

Electron Capture and Loss by Hydrogen Atoms in Molecular Hydrogen*

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Measurements of the single electron capture and loss cross sections for atomic hydrogen in molecular hydrogen are reported for atoms of energies 4 to 35 kev. Peaks in the loss cross section are found which appear to be associated with the formation of negative ions in the target gas.

I. INTRODUCTION

THE sum of the electron loss and capture cross sections for hydrogen in the energy range 4–35 kev has been measured by a method capable of yielding results precise to within 2 or 3%. The difference between the same cross sections has also been measured with comparable accuracy by means of a different technique but one employing the same apparatus. The result has been the discovery of structure in the cross section σ_{01} for electron loss and perhaps in σ_{0-1} for electron capture as well. This structure is probably associated with the formation of negative hydrogen ions in the target gas.

II. APPARATUS

The method employed in the measurement of $\sigma_{01} + \sigma_{0-1}$ has already been described.¹ In brief, a beam of protons accelerated to some energy in the kilovolt range is deflected through 90° by an electromagnet with special pole-tips.² This magnet serves to determine the energy and focus the beam on the entrance slit of a scattering chamber (Fig. 1). In the forepart of this chamber the beam passes through high pressure H₂ and then between condenser plates maintained at several thousand volts for the removal of whatever protons remain. Beams of neutral atoms equivalent to 0.2 to 2 microamps are in this way prepared and sent through collimating slits into the scattering chamber proper.

This consists of an array of nine identical condensers each 3 cm long followed by a Faraday cup in which a thin Nichrome foil is mounted. The beam is incident to this foil which is stretched across an opening in a massive copper block attached to the Faraday cup base. Fine copper wires are soldered to the back of the foil and to the block. The thermal emf developed between the hot copper Nichrome junction in the center of the foil where the beam hits and the cold junction at the copper block can be measured by a special potentiometer built for the purpose. The details of this instrumentation will be described elsewhere.

H₂ is admitted to the scattering chamber after it has

passed through a palladium leak and a liquid nitrogen trap. Several other such traps look directly into the scattering chamber. The chamber is pumped through the hole which admits the atomic beam. During the measurement of $\sigma_{01} + \sigma_{0-1}$ the pressure ranges between 7 and 18 microns. It is measured by means of a McLeod gauge connected to the scattering chamber.

III. $\sigma_{01} + \sigma_{0-1}$

When the atomic beam enters the H₂ collisions occur leading to the loss or capture of an electron by the fast atoms. If this charged component of the beam is removed at once the neutral beam current is attenuated according to

$$I_0(x) = I_0(0) \exp[-n(\sigma_{01} + \sigma_{0-1})x], \quad (1)$$

where $I_0(0)$ is the original neutral current and n is the H₂ density. If x is divided into m equal segments of length x_0 , the condenser length, plus an end correction x_0 this becomes

$$I_0(m) = I_0(0) \exp[-(n\sigma + n'\sigma_1')(mx_0 + x_0)], \quad (2)$$

where σ stands for $\sigma_{01} + \sigma_{0-1}$ and the primed symbols refer to the impurities which may be present. Then

$$\ln[I_0(m)/I_0(0)] = -(n\sigma + n'\sigma_1')(mx_0 + x_0). \quad (3)$$

For fixed values of n and n' , m is varied from 1 to 5 by the application of several thousand volts to the proper number of successive condensers. The reading of the neutral beam detector potentiometer is recorded at each step. (Although the ratio of charged to neutral component changes after the beam leaves the last charged condenser the total beam current does not. It is to this that the “neutral” detector responds.) Fortunately the detector is linear (Fig. 2) and so the logarithm of the detector readings themselves are plotted against mx_0 and fitted by least squares to a straight line whose

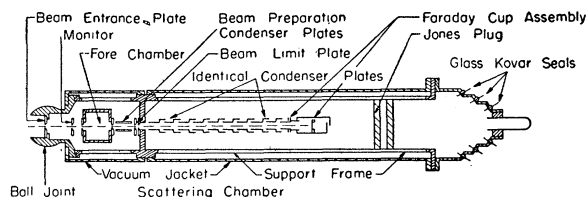


FIG. 1. Sketch, not to scale, of apparatus used in charge transfer experiment.

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¹ R. Curran, T. M. Donahue, and W. H. Kasner, Phys. Rev. **114**, 490 (1959).

² M. Camac, Rev. Sci. Instr. **22**, 197 (1951).

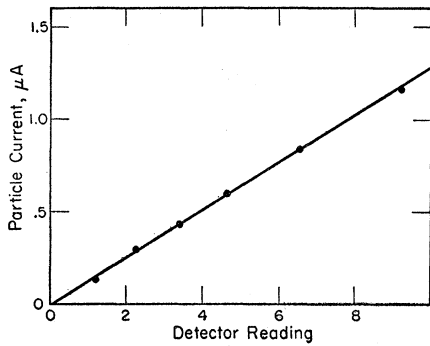


FIG. 2. Variation of "neutral beam" detector with proton current.

slope is $n\sigma + n'\sigma_1'$. This procedure is repeated at each energy for 10 to 20 values of $n+n'$. $n\sigma + n'\sigma_1'$ is then plotted against n and the slope of the resultant curve obtained from a least squares fit gives $\sigma_{01} + \sigma_{0-1}$. The error in the measurement of the pressure is no greater than 1%. The major contribution to the error of $\sigma_{01} + \sigma_{0-1}$ is from the random fluctuations in the neutral beam.

IV. $\sigma_{01} - \sigma_{0-1}$ AND σ_I

In Fig. 3 it can be seen that $\sigma_{01} + \sigma_{0-1}$ ³ does not vary monotonically with energy. To determine whether the structure belongs to σ_{01} or σ_{0-1} a method has been devised for the measurement of $\sigma_{01} - \sigma_{0-1}$. This is essentially the same technique used previously in the measurement of σ_{10} for protons.¹ H_2 is maintained at low pressure (0.2 to 0.8 micron) in the scattering chamber and a neutral atomic hydrogen beam sent into it. Low voltage, ranging from 12 to 35 volts (sufficient to saturate the collected current but not to deflect the charged component in the beam to the plates) is applied to the condensers. The current to any plate or collection of plates can be measured by an electrometer. When m

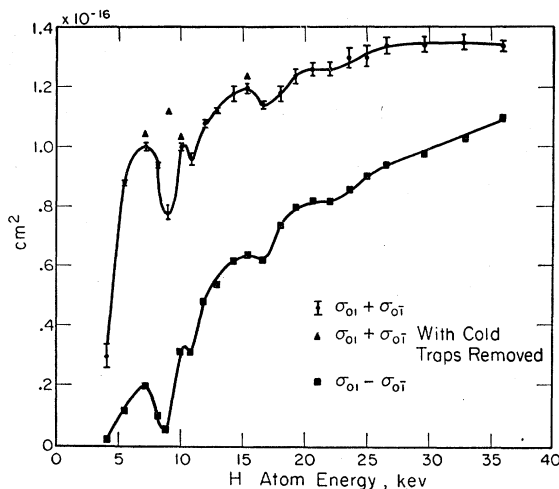


FIG. 3. Sum and difference of electron loss and capture cross sections for H on H_2 .

such positive plates are so connected the current recorded is

$$J_-(m) = I_0(0)[n(\sigma_{01} + \sigma_I) + n'\sigma_2'](mx_c + x_0), \quad (4)$$

where σ_I is the cross section for ion pair production by H in H_2 . The current to the negative plates is

$$J_+(m) = I_0(0)[n(\sigma_{0-1} + \sigma_I) + n'\sigma_3'](mx_c + x_0). \quad (5)$$

In this experiment $I_0(0)$ must be known. The neutral detector is calibrated after each run at a given beam energy by permitting a proton beam to fall on the detector in the evacuated chamber. Since the detector is an integral part of a Faraday cup and the beam current can be varied the sensitivity of the detector is measurable. The leakage current for each condenser is measured also during every run.

From a plot of $n(\sigma_{01} + \sigma_I) + n'\sigma_2'$ and $n(\sigma_{01} + \sigma_I) + n'\sigma_3'$ against pressure $\sigma_{01} + \sigma_I$ and $\sigma_{0-1} + \sigma_I$ are obtained and from them in turn $\sigma_{01} - \sigma_{0-1}$ and σ_I . It is possible to perform the subtraction electrically by a recording of

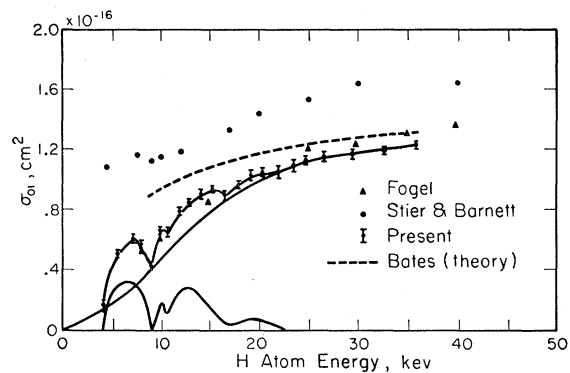


FIG. 4. Electron loss cross section for H on H_2 . The lower most curve is the difference between the measured cross section and the monotonic curve arbitrarily drawn through the minima of the measured curve.

the total current to both positive and negative plates but this foregoes the possibility of measuring σ_I .

When $\sigma_{01} - \sigma_{0-1}$, is plotted against energy (Fig. 3) it is clear that the structure belongs mainly to σ_{01} . The coincidence of details in the structure in both $\sigma_{01} + \sigma_{0-1}$ and $\sigma_{01} - \sigma_{0-1}$, although they are measured by very different techniques and in a different pressure region, confirms the reality of the structure.

The values of σ_{01} and σ_{0-1} are estimated as accurate to within the uncertainty of the vertical line through each experimental point. The contributions to this error arise from the probable error in the values of $\sigma_{01} + \sigma_{0-1}$ and the inaccuracy of the pressure measurements which was about 2% at most for the $\sigma_{01} + \sigma_I$ and $\sigma_{0-1} + \sigma_I$ determinations.

V. RESULTS AND DISCUSSION

In Figs. 4 and 5 there are plotted σ_{01} and σ_{0-1} separately. The results of previous measurements of these

cross sections by Fogel and others,⁴ by Stier and Barnett,⁵ and by Whittier⁶ are also plotted. Our results for σ_{01} agree well with the results achieved by the Russian workers, especially since they estimate an uncertainty of 15% in their measurement. There is clearly a big discrepancy with the Stier and Barnett results. In both instances the previous measurements have been made at energy intervals too large to show the structure. Our measured values of σ_{01} would appear to be asymptotic with the theoretical value calculated by Bates and his co-workers.^{7,8} It is expected from the Born approximation used that the calculated cross section be too high at low energy. As for σ_{0-1} our values agree fairly well with those of Whittier but are far larger than those measured by the other two groups. The structure which is suggested in σ_{0-1} is, we believe, real.

A smooth base curve has been drawn in Fig. 4 and the slowly varying part of σ_{01} subtracted out. The resulting structure is plotted in Fig. 4 and in Fig. 6 as a function

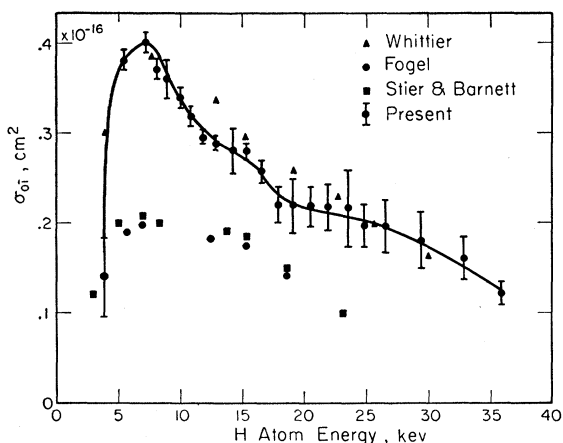


FIG. 5. Electron capture cross section for H on H₂.

of the velocity of the hydrogen atom. In Fig. 6 are plotted also the measurements by Schulz⁹ of the cross section for capture of free electrons by H₂ to form H⁻+H. The last two of our peaks can be made to coincide fairly well with those of Schulz if about 0.30×10^8 cm/sec is added to the atomic velocity, that is if it is assumed that the capture is a two step process in which, during one encounter between a fast hydrogen atom and a molecule, the electron is first stripped from the proton ending about 2.5 volts in the continuum and is then

³ To avoid confusion all cross sections are in units of cm² per molecule.

⁴ I. M. Fogel, V. A. Ankuninov, D. V. Philipenko, and N. V. Topolia, *J. Exptl. Theoret. Phys. U.S.S.R.* **34**, 579 (1958) [translation: *Soviet Phys.-JETP* **7**, 400 (1959)].

⁵ P. M. Stier and C. F. Barnett, *Phys. Rev.* **103**, 896 (1956).

⁶ A. C. Whittier, *Can. J. Phys.* **32**, 275 (1954).

⁷ D. R. Bates and G. W. Griffing, *Proc. Phys. Soc. (London)* **A68**, 90 (1955).

⁸ D. R. Bates and A. Williams, *Proc. Phys. Soc. (London)* **A70**, 306 (1957).

⁹ G. J. Schulz, *Phys. Rev.* **113**, 846 (1959).

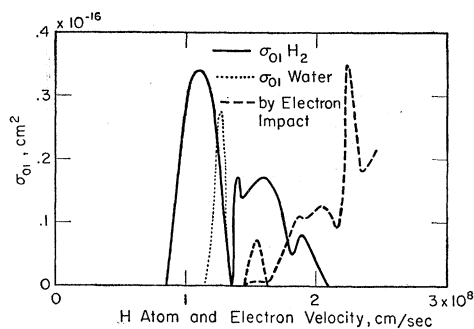


FIG. 6. Structure in the electron loss cross section for H on H₂ plotted against hydrogen atom velocity. For comparison and not on the same scale the results of Schulz (see reference 8) for negative ion formation by electrons in H₂ are plotted as a function of electron velocity.

captured by the H₂. Thus, it resembles the free electrons used by Schulz and by Khvostenko and Dukel'skii.¹⁰ The increment in velocity appears to be a linear function of the atomic velocity in this energy range as is shown in Fig. 7.

Workers who have studied electron capture by H₂ have regularly noticed the formation of H⁻ at about 6.8 ev. Water vapor created in amounts proportional to the quantity of H₂ present is considered responsible. Schulz, for example, has noted a great enhancement in the formation of H⁻ at this energy if traps are removed from his collision chamber. To check our hypothesis we measured $\sigma_{01} + \sigma_{0-1}$ with traps on and off and noticed a large increase in cross section at 8.2 kev when the traps were absent (dotted curves in Figs. 3 and 6). This is just where the peak should be to correspond to the 6.8 ev process for free electrons.

It is to be noted that our partial cross sections—the

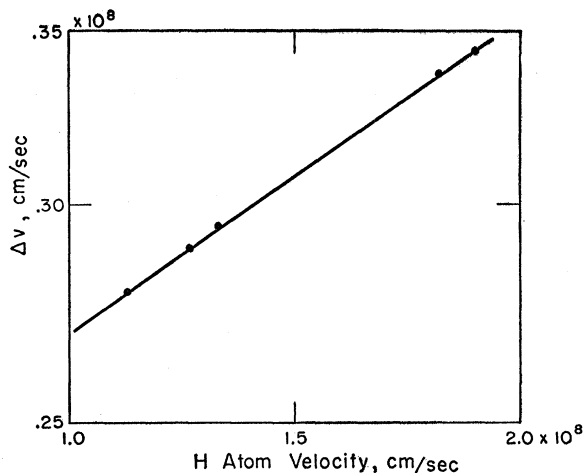


FIG. 7. Correction ΔV which must be applied to H atom velocity to bring about coincidence of peaks in cross sections for atoms and free electrons.

¹⁰ V. I. Khvostenko and V. M. Dukel'skii, *J. Exptl. Theoret. Phys. U. S. S. R.* **33**, 851 (1957) [translation: *Soviet Phys.-JETP* **6**, 657 (1958)].

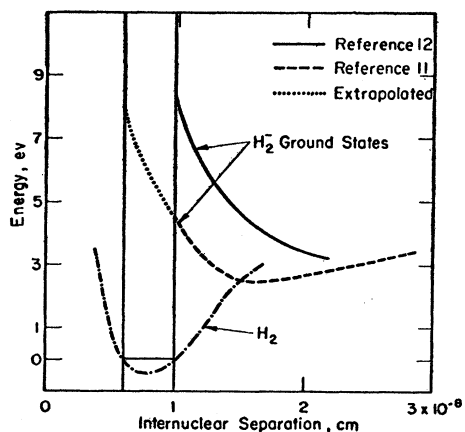


FIG. 8. H_2 and H_2^- potential energy curves. The dotted curve is inferred from the first peak of Fig. 6.

resonant parts of σ_{01} are very large compared to the cross sections normally encountered in negative ion formation processes: $1-3 \times 10^{-17} \text{ cm}^2$ compared with $1-3 \times 10^{-20} \text{ cm}^2$ for free electrons. The presence of the proton as a third body for transfer of energy and momentum apparently improves the chances for the capture of the electron.

The large peak at 6.5 keV has no counterpart in the free electron capture measurements. The electron energy corresponding to this peak would be 5.4 eV if the same assumptions are made in this case concerning the stripping-capture process. This energy would be just about right to fit a transition to the attractive H_2^- state if the calculations of Eyring, Hirschfelder, and Taylor¹¹ give a good approximation to the potential curve (Fig. 8). It would not be compatible with the potential curve calculated by Dalgarno and McDowell.¹²

¹¹ H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.* **4**, 479 (1936).

¹² A. Dalgarno and M. R. C. McDowell, *Proc. Phys. Soc. (London)* **A69**, 615 (1956).

The structure in σ_{0-1} is rather more difficult to explain quantitatively than that in σ_{01} . It may result from the formation of a complex H_3 molecule with breakup into H^- and H_2^+ .

In Fig. 9 the results for σ_I are plotted. This cross section, since it represents the total ion pair creation cross section, has contributions arising from many processes, some of which also contribute to σ_{01} and σ_{0-1} . The results have been corrected for secondary electrons

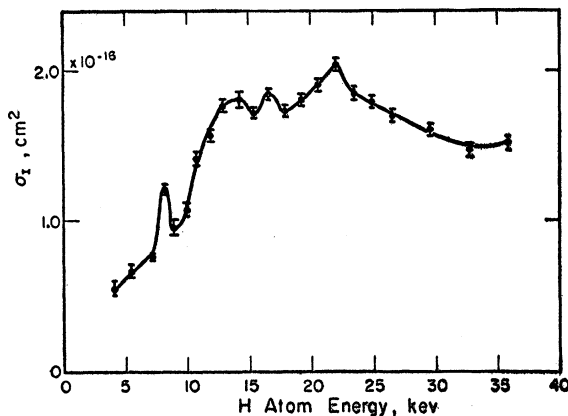


FIG. 9. Cross section for formation of ion pairs by hydrogen atoms in H_2 .

ejected at the negative condenser plate using the results of Ghosh and Sheridan.¹³

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¹³ S. N. Ghosh and W. F. Sheridan, *J. Chem. Phys.* **26**, 480 (1955).