and

$$g(\mathrm{Li}^7)/g(\mathrm{Li}^6) = 2.641\,006. \quad (6)$$

The three hyperfine coupling parameters obtained from Eqs. (3), using observed data in Eqs. (4), are listed in Table I, together with the implied value of $a_{3/2}$. These numbers differ from either set of computed values by roughly 2%. The two sets of computed results, obtained by very different methods, are in substantial agreement with each other and with experiment. The Bethe-Goldstone results (RKN) are within a fraction of 1% of the best established experimental data ($a_{1/2}$ and ΔH for the Li^7 low-field level crossing). The small discrepancy between this calculation and the hyperfine parameters deduced from experimental data is almost entirely due to the difference between computed and observed values of $V_{av}{}^{h}(\mathrm{Li}^6)$. The computed data in Table I should provide useful predictions of those quantities not yet determined experimentally.

The two independent computations, and available experimental data, indicate unequivocally that a_c, a_{dip}, and a_{orb} must be treated as independent parameters. The practice of assuming a fixed relationship among these parameters, obtained from one-electron models, cannot be justified in the analysis of accurate experimental data.

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[1]K. A. Brueckner, Phys. Rev. 96, 508 (1954), and 97, 1353 (1955), and 100, 36 (1955), and in The Many-Body Problem, edited by B. De Witt (Wiley, New York, 1959), pp. 47-241.

[2]R. K. Nesbet, Phys. Rev. 155, 51, 56 (1967), and Advan. Chem. Phys. 14, 1 (1969).

[3]R. K. Nesbet, in Quantum Theory of Atoms, Molecules, and the Solid State, edited by P.-O. Löwdin (Academic, New York, 1966), pp. 157-165, and Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 164, 87 (1967).

[4]H. F. Schaefer, III, and F. E. Harris, Phys. Rev. 167, 67 (1968).

[5]R. K. Nesbet, to be published (RKN).

[6]J. D. Lyons, R. T. Pu, and T. P. Das, Phys. Rev. 178, 103 (1969) (LPD).

[7]H. P. Kelly, Phys. Rev. 131, 684 (1963), and 136, B896 (1964), and 144, 39 (1966), and in Perturbation Theory and its Application in Quantum Mechanics, edited by C. H. Wilcox (Wiley, New York, 1966), pp. 215-241.

[8]J. D. Lyons and T. P. Das, to be published.

[9]C. H. Townes, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958), Vol. 38, Pt. I, p. 377; S. L. Kahalas and R. K. Nesbet, J. Chem. Phys. 39, 529 (1963); L. Wharton, L. P. Gold, and W. Klemperer, J. Chem Phys. 37, 2149 (1962).

[10]T. G. Eck and R. L. Smith, to be published.

[11]K. C. Brog, T. G. Eck, and H. Wieder, Phys. Rev. 153, 91 (1967).

[12]G. J. Ritter, Can. J. Phys. 43, 770 (1965).

$H^+ + H^-$ MUTUAL NEUTRALIZATION CROSS SECTION OBTAINED WITH SUPERIMPOSED BEAMS*

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The ion-ion mutual neutralization cross section for $H^+ + H^-$ has been measured over the barycentric energy range from 0.15 to 300 eV using a merged-beam technique. The results are compared with theoretical calculations and with a recent higher energy experimental measurement. An estimate of the thermal rate coefficient is made.

The ion-ion mutual neutralization cross section has been measured for $H^+ + H^-$ using a superimposed beam technique. The barycentric energy range of the measurements is 0.15 to 300 eV. This is the first measurement of this important cross section at energies below 125 eV. The data compare very favorably with the results of Rundel, Aitken, and Harrison,[1] who used beams intersecting at 20°, in the region of overlap. There has been substantial theoretical interest in ion-ion mutual neutralization,[2-5] and especially in the $H^+ + H^-$ reaction.[2-4] This system is well suited for an experimental test of theoretical calculations because of its simplicity and of the fact that the initial states are well defined.

The technique, which has been described in detail elsewhere,[6] involves merging the positive and negative ion beams of different speeds by magnetic deflection, and observing their interaction over a known path length (see Fig. 1). Both beams have laboratory energies E^+ and E^- in the keV range, but can have relative energies W as low as 0.15 eV while in the interaction region.

After traversing the 30-cm interaction length

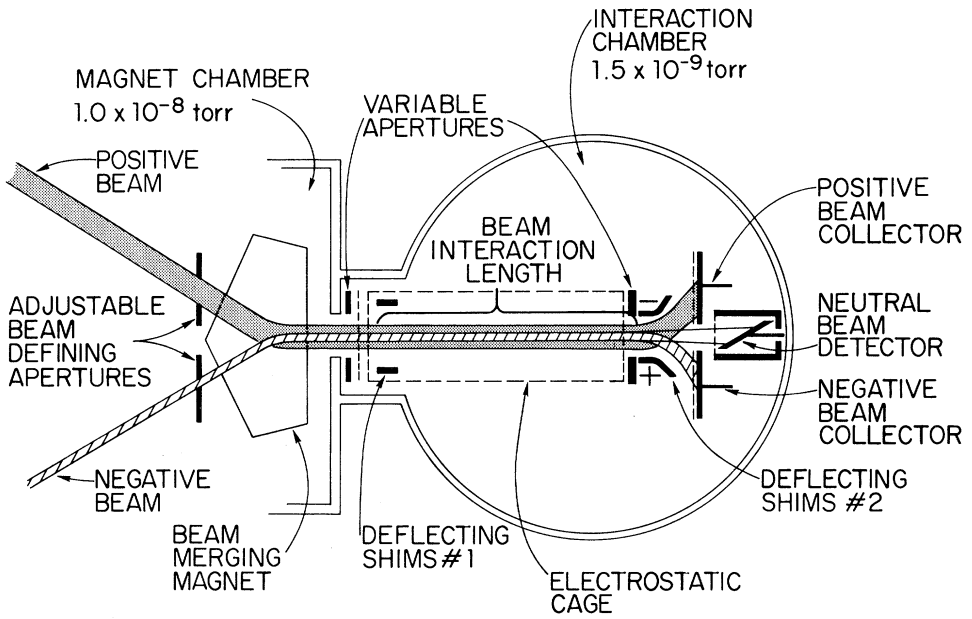

FIG. 1. Schematic of the apparatus.

in superposition, the beams are separated by electrostatic deflection and collected in two Faraday cups. The neutral particles formed by ion-ion neutralization, as well as a much larger background of neutrals formed by electron stripping and capture reactions of the beam ions with the ambient gas, continue along the superimposed beam direction and are detected indirectly by secondary electron emission. An electrical chopping technique[6] is used to separate the ion-ion neutralization signal from that due to beam-background gas interactions.

The relative energy of the merged beams can be varied over a limited range by applying a potential to the electrostatic cage that surrounds the interaction region, and over a larger range by varying the energy and angle with which the beams enter the merging magnet. Data from overlapping relative energies for different angles are in agreement.

The length L of the interaction region is defined by the two pairs of electric deflectors (Fig. 1). Subtracting the neutral current measured when the beams are demerged at the first deflector from the current observed when the beams are allowed to continue to the second pair of deflectors yields the desired signal. No pressure dependence[6] of this net signal was observed when the background pressure was maintained below 2×10^{-9} Torr.

The ion-ion neutralization signal I_0 is proportional to the product of the neutralization cross section Q and the relative speed v_r. This product is given by[6]

$$Qv_r = eI_0(E^+E^-/M^+M^-)^{1/2}(4I^-J_A{}^+L\gamma)^{-1}, \quad (1)$$

where M^+ and M^- are the atomic masses and γ is the neutral-particle secondary-electron emission coefficient. I^- is the total negative beam current, and $J_A{}^+$ is the current density of the (broad) positive beam in the region occupied by the (narrow) negative beam (see Fig. 1). Thus the overlap integral of the beams in the interaction region, $\int J^-J^+dV$, is approximated by $J_A{}^+I^-L$ This approximation and the modifications to Eq. (1) required to account for the effects of chopping both beams are discussed in Ref. 6.

Figure 2 shows the experimental results. The solid dots represent the results of this research. The vertical error bars are the standard deviations of the four to ten separate observations at each energy which were averaged to obtain the point. The horizontal error bars in the low-energy region reflect an uncertainty due to imperfect beam collimation (discussed below). The triangles are the results of Rundel, Aitken, and Harrison.[1] Their error bars represent 90% confidence limits for random errors. The short-dash curve represents the Landau-Zener calculation of Bates and Lewis.[2] The long-dash curve shows results of a recent Landau-Zener calculation by Dalgarno, Victor, Browne, and Webb.[3]

In making these measurements, the secondary-electron emission coefficient γ was taken as the

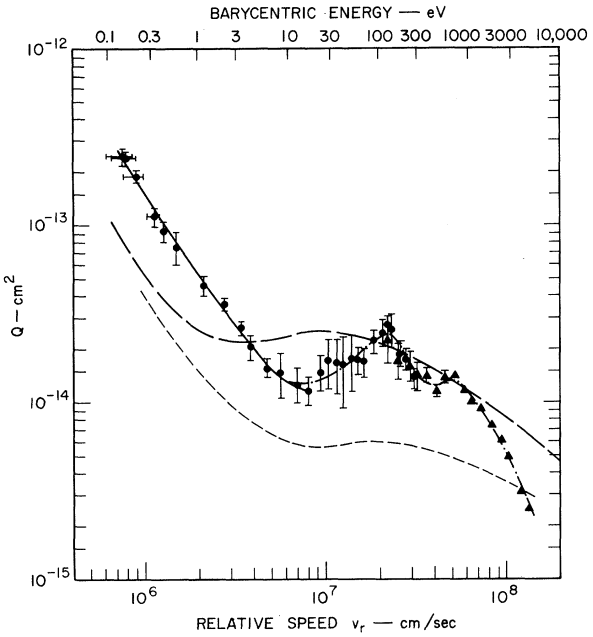

FIG. 2. Ion-ion mutual neutralization cross sections versus velocity for $H^+ + H^-$. Circles, this research; triangles, Ref. 1; short-dashed curve, Ref. 2; long-dashed curve, Ref. 3.

average of measured values for the coefficients of the H^+ and H^- beams. It has been shown[7] that γ for beam energies of this experiment varies only gradually with the energy and charge state of the particle. We have observed that γ's for H^+ and H^- differ by only 15 to 25% over the range of beam energies used, with H^- having the larger value. Chambers[8] found γ for H^0 to be 10% larger than γ for H^+ at 2.5 keV, and Tisone and Branscomb[9] found γ's for H^0 and H^- to be equal to within ±9% at 2.5 keV. Thus the determination of γ as the average of the H^+ and H^- coefficients should be accurate to within ±10%. Because of the nearly linear dependence of γ^+ and γ^- on energy, the average γ is not affected by placing a voltage on the electrostatic cage.

Because of the deamplification effect[10] of the merged-beam technique, the energy spreads (~3 eV) in the dupolasmatron-produced ion beams[11] are negligible in the center-of-mass system. However, as the relative energy of the beams is decreased below 1 eV there is an uncertainty in the relative energy of the beams caused by velocity components transverse to the beam direction (imperfect collimation). To account for these effects, we define the relative energy as

$$W = \mu[(E^+/M^+)^{1/2} - (E^-/M^-)^{1/2}]^2 + \overline{W}_T, \qquad (2)$$

where μ is the reduced mass and $\overline{W}_T$ is the effective low-energy limit due to transverse velocity contributions. The effective relative velocity v_r, used in Eq. (1) to compute the cross section from the signal, is obtained from $v_r = (2W/\mu)^{1/2}$. Estimates of $\overline{W}_T$ using an approximation based on the collimator geometry[10] yields $\overline{W}_T$ in the range 0.05 to 0.25 eV. Use of $\overline{W}_T = 0.2$ eV gives a velocity dependence of Q that reaches $1/v_r^2$ at the lower energies. Since we expect $1/v_r^2$ to be the limiting velocity dependence of Q as thermal energy is approached,[2] $\overline{W}_T = 0.2$ eV provides an upper limit on the transverse energy contribution. When values of $\overline{W}_T$ less than 0.1 eV are used, the result is a velocity dependence for Q that decreases toward $1/v$ as the low-energy limit is approached. Thus it is concluded that $0.1 < \overline{W}_T < 0.2$ eV. For the data points shown, 0.15 eV was used for $\overline{W}_T$ in Eq. (2). The low-energy error bars were determined by using $\overline{W}_T = 0.2$ eV on the right and 0.1 eV on the left.

Another source of possible error is the approximation used to determine the overlap integral.[6] This determination may be in error by ±15%. An uncertainty in the interaction length L is present because the beams are not demerged instantaneously at the deflectors. The 30-cm effective length for L may be in error by ±8%. The ion-ion neutralization current I_0 is determined by integrating for periods up to 15 min. I_0 may be in error by ±15%. Other error contributions are small. I^- is determined to within ±4%, $J_A{}^+$ to ±6%, and E^+ and E^- to ±1%.

A possible, but unlikely, complication is the fact that there are two possible reactions that yield neutral particles: $H^+ + H^- \rightarrow H + H$ (mutual neutralization), and $H^+ + H^- \rightarrow H^+ + H + e$ (electron detachment). Thus in fact this experiment measures the cross section for mutual neutralization plus one-half the cross section for electron detachment. At the relative velocities covered in this study the detachment reaction may be thought of as proceeding through a channel in which a curve crossing takes place to a repulsive $H_2{}^+$ state through an intermediate $H_2{}^*$ excited state. There is no direct crossing between $H^+ + H^-$ and $H^+ + H$. Transitions to the repulsive $H_2{}^+$ state via curve crossings can only occur for impact parameters that are small (<2 Å) compared with those for the neutralization reaction (>5 Å), and the maximum cross sections are probably less than 10^{-15} cm² and thus are negligible in this experiment. The good agreement of the present data with those of Rundel, Aitken, and Harrison,[1] whose measurements did not include the electron-

detachment cross section, further indicates that this reaction does not contribute significantly to the present measurements.

Added linearly, the possible errors sum to ±60%. The root-mean-square error determined from these individual errors is ±26%. We thus assert that, except for velocities between 0.9 and 1.8×10^7 cm/sec, where the scatter in the data is substantially larger, the present results should be correct to within ±50%.

To obtain information about the low-energy rate coefficient the solid curve through the data up to 20 eV (Fig. 2) was determined by a least-squares fit of the data by the functional form $Q = A/v^2 + B/v + C + Dv$. This parametrization allows the proper asymptotic behavior at low energies, and can be viewed as an expansion of the Landau-Zener formula which describes such processes. For the fit shown, $A = 9.2\times10^{-2}$ cm^4/sec^2, $B = 6.3\times10^{-8}$ cm^3/sec, $C = -4.5\times10^{-15}$ cm^2, and $D = 0.89\times10^{-21}$ cm sec. The other curve which joins the parametrized fit at about 10 eV is an average curve through our data and those of Rundel, Aitken, and Harrison.[1]

The low-energy temperature dependence of the thermal rate coefficient $\alpha = \langle Qv_r \rangle$ can be estimated from the parametrization of Q given above by Boltzmann averaging. The result is

$$\alpha(T) = (2\mu/\pi kT)^{1/2}A + B + 2(2kT/\mu\pi)^{1/2} + C + \cdots. \quad (3)$$

Using our values for A, B, and C yields $\alpha(300°\text{K}) = 4.0\times10^{-7}$ cm^3/sec. Error limits on α can be estimated by fitting the results obtained by using $\overline{W}_T = 0.1$ and 0.2 eV to the same functional form. The result is $\alpha(300°\text{K}) = (4.0\pm1.8)\times10^{-7}$ cm^3/sec.

The agreement of the present data with the data of Rundel, Aitken, and Harrison[1] (see Fig. 2) between 125 and 300 eV is seen to be quite good. Since the two experiments are very different in design and execution, this agreement increases confidence in the results of both of these difficult experiments.

The two Landau-Zener calculations show the general characteristics of the measured cross sections. They are both lower than the observed values at low energies. Both have a minimum and a maximum, but these are much less distinct than the major observed ones and occur at different velocities. The Bates and Lewis[2] results are lower than those of Dalgarno, Victor, Browne, and Webb,[3] which are based on more accurate potential curves for the H_2 molecule.[12] The Dalgarno et al. results exceed the experimental ones between about 5 and 100 eV where the experiment shows a minimum. Between 100 and 2000 eV, the Dalgarno et al. calculation is in good agreement with experiment, except that the calculation does not predict the observed minor structure. In this region Bates and Lewis are a factor of 4 lower than the experimental results.

The fact that the results of Landau-Zener calculations do not agree exactly with the present data is not unexpected. Several workers[13-16] have questioned the validity and accuracy of the Landau-Zener formulation, and it is predicted that this formula will tend to underestimate the cross section. The disagreement in slope between the calculated curves and that of Rundel, Aitken, and Harrison above 1000 eV is also expected as a result of the invalidity of the Landau-Zener theory at these high energies.

Victor[4] has also used a close-coupling theory for this reaction, obtaining a cross section which is a factor of 5 smaller than his Landau-Zener calculation at thermal velocities, and which is larger than the experimental results by 20% at 200 eV. At higher energies the calculated cross section decreases much less rapidly with energy than do the experimental results. Final results of this calculation are not yet available.

The experimental data show two maxima and two minima in the cross section. The broad minimum at low velocity can be associated with the minimum predicted by both Landau-Zener calculations. The other extrema are considerably sharper than any theoretically predicted ones. Apparently at higher velocity there is a broad maximum upon which are superimposed two minimaxima and a minimum. In addition, there is considerable scatter in the data between $v_r = (0.9$ and $2.3)\times10^7$ cm/sec, which could obscure or even be caused by additional structure. The three observed extrema are roughly evenly spaced in reciprocal velocity, and may be similar in origin to the oscillations seen in other cases of charge transfer or energy transfer.[17] As shown in Fig. 3, if the peaks are numbered by integers N and the valleys by half-integers, and the theoretical intercept[18] $N_0 = \frac{3}{8}$ is assumed, all the clearly identifiable extrema fall on a linear curve with the slope $v_0 = dN/d(v^{-1}) = 4\times10^7$ cm/sec = 0.2 a.u. The maximum amplitude of the oscillating contribution appears to be about $\Delta Q \cong (2\text{-}3)\times10^{-15}$ cm^2 $\cong$ 80-120 (a.u.)^2, which is of the order of the geometric cross section to be expected for the crossing at $R_x \cong 11$ a.u. resulting in H(1s) + H(n = 2). This amplitude is probably much too large

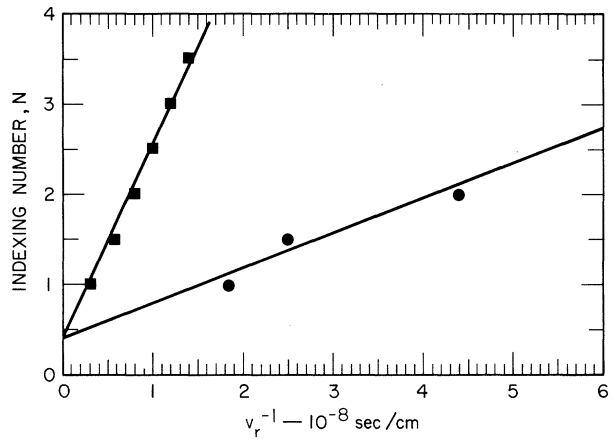

FIG. 3. Plot of the indexing numbers N of the maxima and minimum versus v_r^{-1}. Closed circles, this research; closed squares, Keever et al.

to be associated with the H(1s) final channel, and the characteristic velocity v_0 is entirely different from the value $v_0 = 2.1 \times 10^8$ cm/sec = 1 a.u. obtained from the oscillations seen by Keever, Lockwood, Helbig, and Evehart[19] in the reverse reaction $H(1s) \rightarrow H^+ + H^-$ (measured for 1.5° and 3.0° scattering). The spacing of the oscillations in both forward and reverse reactions should be the same, and is related[20] to the average value of the difference potential $\Delta V(R)$ between two states responsible for the different available trajectories inside the crossing at R_x:

$$2\pi v_0 = 2\hbar^{-1}\int_0^{R_x} \Delta V(R)dR \cong 2\hbar^{-1} R_x \langle \Delta V \rangle. \qquad (4)$$

Assuming $R_x = 11$ a.u., we find $\langle \Delta V \rangle \cong 0.06$ a.u. $\cong 1.6$ eV, which appears quite reasonable if ΔV represents the distance between the largely Coulombic B state and the majority of the other, nonionic, states dissociating to $H(1s) + H(n = 2)$.

Another possible, although less likely, source of this structure is the variation of interaction energies with nuclear separation. Bates[13] and Mordinov and Firsov[14] have shown that inclusion of this effect in a Landau-Zener calculation can lead to two maxima in the cross section.

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[1]R. D. Rundel, K. L. Aitken, and M. F. A. Harrison, J. Phys. B: Phys. Soc. (London) Proc. 2, 954 (1969).

[2]D. R. Bates and J. T. Lewis, Proc. Phys. Soc. (London) A68, 173 (1955).

[3]A. Dalgarno, G. A. Victor, J. C. Browne, and T. G. Webb, to be published,

[4]G. A. Victor, in Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collisions, Boston, 28 July-2 August 1969, Abstracts of Papers (Massachusetts Institute of Technology Press, Cambridge, Mass., 1969), p. 108.

[5]J. L. Magee, Discussions Faraday Soc. 12, 33 (1952); D. R. Bates and T. J. M. Boyd, Proc. Phys. Soc. (London) A69, 910 (1956).

[6]W. H. Aberth and J. R. Peterson, Phys. Rev. (to be published).

[7]H. C. Hayden and N. G. Utterback, Phys. Rev. 135, A1575 (1964); V. G. Tel'kovskii, Dokl. Akad, Nauk SSSR 108, 44 (1956) [Soviet Phys. Doklady 1, 334 (1956)].

[8]E. S. Chambers, Phys. Rev. 133, A1202 (1964).

[9]G. C. Tisone and L. M. Branscomb, Phys. Rev. 170, 169 (1968).

[10]R. H. Neynaber, S. M. Trujillo, and E. W. Rothe, Phys. Rev. 157, 101 (1967), and Rev. Sci. Instr. 37, 1655 (1966).

[11]W. Aberth and J. R. Peterson, Rev. Sci. Instr. 38, 745 (1967).

[12]A. Dalgarno, G. A. Victor, and T. G. Webb, Air Force Cambridge Research Laboratories, Bedford, Mass., Final Report No. AFCRL-68-0428, 1968 (unpublished).

[13]D. R. Bates, Proc. Roy. Soc. (London), Ser. A 257, 22 (1960).

[14]Y. P. Mordinov and O. B. Firsov, Zh. Eksperim. i Teor. Fiz. 39, 427 (1960) [Soviet Phys. JETP 12, 301 (1960)].

[15]C. A. Coulson and K. Zalewski, Proc. Roy. Soc. (London), Ser. A 268, 437 (1962).

[16]D. R. Bates, H. C. Johnston, and I. Stewart, Proc. Phys. Soc. (London) 84, 517 (1964).

[17]J. Perel, R. H. Vernon, and H. L. Daley, Phys. Rev. 138, A937 (1965).

[18]R. E. Olson, Phys. Rev. 187, 153 (1969).

[19]W. C. Keever, G. J. Lockwood, H. F. Helbig, and E. Everhart, Phys. Rev. 166, 68 (1968).

[20]F. P. Ziemba and A. Russek, Phys. Rev. 115, 922 (1959); W. Lichten, Phys. Rev. 131, 229 (1963), and 139, A27 (1965).