Reports

Doubly Charged Negative Atomic Ions of Hydrogen

Abstract. *The existence of a relatively long-lived doubly charged negative atomic ion H^{2-} (and D^{2-}), isoelectronic with the lithium atom, has been demonstrated by mass spectrometry through a combined analysis of ion energy, velocity, and momentum. This species, formed in a hydrogen plasma, has a half-life of 2.3×10^{-8} seconds before it spontaneously dissociates to produce H^- ions.*

Hydrogen is the most abundant and simplest element in the universe. The hydrogen atom was the first atom to be understood from first principles, and the H_2 molecule may very well be the best theoretically understood molecular species. In fact, theoretical chemistry predicted the existence of the H^- ion (*1*) before it was demonstrated by mass spectrometry (*2*) and long before its role was postulated in astrophysics (*3*). The existence of H_2^- was also theoretically predicted (*4*), but it took almost 40 years before a long-lived H_2^- ion was unambiguously (*5*) demonstrated in the laboratory (*6*). On the other hand, the existence of a long-lived H_3^- ion, which was demonstrated in the same study (*5*), was not predicted on theoretical grounds (*7*).

A recent series of experiments has demonstrated the existence of yet another hydrogen species, a relatively long-lived doubly charged negative hydrogen ion, H^{2-}. Although H^{2-} has been suggested previously as a short-lived transient in the reaction $e + H^- \rightarrow H + 2e$ (*8*), this finding of a long-lived H^{2-} is significant. In addition to its theoretical significance, it has implications in plasma physics, including fusion research, and in astrophysics, since H^- is recognized as a predominant source of opacity in solar and stellar photospheres (*9*). This report is meant to bring this discovery to the attention of the scientific community. A paper giving the details of the experimental system and the results is being published elsewhere (*10*).

The experimental arrangement used in this study is the same as that used in the study of H_2^- and H_3^- (*5*). However, in this investigation (see Fig. 1) we made extensive use of the tandem operation of (i) an einzel lens system as an energy/charge analyzer; (ii) an $\boldsymbol{E} \times \boldsymbol{B}$ filter ($\boldsymbol{E}$ = electrostatic field; $\boldsymbol{B}$ = magnetic field) as an ion velocity selector, independent of the mass or charge of the selected species; and (iii) a sector magnet as a momentum/charge analyzer.

We consistently observed ions formed in a hydrogen plasma passing the ion velocity filter $2^{1/2}$ times faster than H^- ions—that is, at an apparent mass 1/2—while being identified by the momentum analyzer at an apparent mass 2. From a deuterium plasma we observed ions with a velocity of apparent mass 1 and momentum of apparent mass 4. Furthermore, these "unusual" H^- ions extracted from the plasma ion source comprise two populations, those focused by the einzel lens at the same voltage as the regular H^- ions and those focused at twice this voltage. The ratio between the ion currents of the first and the second type ranged between 10^{-2} and 10^{-3}, depending on the extraction voltage and on the length of the drift space between the extraction electrode and the einzel lens. The ratio between the ion currents of the regular H^- ions and the fast ions that were focused by the einzel lens at twice the voltage was of the order of 10^6.

These observations may be explained along the following lines. The detection of an ion with $2^{1/2}$ times the velocity, or twice the energy, of H^- indicates that we extract a doubly charged ion from the ion source. Such an ion acquires twice the kinetic energy on acceleration between the ion source and the extraction electrode. Furthermore, such a doubly charged ion, H^{2-}, would have to be detected by momentum/charge analyzer (the sector magnet) at apparent mass 1/2. As we did not observe any ions at this apparent mass, but rather at apparent mass 2, it appears that the original extracted H^{2-} dissociates to $H^- + e$ before reaching the sector magnet. The resulting H^-, which still possesses the original kinetic energy of its precursor, will have a momentum/charge ratio $2^{1/2}$ times higher than that of the primary H^- ion extracted at the same voltage. Since the sector magnet is calibrated in momentum (mass $\times$ velocity) units, these faster secondary H^- ions will be detected at apparent mass 2.

Because these fast secondary H^- ions have an energy/charge ratio twice that of the primary H^- ions, they will be focused by the einzel lens at twice the voltage. About 1 percent of the original H^{2-} ions do reach the einzel lens, having the same energy/charge ratio as the primary H^- ions, but they dissociate completely to fast H^- ions before reaching the momentum analyzer. From the change in the ratio between the two populations of detected fast H^- ions with the drift time between the extraction electrode and the einzel lens, we determined a half-life of 23 ± 4 nsec for the $H^{2-} \rightarrow H^- + e$ dissociation.

The ion currents of both types of fast H^- ions increased with the pressure prevailing in the region between the plasma ion source and the extraction electrode. The pressure effects of molecular hydrogen, helium, and argon were studied. At low pressures ($< 10^{-5}$ torr), the H^- ion currents were highest for argon and next highest for

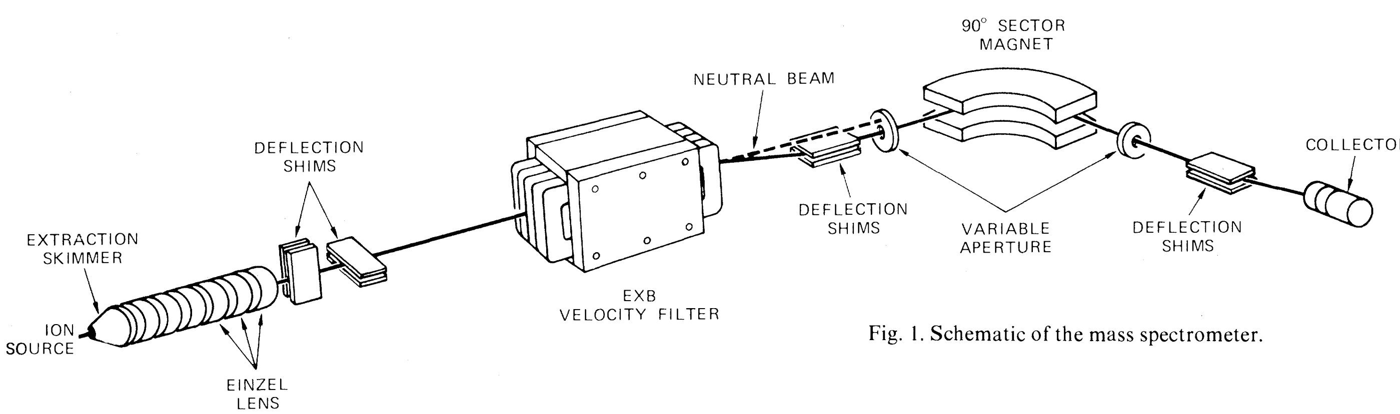

Fig. 1. Schematic of the mass spectrometer.

Table 1. Formation and decomposition of H^{2-} ions. Abbreviations: M, third body; *, excited species; k, specific rate constant; and ΔV, voltage gradient.

Reaction	Description
	Formation
$M + e \longrightarrow M^+$	Ionization of neutral gas in the ion extraction region, pressure dependent
$H^- + M^+ \longrightarrow H^{-*}$	Excitation by collision
$H^{-*} + e + M \longrightarrow H^{2-} + M$	Three-body process, pressure dependent
	Decomposition
$H^{2-} \xrightarrow{k} H^- + e$	Spontaneous dissociation
$H^{2-} + M \left\langle \begin{matrix} \rightarrow H^- + M + e \\ \rightarrow H + M + 2e \end{matrix} \right.$	Collisional dissociation
$H^{2-} \xrightarrow{\Delta V} H^- + e$	Field-induced dissociation

hydrogen. The currents increased with the second power of pressure for both hydrogen and helium, but somewhat more slowly for argon.

All the experiments carried out with a hydrogen plasma were corroborated with parallel experiments with deuterium plasma; the existence and behavior of analogous fast D^- ions were demonstrated in every instance.

This diversity of experimental results is consistent qualitatively and quantitatively with the sequence of processes shown in Table 1. Our suggested mechanism for the formation of H^{2-} is that an excited H^- ion attaches an electron to give the doubly charged atomic ion. The excited H^- can be produced efficiently by collisions with positive ions, formed in our experimental setup by electron impact ionization in the extraction region and accelerated in the opposite direction. Under our conditions, a thousandfold higher electron current (milliamperes) accompanies the H^- ion current (microamperes). The formation of H^{2-} from $e + H^{-*}$ requires removal of the excess energy by a third body. This mechanism explains the second power dependence on the pressure of hydrogen or noble gases in the extraction regions.

Under our experimental conditions (*5*), the contribution of collisional dissociation of H^{2-} to give H atoms was not studied. Also, H^{2-} undergoes field-induced dissociation to give H^- or H. This phenomenon, which contributes to the attenuation of the H^{2-} beam in our experimental setup, will be described elsewhere (*10*).

In summary, we have experimental evidence for the existence of a relatively long-lived H^{2-} ion. Since H^{2-} is isoelectronic with He^-, Li, or Bi^+, it represents an extreme case of the three-electron system (*11*). We believe that this species may play an important role in hydrogen plasmas. We do not know the lifetime of the excited H^- that is presumably the precursor of H^{2-}. If this is a long-lived state and if it can be produced by photoexcitation, then there is room to believe that an equilibrium concentration of H^{2-} may exist in interstellar space. The photoionization of this species, which is expected to take place in the infrared, may thus be observable in the astronomical infrared spectrum. The autodetachment of H^{2-} leaves H^- in an excited state and may also result in single or multiple photon emission. Since we have no information about the electronic structure of H^{2-} at present, the assignment of possible absorption or emission lines will have to wait until appropriate theoretical calculations are performed. We hope that this report will stimulate theoretical work leading to a utilization of our experimental findings to their full capacity.

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References and Notes

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6. The mass spectrometric detection of H_2^- negative ions was reported first by V. I. Khvostenko and V. M. Dukel'skii [*Zh. Eksp. Teor. Fiz.* **34**, 1026 (1958); *Sov. Phys. JETP* **7**, 709 (1958)] and recently by R. E. Hurley [*Nucl. Instrum. Methods* **118**, 307 (1974)], who also reports observing H_3^-. No isotopic confirmation of these measurements was made, however, and consequently the results have remained in doubt.
7. The structure of the ground state of H_3^- has been studied theoretically and shown to be unstable [A. Macias, *J. Chem. Phys.* **48**, 3464 (1968); *ibid.* **49**, 2198 (1968)].
8. A very short-lived H^{2-} was postulated as a resonance state in the reaction $H^- + e \longrightarrow H + 2e$ by D. S. Walton, B. Peart, and K. T. Dolder [*J. Phys. B* **3**, 2148 (1970); *ibid.* **4**, 1343 (1971); *ibid.* **6**, 1497 (1973)]. Its structure was theoretically evaluated by H. S. Taylor and L. D. Thomas [*Phys. Rev. Lett.* **28**, 1091 (1972)]. However, we do not know of any theoretical information on longer-lived H^{2-} ions.
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11. The lifetimes of two autoionization states in He^- have been studied experimentally by L. M. Blau, R. Novick, and D. Weinflash [*Phys. Rev. Lett.* **24**, 1268 (1970)] and theoretically by G. N. Estberg and R. W. LaBahn (*ibid.*, p. 1265). Metastable autoionization states in Li have been studied by P. Feldman and R. Novick [*ibid.* **11**, 278 (1963)] and calculated theoretically by J. L. Pietenpol [*ibid.* **7**, 64 (1961)].
12. The mass spectrometer used in this study was constructed as part of a program sponsored by the National Science Foundation under grant GA-37729.

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Reversal of Acetylcholine Potentials in Eel Electroplaque

Abstract. *Although the eel electroplaque is a major source of purified acetylcholine (ACh) receptor, the electrophysiological properties of the receptor have not been studied in detail. In particular, the reversal potential for the action of ACh on the postsynaptic membrane has not been measured directly. In order to obtain the reversal potential, ACh was applied iontophoretically from a micropipette onto the innervated membrane. The resulting depolarization (ACh potential) decreased in amplitude as the cell was depolarized, reached zero at a reversal potential of about –4 millivolts, and then reversed in sign as the inside of the cell was made increasingly more positive. The relation between ACh potential amplitude and membrane potential was nonlinear because of a decrease with depolarization of the peak conductance change produced by the drug.*

The eel electroplaque is one of the major sources of purified acetylcholine (ACh) receptors for chemical studies and for immunological studies on the interaction of ACh receptor antibodies with postjunctional receptors in vertebrate skeletal muscle (*1*). The fact that antibodies to electroplaque ACh receptors cross-react with ACh receptors in skeletal muscle suggests that the structures of the two receptors are similar. However, the electrophysiological properties of the electroplaque receptor, as far as they have been studied, appear to be somewhat different from those of the receptors at the motor end plates of skeletal muscle. For example, it is known that the major effect of ACh at the muscle end plate is to produce an increase in membrane conductance to Na and K, with the conductance ratio of the two ions being such that the end-plate current, and hence the end-plate potential, reverses at a membrane potential of about –15 mv (*2*). In the electroplaque, on the other hand, the reversal potential has not been measured directly; indeed, with bath-applied ACh agonists, the agonist-induced current through the postsynaptic membrane does not reverse at any potential (*3*), apparently because the overall conductance of the drug-activated channels is reduced to zero by extreme membrane depolarization. Because of this, the reversal potential has been estimated only by extrapolation of