TECHNICAL REPORT 31

FORMATION OF H^- BY ELECTRON IMPACT ON H_2 AT LOW ENERGY

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ARPA Order Number: 125-63 (Amd. 11)

Contract Number: NONR-2584(00)

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Atomic and Molecular Sciences
Research and Development
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

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Approved R. E. Fox

L. E. Fox, Director
Atomic and Molecular Sciences
Research and Development

Scientific Paper 65-9E3-113-P3
Proprietary Class 3

October 29, 1965

Formation of H^- by Electron Impact on H_2 at Low Energy*

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This letter reports the formation of the atomic hydrogen negative ion by electron impact on H_2 very close to the theoretical threshold for the production of H^- and H with zero kinetic energy via the process $e + H_2 \rightarrow H^- + H$. We find H^- formation with a very sharp onset at an electron energy of 3.73 ± 0.07 eV and a very steeply rising, albeit small, cross section which peaks very close to its onset. This observation leads to a better understanding of the potential-energy curves of the H_2^- system and has a bearing on the interpretation of vibrational excitation in H_2.

Dissociative attachment by electron impact on H_2 has been the subject of repeated studies, both without[1,2] and with[3] mass spectrometry.

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1. D. Rapp, T. E. Sharp, D. D. Briglia, Phys. Rev. Letters 14, 533 (1965).
2. G. J. Schulz, Phys. Rev. 113, 816 (1959).
3. V. I. Khvostenko and V. M. Dukel'skii, JETP 6, 657 (1958).

* This work has been supported in part by the Advanced Research Projects Agency through the Office of Naval Research.

The identity of the negative ions as well as the energy dependence of the cross section are rather well established[1,2] above electron energies of about 6 eV. One observes a broad peak in the energy range about 11 eV with a cross section in the range 1.3 to 1.5 x 10^{-20} cm^2. The first value is from Ref. (1) and the second Ref. (2); the agreement in this energy range is therefore extremely good. A sharply rising peak in H^- formation at an energy 14.0 - 14.2 eV has a cross section[1,2] in the range 2.1 to 3.5 x 10^{-20} cm^2. In the energy range 6 to 13.6 eV, the formation of H^- proceeds via a repulsive energy curve, leading to H^- ions and H atoms with kinetic energy. In the region of the peak near 14 eV, hydrogen atoms and H^- with low kinetic energy are produced, the hydrogen atoms being in the n = 2 excited states.

In previous experiments on H^- formation in this[1] and in other laboratories,[4] a small negative signal was observed at an energy about 3.7 eV, but these results were not published because doubts persisted whether scattered electrons falsify the collected currents at these low energies. It should be noted that the early theory[5] predicted that no state of H_2^- could lie at these low energies. The predictions of this theory have recently been found to be in error.[6,7] Curran,

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4. D. Rapp and D. D. Briglia, Lockheed Report LMSC6-74-64-40, state that the "peak at 3.9 eV in H_2 may possibly be caused by something other than negative ions."

5. H. Eyring, J. O. Hirschfelder and H S. Taylor, J. Chem. Phys. 4, 479 (1936) found that the lowest lying potential energy curve of H_2 traverses the Franck-Condon region at an energy about 5 eV.

6. H. S. Taylor and F. E. Harris, J. Chem. Phys. 39, 1012 (1963).

7. Yu. N. Demkov, JETP 19, 762 (1964).

working in this laboratory,[8] used a mass spectrometer to identify the 3.7 eV process as the formation of H^- from H_2 but was unable to establish that the H^- current is proportional to gas pressure, as required for a two body collision process.

Experiment

An electron beam, aligned by a magnetic field of about 150 gauss, traverses a differentially pumped collision chamber where the ions are produced by dissociative attachment. The effective energy distribution of the electron beam is reduced by use of the retarding potential difference method.[9] The ions produced in the collision chamber are expelled by a repeller which is usually operated about 2.7 volt negative with respect to the collision chamber and are analyzed by a 90 degree magnetic mass spectrometer equipped with an electron multiplier. Since the collision chamber, as well as the mass spectrometer, are differentially pumped, it is possible to reach pressures up to about 0.1 Torr in the collision chamber without appreciably scattering ions in the mass spectrometer focussing and analyzer regions.

The pressure in the collision chamber is determined by measuring the total saturated ion current at an electron energy of 70 eV on the repeller electrode; the pressure is then calculated using the known ionization cross section.

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8. R. K. Curran, private communication.

9. R. E. Fox, W. M. Hickam, D. J. Grove, and J. Kjeldaas, Rev. Sci. Instr. 26, 1101 (1955).

Results in Hydrogen

Figure 1 shows a plot of the H^- ion current as a function of electron energy. A retarding curve on the electrons, shown by the dashed curve in Fig. 1, determines the energy scale.[10] The onset of the negative ion current is determined from the high energy tail of the retarding curve, and we obtain a value of 3.73 eV for the onset. The peak of the negative ion curve is determined from the half-power point of the retarding curve and the mean of 10 determination gives a value 3.75 ± 0.07 eV. These results indicate that the H^- curve rises more steeply than can be determined from the presently available energy distribution, and the data, therefore, are not inconsistent with a much more steeply rising excitation function at threshold. Using accepted values for the dissociation energy, D, of H_2 and the electron affinity, A, for H, the onset of H^- with zero kinetic energy occurs at an energy (D-A) = (4.48 - 0.75) = 3.73 eV, in agreement with the onset observed in the present experiment.

The peak current at 3.75 eV is found to be 8% of the peak current at 14 eV. Since both these processes lead to H^- with essentially zero kinetic energy, kinetic energy discrimination should be absent, and one can obtain a cross section for the 3.75 eV process by normalizing to the previously measured cross section at the 14.0 eV peak. Depending on the value one chooses to accept for the cross section[1,2] at 14 eV, one obtains

10. When a negative potential with respect to the collision chamber is applied to the repeller--as is customary in negative ion studies--then the retarding curve on the electrons yields the correct energy scale calibration. /G. J. Schulz, J. Appl. Phys. 31, 1134 (1960)/.

a value of 1.6×10^{-21} or $2.8 \times 10^{-21} cm^2$ for the cross section at the 3.75 eV peak. It should be noted that, since the actual energy dependence near the peak could not be traced out in the present experiment because of insufficient energy resolution, the actual cross section at 3.75 eV is probably somewhat larger.

Figure 2 shows the pressure dependence of the ion currents at an electron energy, W, of 3.75 and 14.0 eV showing that both processes are linear with pressure indicating that we are dealing with two-body processes.

Isotope Effect

We have attempted to observe the isotope effect by measuring the cross section of D^- formation from D_2 in the energy range of Figure 1; in our experiments to date, we were unable to observe a D^- signal around 3.8 eV although we could observe a D^- signal at 14 eV (where the cross section[1] for D^- formation is 1×10^{-20} cm^2) with a signal to noise ratio of more than 100. This observation places an upper limit of $1 \times 10^{-22} cm^2$ on the D^- cross section in 3.8 eV range. An expression for the negative ion formation via a compound state, where "backward decay" is present, is given[7,11] by $Q_- = Q_o \exp(-2 \bar{\Gamma} \tau/\hbar)$ here Q_- is the cross section for negative ion formation, Q_o is the cross section for formation of the compound state (H_2^-), $\bar{\Gamma}$ is the mean width of the potential energy curve and τ is the time for the atoms to move to a distance where they are stabilized. This stabilization time for D^- is $\sqrt{2}$ times the stabilization time for H^-; from these considerations we arrive at a limit $2 \bar{\Gamma} \tau \geqslant 3 \times 10^{-14}$ eV sec. Assuming τ to be of the order of a vibration time, $\tau \sim 10^{-14}$ sec, we obtain

11. T. D. Holstein, Conference on Gaseous Electronics, Schenectady, N.Y. (1951).

$\bar{\Gamma} \gtrsim 1.5$ eV. Although this width seems large, it is not inconsistent with the hypothesis that the same compound state of H_2^- leads to vibrational excitation.[12] The large width of the H_2^- state causes the vibrational cross section to be broad and without appreciable structure, in agreement with previous experimental observations.[13,14] The large isotope effect observed in the present work at low energy (~3.8 eV) is in striking contrast with the small isotope effect previously reported[1] in the energy range 7-18 eV. It indicates that the level width $\bar{\Gamma}$ is considerably smaller for the high energy process of negative ion formation.

Conclusions

The fact that we observe H^- negative ion formation at 3.7 eV indicates that a potential energy curve traverses the Franck-Condon region at this energy. The large isotope effect observed in the present experiment leads us to the conclusion that the state involved here is short lived and therefore the potential energy "curve" is broad. This state may be responsible[12] not only for the H^- production observed in this experiment but also for vibrational excitation of the H_2 molecule observed previously[13,14,15]

12. J. N. Bardsley, A. Herzenberg, F. Mandl, IVth International Conference on the Physics of Ionized Gases (Science Bookcrafters, New York) 1965, p. 359, and private communication.

13. G. J. Schulz, Phys. Rev. 135, A988 (1964).

14. A. G. Engelhardt and A. V. Phelps, Phys. Rev. 131, 2115 (1963).

15. It should be noted, however, that K. Takayanagi, J. Phys. Soc. Japan 20, 562 (1965) calculates the vibrational excitation in H_2 without invoking a compound state and obtains agreement with experiment. The two viewpoints, namely "direct" excitation of vibration with the polarization force dominant, and the "compound state" viewpoint described above may not be irreconcilable.

as well as the peak in the elastic cross section[16] around 2 eV. These observations are substantially in agreement with the viewpoint of Taylor and Harris[6] and of Bardsley, Herzenberg and Mandl[12] who point out that a short-lived state of H_2^- traverses the Franck-Condon region at energies below the $H^- + H$ dissociation limit and that a small portion of this curve extends above this limit.

Acknowledgment

The authors wish to express their thanks to A. V. Phelps and P. J. Chantry for many helpful comments.

16. R. Kollath, Physikalische Zeitschrift 31, 985 (1930) and H.S.W. Massey and E.H.S. Burhop, Electronic and Ionic Impact Phenomena, Clarendon Press, Oxford, 1952, p. 215.

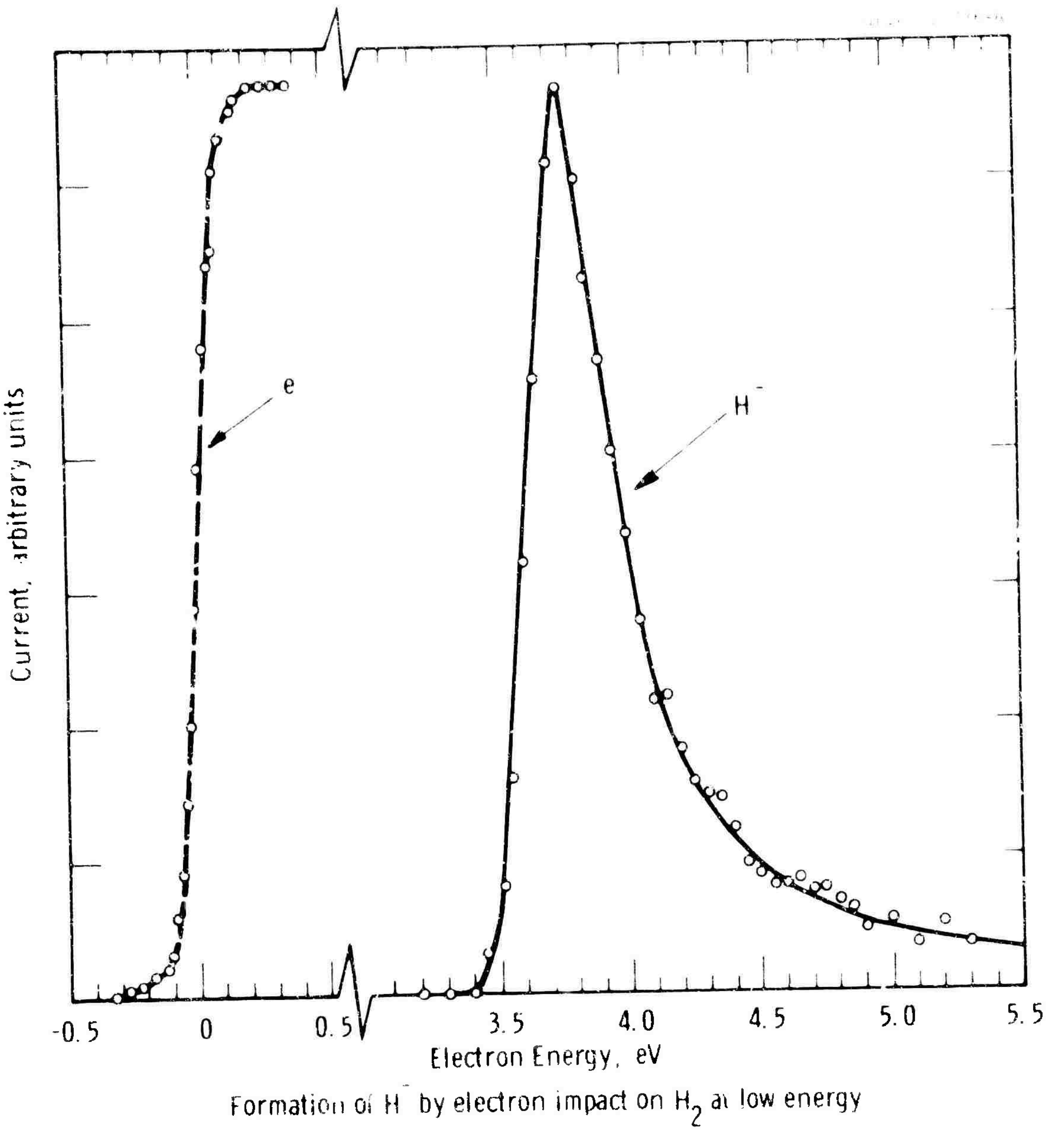

Fig. 1 Energy dependence of H^- formation from H_2 at low energies. The dashed curve is the electron retarding curve used to obtain the energy scale. The onset of H^- formation occurs at 3.73 ± 0.07 eV and the peak H^- current occurs at 3.75 ± 0.07 eV. The value of the cross section at 3.75 eV is about $2 \times 10^{-21} cm^2$. See text.

Curve 575395-A

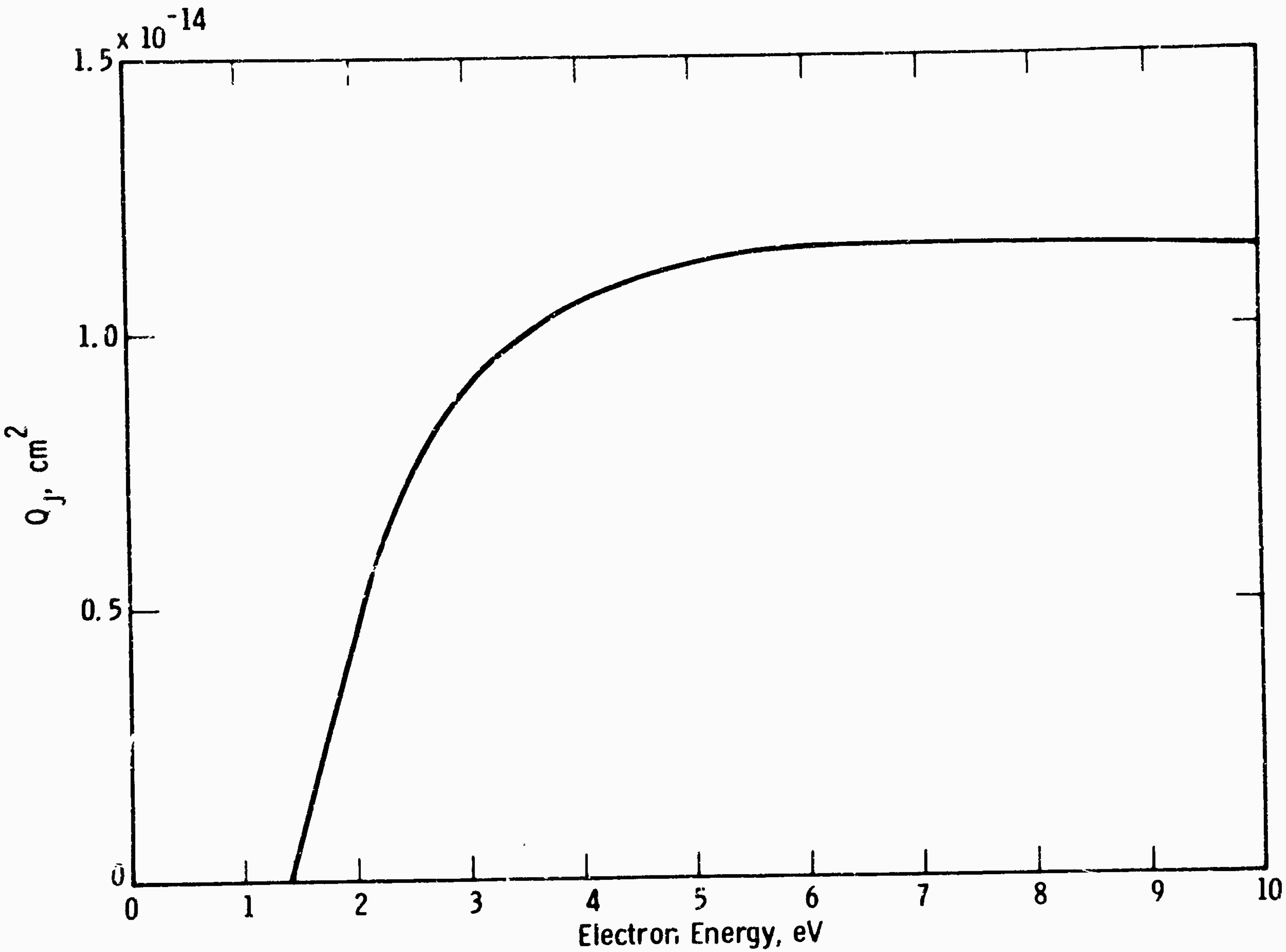

Fig. 2. Pressure dependence of two peaks involving H^- formation from H_2 with zero kinetic energy. The ratio of the ion peak at an electron energy, W, of 14 eV to that at W = 3.75 eV is 12.5.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Westinghouse Research Laboratories Pittsburgh, Pennsylvania 15235	2a REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b GROUP

3 REPORT TITLE

FORMATION OF H^- BY ELECTRON IMPACT ON H_2 AT LOW ENERGY

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report 31

5 AUTHOR(S) (Last name, first name, initial)

Schulz, G. J., Dr. PI
Asundi, R. K., Dr.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
October 29, 1965	9	16

8a CONTRACT OR GRANT NO. NONR-2584(00) b. PROJECT NO 4720 c d	9a ORIGINATOR'S REPORT NUMBER(S) 65-9E3-113-P3 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 AVAILABILITY/LIMITATION NOTICES

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
2 figures	ARPA Department of Defense Washington 25, D. C.

13 ABSTRACT

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DD FORM 1 JAN 64 1473

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Security Classification

14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
hydrogen						
deuterium						
isotopes						
cross sections						
negative ions						
electrons						
vibration						
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