FORMATION OF H⁺ BY ELECTRON IMPACT ON H₂ 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
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TECHNICAL REPORT 31

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Approved

I. E. Fox, Director
Atomic and Molecular Sciences
Research and Development
Formation of \( \text{H}^- \) by Electron Impact on \( \text{H}_2 \) at Low Energy

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This letter reports the formation of the atomic hydrogen negative ion by electron impact on \( \text{H}_2 \) very close to the theoretical threshold for the production of \( \text{H}^- \) and \( \text{H} \) with zero kinetic energy via the process \( \text{e} + \text{H}_2 \rightarrow \text{H}^- + \text{H} \). We find \( \text{H}^- \) formation with a very sharp onset at an electron energy of \( 3.73 \pm 0.07 \) 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 \( \text{H}_2^- \) system and has a bearing on the interpretation of vibrational excitation in \( \text{H}_2 \).

Dissociative attachment by electron impact on \( \text{H}_2 \) has been the subject of repeated studies, both without\(^1,2\) and with\(^3\) mass spectrometry.


\* 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 \(1.5 \times 10^{-20} \text{ cm}^2\). 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 \(\text{H}^-\)
formation at an energy 14.0 - 14.2 eV has a cross section\(^1,2\) in the range
2.1 to \(3.5 \times 10^{-20} \text{ cm}^2\). In the energy range 6 to 13.6 eV, the formation
of \(\text{H}^-\) proceeds via a repulsive energy curve, leading to \(\text{H}^-\) ions and \(\text{H}\)
atoms with kinetic energy. In the region of the peak near 14 eV, hydrogen
atoms and \(\text{H}^-\) with low kinetic energy are produced, the hydrogen atoms
being in the \(n = 2\) excited states.

In previous experiments on \(\text{H}^-\) 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 \(\text{H}_2^-\) could lie at these low energies. The predictions of this
theory have recently been found to be in error.\(^6,7\) Curran,

\(^4\) D. Rapp and D. D. Briglia, Lockheed Report LMSC6-74-64-40, state that
the 'peak at 3.9 eV in \(\text{H}_2\) 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 \(\text{H}_2\)
traverses the Franck-Condon region at an energy about 5 eV.


\(^7\) 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 focusing 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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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. 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 $3.75 \pm 0.07$ 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 $^1$, at 14 eV, one obtains

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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 $1.6 \times 10^{-21}$ or $2.6 \times 10^{-21}$ 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 $\text{D}^-$ formation from $\text{D}_2$ in the energy range of Figure 1; in our experiments to date, we were unable to observe a $\text{D}^-$ signal around 3.8 eV although we could observe a $\text{D}^-$ signal at 14 eV (where the cross section for $\text{D}^-$ formation is $1 \times 10^{-20}$ 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 $\text{D}$ 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 by

$$Q_\text{D}^- = Q_\text{H}^- \exp \left(-2 \frac{\Gamma}{\hbar} \sqrt{\frac{2}{\tau}}\right)$$

Here $Q_\text{D}^-$ is the cross section for negative ion formation, $Q_\text{H}^-$ is the cross section for formation of the compound state ($\text{H}_2^-$), $\Gamma$ is the mean width of the potential energy curve and $\tau$ is the time for the atoms to move to a distance where they are stabilized. This stabilization time for $\text{D}^-$ is $\sqrt{2}$ times the stabilization time for $\text{H}^-; \quad$ from these considerations we arrive at a limit $2 \frac{\Gamma}{\hbar} \tau \gg 3 \times 10^{-14}$ eV sec. Assuming $\tau$ to be of the order of a vibration time, $\tau \sim 10^{-14}$ sec, we obtain

\[ \Gamma \gtrsim 1.5 \text{ eV}. \] Although this width seems large, it is not inconsistent with the hypothesis that the same compound state of \( \text{H}_2^- \) leads to vibrational excitation.\(^{12}\) The large width of the \( \text{H}_2^- \) 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 (\( \sim 3.8 \text{ eV} \)) 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 \( \Gamma \) is considerably smaller for the high energy process of negative ion formation.

**Conclusions**

The fact that we observe \( \text{H}^- \) 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 \( \text{H}^- \) production observed in this experiment but also for vibrational excitation of the \( \text{H}_2 \) molecule observed previously.\(^{13,14,15}\)

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15. It should be noted, however, that K. Takayanagi, J. Phys. Soc. Japan 20, 562 (1965) calculates the vibrational excitation in \( \text{H}_2 \) 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$^{12}$ around 2 eV. These observations are substantially in agreement with the viewpoint of Taylor and Harris$^6$ and of Bardsley, Herzenberg and Mendl$^{12}$ who point out that a short-lived state of $\text{H}_2^-$ traverses the Franck-Condon region at energies below the $\text{H}^- + \text{H}$ dissociation limit and that a small portion of this curve extends above this limit.

Acknowledgment

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Formation of $H^-$ by electron impact on $H_2$ at low energy.

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 $3.73 \pm 0.07$ eV and the peak $H^-$ current occurs at $3.75 \pm 0.07$ eV. The value of the cross section at 3.75 eV is about $2 \times 10^{-21}$ cm$^2$. See text.
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 $1/2$. 
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 \(^-\) and with mass spectrometry.
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