Absolute Total Electron Scattering Cross Sections in H_2 and D_2 for Low Electron Energies*

D. E. GOLDEN, H. W. BANDEL, AND J. A. SALERNO
Lockheed Palo Alto Research Laboratories, Palo Alto, California
(Received 2 January 1966)

The Ramsauer technique has been used to measure the total electron scattering cross sections in H_2 and D_2 as a function of electron energy from 0.25 to 15 eV with an estimated probable error of $\pm 3\%$. Within the experimental error, the cross sections in H_2 and D_2 are identical. The cross section first increases smoothly with increasing electron energy from 9.2 Å^2 at 0.25 eV to a maximum of 15.7 Å^2 at about 2.8 eV and then decreases smoothly to 7 Å^2 at 15 eV. A modified effective-range formula has been used to fit the data for energies less than 1 eV, yielding a zero-energy scattering cross section of 5.53 Å^2. A gas-cathode interaction which may affect the determination of the absolute energy scale in some experiments by as much as 0.35 eV is discussed.

INTRODUCTION

THE subject of low-energy electron-molecule scattering has received considerable attention in recent years.[1,2]

For e^--H_2 scattering, there have been many early direct measurements of the total scattering cross section for electron energies greater than about 0.25 eV.[3–7] There is in general, disagreement as to the shape of the e^--H_2 scattering cross section as a function of energy.[8] The agreement in the magnitude of the cross section at a given energy in some cases is worse than a factor of 2.

The more indirect methods which measure the momentum-transfer cross section agree in general about the shape of the variation of cross section with energy[9–13] However, there are still serious differences in the magnitude of the cross section at a given energy ($\sim 50\%$). This is especially true for extermely low values of electron energy.

Theoretically, hydrogen is in many ways the simplest molecule to handle. Nevertheless, the problem of low-energy electron-molecule scattering is inherently more complicated to calculate than the comparable problem of electron-atom scattering. The calculational difficulties arise from the nonspherically-symmetric nature of the potential.

Following the method of assuming a simplified potential, successfully applied by Allis and Morse[14] to the Ramsauer effect for atoms, Fisk,[15] as early as 1935, calculated e^--H_2 total elastic scattering cross sections for very low electron energies. This empirical method, which used adjustable constants, gave reasonable order-of-magnitude results. More recently, Massey and Ridley[16] have applied the variational method of Hulthén[17] and Kohn[18] to the theory of e^--H_2 total elastic scattering for low electron energies including electron-exchange effects. Carter *et al.*[19] have obtained the ground-state H_2 wave functions using a self-consistent field approach. Using this wave function in a static field approximation with an approximate allowance for exchange they have calculated total elastic cross sections,[19] which are in good agreement with the results of Massey and Ridley.[16] Nevertheless, both of these calculations differ at some energies by as much as 50% from any of the experimental data. Recently, Lane[20] has combined for elastic scattering the "modified effective range" formulas given by O'Malley separately for a scattering system including the effects of the long-range polarization interaction,[21] and for a scattering system including the effects of a permanent quadrupole moment.[22] The result of this calculation is that the form of the effective range formula given by O'Malley[21] is still valid. Nevertheless, for low-energy electron scattering from a molecular system one cannot compare total and momentum transfer cross sections without knowledge of the differential cross sections. The only available information concern-

* This work was supported by the Lockheed Independent Research Program.

[1] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).
[2] D. R. Bates, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962).
[3] R. B. Brode, Phys. Rev. **25**, 636 (1925).
[4] M. Rusch, Physik. Z. **26**, 748 (1925).
[5] E. Brüche, Ann. Physik **82**, 912 (1927).
[6] C. Ramsauer and R. Kollath, Ann. Physik **4**, 91 (1929).
[7] C. E. Normand, Phys. Rev. **35**, 1217 (1930).
[8] Many of the discrepancies between these early measurements may have been due to the difficulties involved in purifying the hydrogen at the time.
[9] A. V. Phelps, O. T. Fundingsland, and S. C. Brown, Phys. Rev. **84**, 559 (1951).
[10] L. J. Varnerin, Jr., Phys. Rev. **84**, 563 (1951).
[11] R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) **A215**, 467 (1952).
[12] G. Bekefi and S. C. Brown, Phys. Rev. **112**, 159 (1958).
[13] L. S. Frost and A. V. Phelps, Phys. Rev. **127**, 1621 (1962); A. G. Englehardt and A. V. Phelps, *ibid.* **131**, 2115 (1963).
[14] W. P. Allis and P. M. Morse, Z. Physik **70**, 567 (1931).
[15] J. B. Fisk, Phys. Rev. **49**, 167 (1935).
[16] H. S. W. Massey and R. O. Ridley, Proc. Phys. Soc. (London) **A69**, 659 (1956).
[17] L. Hulthén, Kgl. Fysiograf. Sällskap. Lund, Förh. **14**, No. 21 (1944).
[18] W. Kohn, Phys. Rev. **74**, 1763 (1948).
[19] C. Carter, N. H. March, and D. Vincent, Proc. Phys. Soc. (London) **71**, 2 (1958).
[20] N. F. Lane, in *Abstracts of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965).
[21] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).
[22] T. F. O'Malley, Phys. Rev. **134**, A1188 (1964).

ing low-electron-energy differential scattering cross sections in H_2 are the early measurements of Bullard and Massey,[23] and Ramsauer and Kollath.[24]

Thus, although e^--H_2 has been stated to be the simplest electron-molecule scattering system, much work both experimentally and theoretically, is still needed in order to understand this system.

This paper presents careful measurements of the total e^--H_2 and D_2 scattering cross sections as a step in the understanding of these systems.

APPARATUS AND PROCEDURE

The apparatus and procedure are the same as those described previously for Ramsauer-type measurements in helium,[25] with the following exception. It was found necessary, when either H_2 or D_2 was introduced, to increase the accelerating voltage in order to peak the current reaching the collector, while keeping all other parameters constant. The effect increased with increasing gas pressures at the cathode until a pressure of about 1×10^{-4} Torr was reached for either H_2 or D_2. Further increase in gas pressure caused no further detectable change. However, for cathode pressures $\geqslant 1\times10^{-4}$ Torr of H_2 or D_2 it was found necessary to increase the accelerating voltage by about 0.35 V in order to peak the collector current. Further inspection revealed that when the collector current was peaked in this way, the electron-beam energy measured either at the scattering chamber or at the collector was the same as that obtained *in vacuum*. Hence, it was concluded that the introduction of a small amount of either H_2 or D_2 caused the cathode surface to become more positive by about 0.35 V, with a corresponding decrease in the accelerating voltage applied to the electrons leaving the cathode. In the apparatus used in the present experiment, the energy of the electrons which can get through the slit system is determined by the applied magnetic field.[25] Therefore, if the applied magnetic field is kept constant, the accelerating voltage may be readily adjusted without varying the electron energy. However, if an electrostatic-type gun[26] is used, where to some extent the electron-energy determination may be dependent on the value of the applied accelerating potential, great care must be exercised in order to ensure that the shift in accelerating voltage actually felt by the electrons leaving the cathode is accounted for in an absolute energy determination. The effect described above could cause a rather large error in the determination of appearance potentials made in gas mixtures.

The energy scale for the present experiment as well as that for the resonances in H_2 and D_2 reported previously[27] was determined from retarding potential measurements at the collector. Both of these experiments account for the cathode effect described above.[28]

RESULTS

The total cross section was determined at various values of electron energy between 0.25 and 15 eV using the procedure previously described[25] with the modification discussed above. The resulting values of total cross section are plotted versus electron energy in Fig. 1 for three different samples each for H_2 and D_2,[29] and two different pressure gauges. It is not surprising that no differences are found between the cross sections in H_2 and D_2 since the polarizabilities are closely the same.[30] The earlier direct measurements of Brüche[5] and Normand[7] are also shown on the plot. The present measurements are in good agreement ($\sim5\%$) with the measurements of Brüche.[5] Aside from some scaling factors, the shape of the variation of cross section with energy in H_2 and D_2 is quite similar to that observed in He.[25] For electron energies $\geqslant 6.5$ eV, the present

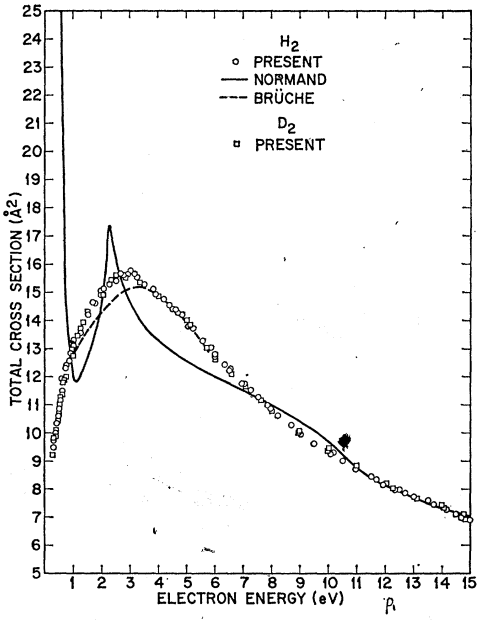

FIG. 1. Total e^-—H_2 and e^-—D_2 scattering cross sections versus electron energy 0–15 eV.

[23] E. C. Bullard and H. S. W. Massey, Proc. Roy. Soc. (London) A133, 637 (1931).
[24] C. Ramsauer and R. Kollath, Ann. Physik 12, 529 (1932).
[25] D. E. Golden and H. W. Bandel, Phys. Rev. 138, A14 (1965).
[26] A. L. Hughes and J. H. McMillen, Phys. Rev. 34, 291 (1929).
[27] D. E. Golden and H. W. Bandel, Phys. Rev. Letters 14, 1010 (1965).
[28] The difference in the energy scale for the H_2 resonances as determined in C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. Letters 12, 293 (1964), and that determined in Ref. 27 is discussed in Ref. 27.
[29] The H_2 and D_2 used in this work was Matheson assayed reagent-grade gas in 1.1-liter Pyrex flasks. A complete analysis supplied by the manufacturer showed: for H_2 no detectable impurities of greater than 4 ppm by volume; for D_2, $D_2=92.6\%$, $HD=6.9\%$, $H_2=0.5\%$ by volume.
[30] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York 1964).

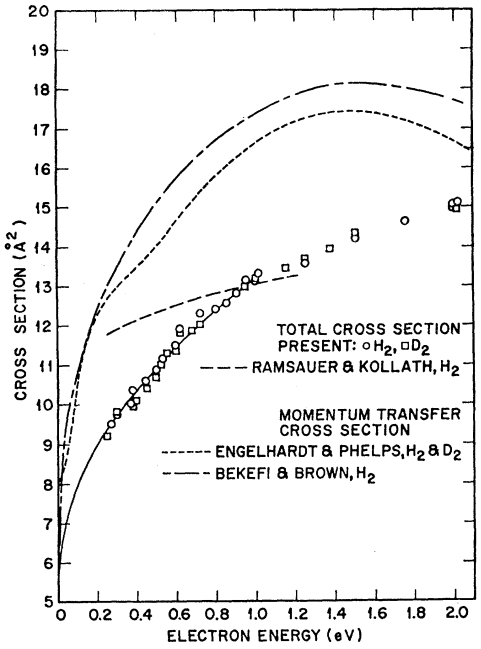

FIG. 2. e^-—H_2 and e^-—D_2 scattering cross sections versus electron energy 0–2 eV.

measurements are in good agreement ($\sim 5\%$) with the previous measurements of Normand.[7] However, for electron energies <6 eV, serious differences are seen on the plot.

The present results for energies $\leqslant 2$ eV are shown in Fig. 2 with the energy scale expanded from that of Fig. 1 by about a factor of 7. The direct measurement of Ramsauer and Kollath for H_2,[6] which are also shown, disagree with the present measurements by as much as 30%. The values of momentum-transfer cross section determined by Bekefi and Brown[12] and Engelhardt and Phelps[13] are also shown. For the most part these momentum-transfer cross sections do not seriously disagree ($\lesssim 8\%$) with each other.[31] The solid line going through the present data points was obtained by fitting the modified effective range formula,

$$\sigma_t(\text{Å}^2) = A + BE^{1/2} + CE\ln E + DE, \quad (1)$$

to the experimental data between 0.25 and 1.0 eV,[32] and extrapolating to zero eV.[20] In this equation σ_t is the total cross section in Å^2 and E is the electron energy in eV. The best fit[32] to the experimental data using Eq. (1) was determined to be

$$\sigma_t(\text{Å}^2) = 5.53 + 8.71E^{1/2} + 0.931E\ln E - 1.05E. \quad (2)$$

The extrapolation of the present total cross section data to zero energy is in very good agreement with the comparable momentum transfer cross section result of Bekefi and Brown.[12] However, the momentum-transfer results of Englehardt and Phelps[13] give an extrapolated zero-energy momentum-transfer cross section of 8 Å^2 which is more than 35% greater than the present result.

Structure in the e^--H_2 and e^--D_2 cross sections as a function of electron energy for energies less than about 11 eV was not found in this experiment. This negative result is not in disagreement with the previously reported more sensitive experiments of Golden and Nakano[33] or Schulz and Asundi.[34] The experiment of Schulz and Asundi gives a peak in the cross section for formation of H^- by electron impact on H_2 at 3.75 eV of $1.6\text{–}2.8\times 10^{-21}$ cm^2 with a half-width of about 0.5 eV.[34] The experiment of Golden and Nakano found no change in the e^--H_2 total cross section at 3.75 eV, with a lower limit of detectibility for cross-section changes of $(3.0-4.5)\times 10^{-19}$ cm^2 using a beam of electrons of 0.045–0.055 eV half-width.[33]

Until more information is forthcoming concerning the differential scattering cross sections, not much more can be said about the relationship between low-energy total and momentum-transfer cross sections for e^--H_2 and D_2.

EXPERIMENTAL ERROR

All the contributing factors to the probable percentage error in these determinations of absolute total cross sections are essentially the same as discussed previously for He.[25]

[31] It should be noted that total and momentum-transfer cross sections may be compared only if the scattering is isotropic.

[32] The sum of the squares of the percentage differences between measured and calculated values of σ_t was minimized by variation of the parameters A, B, C, and D in Eq. (1).

[33] D. E. Golden and H. Nakano (to be published).

[34] G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965).