyaev, Brezhnev, and Erastov¹ and in Ar by Neynaber, Trujillo, and Rothe.² The technique can also be applied to the study of ion-molecule (defined for this paper as heavy-particle transfer), ion-ion, electron-ion, and neutral-neutral reactions. The study of $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ at low energy is discussed in the present paper and represents the first application of the technique to ion-molecule reactions.

EXPERIMENTAL

Except for one modification, the apparatus used for the present measurements is identical to that employed in studies of symmetric-resonance charge transfer in Ar and described previously.² A schematic of the apparatus used for the ion-molecule work is shown in Fig. 1.

The sources were of a low-pressure, oscillating-electron-bombardment type which produced beams with a spread (i.e., full width at half-maximum) of about 1.5 eV. An H_2^+ beam from source 1 was merged with a mechanically chopped H_2 beam. The energies of the particles in each beam were 3000 eV. The H_2 beam was obtained by passing H_2^+ from source 2 through a charge-transfer cell containing H_2 . An electric field between the condenser plates that follow

the cell was used to remove H_2^+ which did not undergo charge transfer. The superimposed beams were then collimated to eliminate large transverse velocities and were passed into a decelerating-accelerating system containing the interaction region. The energy difference between H_2^+ and H_2 that was necessary to obtain the desired interaction energy W was established by raising or lowering the potential of the interaction region by an appropriate amount ΔE . The product ions H_3^+ were then separated from the reactants by the demerging magnet. Other undesired particles were eliminated from the detector (a Bendix multiplier) by passing H_3^+ through a retarding grid and a hemispherical electrostatic energy analyzer tuned for passage of these ions.

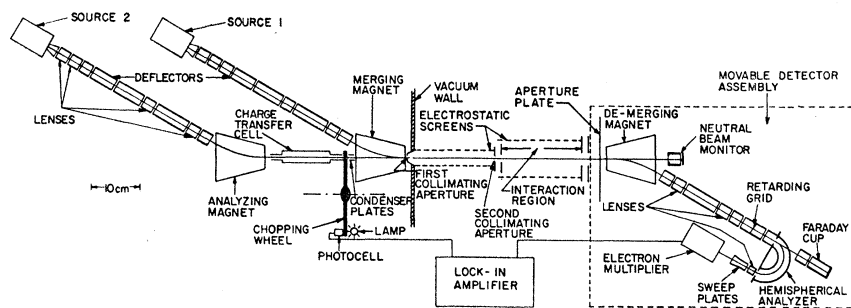
Before the addition of a set of sweep plates after the electrostatic analyzer (these plates were not used in the apparatus employed for charge-transfer studies and represent the one modification of that apparatus), the multiplier output was fairly sensitive to small changes in the fields of the demerging magnet and electrostatic analyzer. Such changes could cause small movements of the H_3^+ beam over the multiplier face, and assuming gain irregularities over the face, could result in output variations. The plates were designed to sweep the H_3^+ beam over an area on the multiplier face and so smooth output variations caused by gain irregularities. The use of these plates did solve the above problem.

A retarding potential curve for the product ions could be obtained for each W . From the plateaus of these curves relative cross sections could be derived. For positive and negative ΔE 's associated with the same W , ion currents at plateaus had the same value, within experimental error. The energy resolutions of the demerging magnet and electrostatic analyzer were such that, for a given ΔE , and therefore, W , H_3^+ of all possible energies would be passed for fixed settings of these detector components.

* Supported in part by Advanced Research Projects Agency (Project DEFENDER) through the U. S. Office of Naval Research.

¹ V. A. Belyaev, B. G. Brezhnev, and E. M. Erastov, *Zh. Eksperim. i Teor. Fiz.* **52**, 1170 (1967) [English transl.: *Soviet Phys.—JETP* **25**, 777 (1967)].

² R. H. Neynaber, S. M. Trujillo, and E. W. Rothe, *Phys. Rev.* **157**, 101 (1967).



MERGING BEAMS APPARATUS

FIG. 1. Schematic of merging-beams apparatus for studying $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. Apertures are not to the scale shown. After the hemispherical analyzer there are four sweep plates, each 5 cm long. Along the first 2.5 cm, the plates form a cylinder of 1.3 cm diam, and along the last 2.5 cm, a frustrum which has a 1.3 cm diam at its small end and a 2.5 cm diam at the other.

Because of transverse velocities, H_3^+ was formed along path lengths of the merged beams where the reactants had the same energy. Therefore, from this mechanism, H_3^+ was continually being generated outside the interaction region and, when $\Delta E = 0$, inside as well. If the potential of the retarding grid in the detector were sufficiently low, these ions would be detected.

When $\Delta E \neq 0$, the detector signal was due to H_3^+ formed inside the interaction region at energy W , and, if the retarding grid were at a sufficiently low potential, to H_3^+ formed outside. The contribution from H_3^+ outside could be measured independently by applying any ΔE that would result in no measurable signal from inside the interaction region. For this purpose we determined that the ΔE associated with $W = 10$ eV, which we will label $\Delta E'$ ($\Delta E' = +470$ or -510 V), was satisfactory.

The contribution associated with W due to H_3^+ formed inside the interaction region was the difference between signals measured with the potential of this region at ΔE and at $\Delta E'$. The retarding potential curve for a given W could be derived from this difference.

TABLE I. Ratio of cross section at W , Q_W , to cross section at 1 eV, Q_1 .

W (eV)	Present experiment Q_W/Q_1	Giese and Maier ^a $(Q_W/Q_1)_{GM}$	Reuben and Friedman ^b $(Q_W/Q_1)_{RF}$	$W^{-1/2}$ $(Q_W/Q_1)_{theor}$
0.1	3.22	3.16
0.2	2.45	2.24
0.3	2.04	1.82
0.4	...	1.63	...	1.58
0.6	1.45	1.39	1.35	1.29
1.0	1.00	1.00	1.00	1.00
1.5	0.69	0.65	0.78	0.82
2.0	0.53	0.44	0.63	0.71
2.5	0.33	0.29	0.52	0.63
3.0	0.20	0.19	0.45	0.58
4.0	0.15	0.08	0.35	0.50
5.0	0.07	0.04	0.29	0.45
7.0	0	...	0.28	0.38
10.0	0	...	0.27	0.32
12.0	0.18	0.29
13.5	0	0.27

^a Reference 4.^b Reference 5.

Each cross-section measurement at W was accompanied by a measurement at 1 eV so that we obtained ratios of cross sections, Q_W/Q_1 . It was not necessary to take measurements for complete retarding potential curves (i.e., curves for a succession of retarding potentials beginning with potentials sufficiently large to result in no measurable signal to potentials well into the region of the plateau) to derive a given ratio. Only a single measurement on each plateau was required, and, in general, this was the technique followed. Data for a given cross-section ratio could be obtained in a few minutes.

Absolute cross-section measurements could be made by a technique discussed previously.²

RESULTS

Our results for Q_W/Q_1 are shown in Fig. 2. Included are data for positive and negative ΔE 's associated with the same W . To give an idea of the accuracy of ratios designated by crosses, we estimate the error for the ratio at 0.1 eV to be -11% to $+6\%$. At 3 eV the standard deviation is about $\pm 18\%$. Also shown in Fig. 2 is a $W^{-1/2}$ straight-line fit to our data for $0.1 \text{ eV} \leq W \leq 1 \text{ eV}$ and the theoretical straight-line prediction of Gioumouis and Stevenson (GS).³ We could measure no signal for $W = 7$ eV and, considering experimental errors, estimate that $Q_W/Q_1 < 0.02$ at this energy. Complete retarding potential curves were taken for $W = 0.3, 1, \text{ and } 3$ eV.

The values of the crosses in Fig. 2 are given in Table I. Also included are the ratios Q_W/Q_1 for a tandem mass-spectrometer experiment by Giese and Maier (GM),⁴ for a single-stage mass-spectrometer experiment by Reuben and Friedman (RF),⁵ and for a linear dependence of the cross section on $W^{-1/2}$.

³ G. Gioumouis and D. P. Stevenson, *J. Chem. Phys.* **29**, 294 (1958).⁴ C. F. Giese and W. B. Maier, II, *J. Chem. Phys.* **39**, 739 (1963). The GM values in Table I were taken from their curve labeled $Q=0$.⁵ B. G. Reuben and L. Friedman, *J. Chem. Phys.* **37**, 1636 (1962). The RF values in Table I are the result of an analysis of their data as outlined by G. Gioumouis, Lockheed Palo Alto Research Laboratory Report No. 2-12-66-4, 1966 (unpublished).

An absolute measurement was made at 1 eV with the result that $Q_1 = 12 \text{ \AA}^2$ with an estimated error of -26 to $+37\%$.

Tests were made to ensure that all product ions from the interaction region passed into the detector assembly (see Fig. 1). A 0.1-in.-diam hole in the aperture plate was substituted for the usual 0.5-in.-diam hole. By laterally moving the detector assembly, a search was then made for ions at distances normal to the axis of the interaction region that were greater than or equal to 0.25 in. No ions were detected.

DISCUSSION OF RESULTS

Considerably more reliability should be placed on our ratios Q_W/Q_1 than on the absolute determination as evidenced by the estimated errors indicated above. This is primarily because the absolute determination depended upon measurements of the transmissions of the grids in the decelerating-accelerating system, the secondary-electron coefficient of the collecting plate in the neutral beam monitor, the primary ion and neutral beam shapes, the relative positions of the primary beams, and the gain of the detector assembly.⁶ These quantities were subject to rather large errors. The determinations of ratios did not depend on these quantities. Our Q_1 , subject to its rather large uncertainty, overlaps the value of 15 \AA^2 predicted by the GS theory.

The experimental errors associated with Q_W/Q_1 become larger as W increases because the Q_W became smaller and are more difficult to measure. Our experience with crossed beams, on the other hand, has been that the cross-section errors become larger as beam energies decrease. This is attributed to beam intensities (which largely dominate such errors) becoming smaller with decreasing energy.

From Fig. 2 it is noted that for $0.1 \text{ eV} \leq W \leq 1 \text{ eV}$, a straight line passing through the origin could be fitted, within experimental error, to our cross-section ratios. This line is in fair agreement with that predicted by GS.³ For $W \geq 1.5 \text{ eV}$ our ratios fall below the $W^{-1/2}$ fit. These facts are also evident in Table I. From the table it is also observed that the agreement between our results and those of GM is fair for W 's between 0.6 and 3 eV. The GM result at 0.4 eV comes quite close to the $W^{-1/2}$ fit to our points. Much of the difference between our results and those of GM above 3 eV, where the cross section is quite small, could be explained by experimental errors.

Uncertainties in W caused by the effects of transverse velocities^{2,6} were negligible for our data except for $W \leq 0.1 \text{ eV}$. An uncertainty in W would also result in an uncertainty in Q_W since the latter was extracted from a measured quantity which was proportional to $Q_W W^{1/2}$. The effects of transverse velocity at 0.1 eV

⁶ S. M. Trujillo, R. H. Neynaber, and E. W. Rothe, Rev. Sci. Instr. **37**, 1655 (1966).

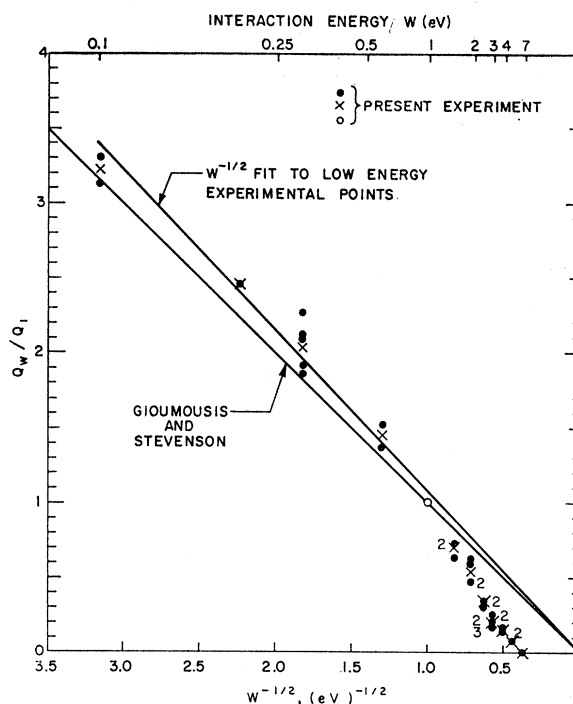


FIG. 2. Q_W/Q_1 versus $W^{-1/2}$ and W for $H_2^+ + H_2 \rightarrow H_3^+ + H$. Each dot represents a value obtained for a single measurement; a dot accompanied by a digit means that number of measurements resulted in the same quantity. Crosses indicate arithmetic averages of dots.

are reflected in the estimated, composite error of -11% (-9% is directly due to transverse velocities) for the cross-section ratio. Since our data indicate that, to a first approximation, $Q_W \propto W^{-1/2}$ near $W = 0.1 \text{ eV}$, the measured quantity $Q_W W^{1/2}$ was independent of uncertainties caused by transverse velocities. Therefore, whatever correction should be applied to the energy of the 0.1-eV point in Fig. 2, the cross-section ratio will still lend the same support to the $W^{-1/2}$ fit shown.

In Table I it is noted that for $W > 1.5 \text{ eV}$ the RF results neither agree with the $W^{-1/2}$ dependence nor fall off as rapidly with energy as do those of GM and of the present experiment. Our results indicate that, within experimental error, the cross-section ratio vanishes (i.e., < 0.02) between 5 and 7 eV and probably remains zero for $W > 7 \text{ eV}$. An extrapolation of the GM cross-section curve gives results consistent with these conclusions. The RF data, on the other hand, indicate a nonzero ratio up to $W = 13.5 \text{ eV}$.

A spectator-stripping model⁷ has been used to explain deviations from the GS theory such as shown by the present results. For given energies of the reactants and one reaction channel for H_3^+ , a single energy for the product ion is predicted from the model. From retarding potential curves of H_3^+ , our results indicate a continuous distribution of energies with a

⁷ For a discussion of the spectator-stripping model see chapter by A. Henglein, Adv. Chem. Ser. **58**, 63 (1966).

spread of 50–100 eV for $W=0.3$ and 1 eV. At 3 eV, where the cross-section ratio is small and considerably below the $W^{-1/2}$ fit, there was a rather large statistical spread in H_3^+ signals at the higher retarding potentials. Because of this spread, it is not clear whether there is a continuous distribution of H_3^+ energies with a 50–100 eV spread, or several discrete energies. The existence of more than one energy for H_3^+ would not be inconsistent with a spectator-stripping model if there were more than one reaction channel for this ion. It should be noted that for similar reactions Durup and Durup⁸ and Doverspike and Champion⁹ find several reaction channels for a given product ion.

From Fig. 2 it appears that the best fit to our data between 0.1 and 1 eV is a smooth curve that is concave downwards. We do not want to discount the possibility that this curve represents an actual departure of the cross-section ratio from a linear dependence on $W^{-1/2}$. We have concrete evidence from signals at an extremely low energy (i.e., $W \leq 0.03$ eV) that the quantity $(Q_W/Q_1)W^{1/2}$ is from 15 to 30% less than the corresponding value given by the slope of the $W^{-1/2}$ fit in Fig. 2. In other words, the $W^{-1/2}$ fit shown does not apply at this low energy. These signals arise when $\Delta E=0$. Transverse velocities account for the interaction energy. An upper bound to the energy has been calculated as 0.03 eV.⁶ Uncertainty in the energy prevents a determination of the cross-section ratio.

Wolf¹⁰ has used a modified phase-space theory to calculate cross sections for the process under discussion. He predicts a curve of cross-section ratio versus W that has the same general shape as a smooth curve that fits our data.

⁸ J. Durup and M. Durup, *J. Chim. Phys.* **2**, 386 (1967).

⁹ L. D. Doverspike and R. L. Champion, *J. Chem. Phys.* **46**, 4718 (1967).

¹⁰ F. A. Wolf, in *Proceedings of the Twentieth Annual Gaseous Electronics Conference*, San Francisco, 1967 (unpublished).

It should be noted that the states of our reactants are unknown. If excited states did exist, cross sections for ground-state reactants could be obtained, in principle, by applying corrections to our quoted values. The percentage correction to our value for Q_1 would probably be considerably larger than the percentage correction to our cross-section ratios.

From mass-spectrometric experiments on $H_2^+ + H_2 \rightarrow H_3^+ + H$, Weingartshofer and Clarke¹¹ report that only the first four vibrationally excited states of H_2^+ contribute significantly towards the formation of H_3^+ and that the ground-state contribution is greater than that from each of the other three states. In another study, Chupka¹² finds that the reaction probability decreases with increasing vibrational and rotational excitation of H_2^+ . Therefore, the existence of such excitation in our experiment would result in a smaller Q_1 than would be obtained from just ground-state H_2^+ . On the other hand, if the GS theory applies at 1 eV, electronically excited H_2 primaries would be expected to result in a Q_1 larger than would be extracted from measurements with a pure, ground-state neutral beam. This follows from the larger polarizability of an excited neutral.

ACKNOWLEDGMENTS

The authors wish to thank Dr. E. W. Rothe for stimulating their interest in the application of merging beams to this problem and for valuable suggestions during the experiment. Helpful discussions with Dr. B. F. Myers and Dr. P. K. Rol are also acknowledged.

¹¹ A. Weingartshofer and E. M. Clarke, *Phys. Rev. Letters* **12**, 591 (1964).

¹² W. A. Chupka, in *Proceedings of the Fifteenth Annual Conference on Mass Spectrometry and Allied Topics*, Denver, Colorado, 1967 (unpublished).