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Observations of Diatomic and Triatomic Hydrogen Negative Ions*

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Mass-spectrometric observations have been made of HD^-, D_2^-, H_3^-, H_2D^-, HD_2^-, and D_3^-, using a hollow-cathode duoplasmatron negative-ion source operating between 0.1 and 2 Torr. Both the diatomic and triatomic hydrogen negative ions appear stable, with half-lives greater than 10^{-5} sec. Attenuation-cross-section measurements of D_2^- and D_3^- with helium between 3 and 5 keV yield average values of (5.5 and 7.0) $\times 10^{-15}$ cm^2, respectively.

The investigation of hydrogen negative molecular ions is important for understanding the electronic structure of molecular hydrogen. Most information on H_2^- has been obtained from the resonant cross-section structure observed in electron-scattering experiments and from the associative detachment production of H^- from $e + H_2$.[1] The information obtained from these experiments and the theoretical calculations imply the existence of compound H_2^- states with lifetimes between 10^{-10} and 10^{-15} sec. The present experimental results indicate, however, that stable excited states of diatomic and triatomic hydrogen negative ions exist with lifetimes in excess of 10^{-5} sec.

The mass-spectrometric detection of H_2^- negative ions was first reported by Khvostenko and Dukel'skii[2] in 1958 and recently by Hurley[3] in 1974 who also reports observing H_3^-. No isotopic confirmation of these measurements was made, however, and consequently the results have remained in doubt.

The measurements presented here were performed with a tandem mass spectrometer (see Fig. 1). This instrument combines a 30-cm Wien-type velocity filter[4] for the first-stage mass separation and a 15-cm-radius 90°-sector magnet momentum filter for the second-stage separation. This arrangement of velocity and momentum analysis ensures correct mass identification of the ionic species as well as high isotope-abundance sensitivity.[5]

The negative-ion source used is a hollow-cathode duoplasmatron[6] operating with the Z electrode offset from the anode extraction aperture by about 0.1 cm. During most of the measurements the ion source was operated at an absolute pressure of 1 Torr (calibrated by an MKS Baratron capacitance manometer), an anode-cathode voltage of 500 V, and an arc current varying between 60 and 100 mA. The H^- and D^- signals were monitored by a Faraday cup located between

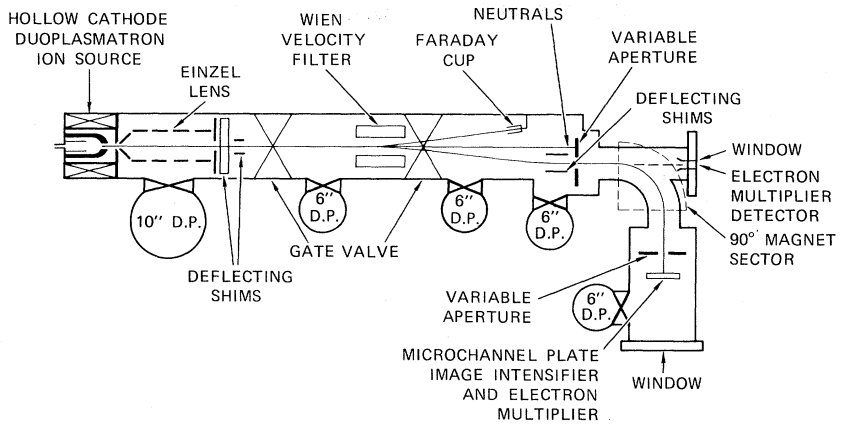

FIG. 1. Schematic of the apparatus.

the Wien filter and magnetic sector (see Fig. 1). The higher-mass-ion signals were monitored following momentum selection by pulse counting using a microchannel plate electron multiplier as detector.

A series of measurements was performed to establish the existence of diatomic and triatomic hydrogen negative ions. The signals at masses 1, 2, 3, 4, 5, and 6 (H^-, D^-, HD^-, D_2^-, HD_2^-, and D_3^-, respectively) were monitored while the H_2/D_2 pressure ratio in the ion source was changed. The total pressure of H_2+D_2 was maintained at 1 Torr during the series. The results of this work, shown in Fig. 2, indicate the following:

(1) The signal levels of H^- and D^- are proportional to the concentration of hydrogen and deuterium in the source.

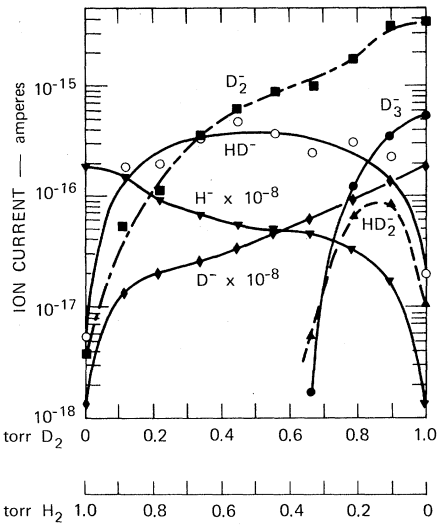

FIG. 2. Production efficiencies of H^-, D^-, HD^-, D_2^-, D_2H^-, and D_3^- as a function of the H_2-D_2 source pressure ratio. The total source is maintained at 1 Torr.

(2) Under the conditions of source operation, complete isotopic scrambling of the H_2 and D_2 gas molecules takes place.[7] The HD^- and D_2^- signals follow the source concentration of HD and D_2; however, a certain DH isotope effect is observed.

(3) The production of the D_3^- and HD_2^- signals follows the relative concentrations of H_2 and D_2 source pressure. Again a DH isotope effect is observed. (In the present study we were not able to measure the relative production efficiencies of H_2^-, H_3^-, and H_2D^- because of the interferences by D^-, HD^-, and D_2^-, respectively.)

(4) The relative production efficiencies of $D^-:D_2^-:D_3^-$ are about $1:2\times10^{-7}:3\times10^{-8}$ at 1 Torr of D_2 source pressure. These relative efficiencies vary considerably with source pressure, but the production of D^- is consistently over six orders of magnitude greater than that of D_2^- and D_3^-.

The existence of these species was further verified by operating the apparatus at a higher resolution and introducing ^3He and ^4He with the hydrogen to produce $^3He^-$ and $^4He^-$ mass markers. The Wien-filter resolution was increased to about 500 and the sector-magnet analyzer resolution was reduced to about 10 for these measurements. The mass scale was calibrated from the relation

$$\Delta m = 2m\Delta V/V, \qquad (1)$$

where V represents the potential producing the deflecting electric field in the Wien filter. Mass scanning was performed by varying this voltage. The vertical lines in Figs. 3(a) and 3(b) are the calculated positions for H_3^- and HD^- relative to $^3He^-$. With an inlet-gas mixture of equal parts

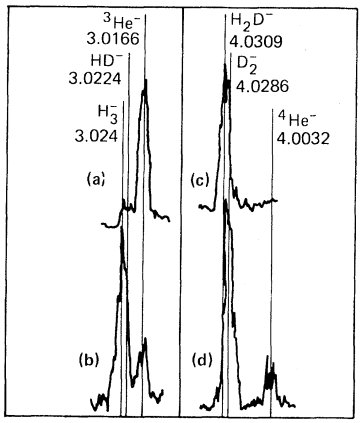

FIG. 3. Analysis of masses 3 and 4 with different source compositions. The vertical lines in (a) and (b) represent calculated positions of H_3^- and HD^- relative to that of $^3He^-$, and in (c) and (d) of H_2D^- and D_2^-. In (a) the source is fed with 40% H, 40% D_2, and 20% He. In (b) 99% H_2 and 1% ^3He is used. In (c) the source-gas feed is 80% H_2, 20% D_2, and (d) has 90% D_2 and 10% ^4He.

H_2 and D_2, predominantly HD^- ions can be anticipated at mass 3. Figure 3(a) shows a Wien-filter mass scan obtained under these conditions. The mass scan of Fig. 3(b) was obtained using H_2 gas in the source in addition to the ^3He marker. Since the resolution $m/\Delta m$ of the mass spectrometer was about 500 (full width at half-maximum), it was not possible to separate fully the H_3^- and the DH^- peaks ($m/\Delta m = 1500$). However, a shift in the peak position when the source conditions favored either H_3^- or HD^- is clearly discernible. In a similar fashion [Figs. 3(c) and 3(d)] the molecular isotopes H_2D^- and D_2^- were inferred from the shift in the mass peak occurring when the source composition was changed from pure D_2 (D_2^-) to 30% D_2, 70% H_2 (H_2D^-).

An attempt was made to determine the lifetime of the D_3^- and D_2^- species by measuring the attenuation of beam current with increasing flight time. The travel length of beam ions in the instrument is about 4 m and changing the ion energy from 15 to 3 keV increases the D_3^- and D_2^- flight time from 5.8 to 12.9 μsec and 4.7 to 10.1 μsec, respectively. To compensate for changing beam extraction and transmission efficiencies with energy, both the D_3^- and D_2^- signals were normalized to the D^- value. No decrease in D_3^- or D_2^- signal with increasing time of flight was observed, indicating that the half-life of these species is greater than 10 μsec.

The attenuation cross sections of D_3^-, D_2^-, and

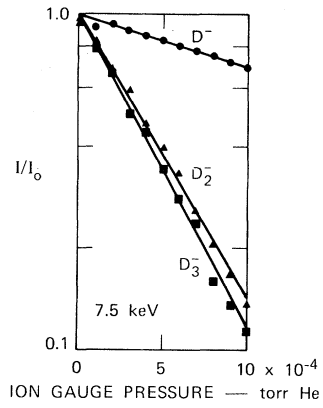

FIG. 4. Attenuation of D_3^-, D_2^-, and D^- by helium.

D^- by helium were measured as a function of energy. The cross sections were obtained from the slope of the semilog plot of the transmitted beam current versus the helium collision pressure (see Fig. 4). No significant deviation from a straight-line curve was observed in any of these plots.

Figure 5 shows the attenuation measurements for D_3^-, D_2^-, and D^- collision in helium between 3 and 15 keV. The cross sections were normalized against the D^- on He data of Risley.[8] The present D^- results show an increase in cross section with decreasing energy. This is probably due to increasing elastic-scattering contributions at lower energies, which would be more pronounced for us because our acceptance-scattering half-angle is small (0.06°) compared with that of Risley (1.1°). The D_3^- and D_2^- cross sections shown in Fig. 5 include the additional channel of collisional dissociation. The He^- cross-

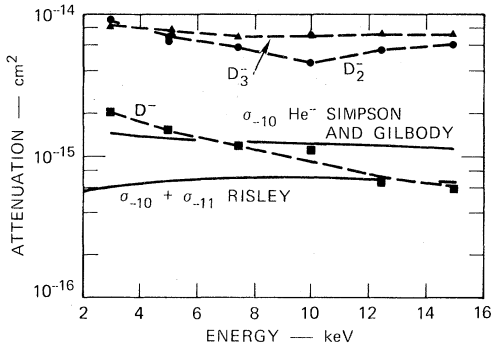

FIG. 5. Plot of attenuation cross section of D_3^-, D_2^- and D^- by helium. The dashed curves represent the present data normalized to those of Risley (Ref. 8). The measurements for $^4He^-$ detachment of Simpson and Gilbody (Ref. 9) are presented for comparison.

section data are shown for comparison.

It appears from the large cross sections and long lifetime observed for D_2^- that these species may be in a quartet electronic state analogous to that of He^- $(1s2s2p)^4P_J$.

Calculations on H_3^- indicate that this ion is unstable with respect to $H_2^- + H$ clustering.[10] The similarity between the D_3^- and D_2^- attenuation cross sections indicates that D_3^- may also be electronically excited.

The isotopic and pressure effects on the relative production efficiency of the diatomic and triatomic hydrogen negative ions are being studied further in order to elucidate the mode of formation of these species.

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Photodissociation Spectrum of CO_3^-: Evidence for a Bound Excited State*

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The photodissociation cross section for $CO_3^- + h\nu \rightarrow CO_2 + O^-$ has been measured from 6400 to 5650 Å using a drift-tube mass spectrometer and a continuously tunable dye laser. The cross section has very detailed structure, which is interpreted as reflecting the vibrational levels of a bound, predissociating state of CO_3^-.

The existence of bound excited states for negative ions is the subject of considerable current interest. Autodetaching states of atomic negative ions have been discussed in several recent Letters,[1-4] and such a state has also been observed for a molecular ion.[5] Molecular negative ions, particularly those with a large electron attachment energy, may have bound excited states that do not autodetach. Such a state has been observed[6] in C_2^-, and one probably exists[7,8] in O_3^-. We report here on the observation of a bound excited state in CO_3^- by measurement of the photodissociation cross section of this ion.

The experimental apparatus, consisting of a drift-tube mass spectrometer and a laser, is basically the same as that previously[9,10] used to measure the photodissociation cross section for CO_3^- at seven discrete wavelengths between 5287 and 4579 Å. However, the argon-ion laser used in that work has been replaced by a tunable dye laser having a resolution of 0.5 Å. The CO_3^- ions are formed by reaction[9,10] between O^- and CO_2, and drift under the influence of a weak applied electric field through CO_2 gas toward an extraction aperture. The ratio of the electric field strength to the neutral-gas density, E/N, is chosen such that the directed drift velocity is only about one tenth the mean thermal speed of the ions and gas molecules at room temperature. Thus, the ions experience a large number of thermalizing collisions following their production. Just before passing through the extraction aperture, the ions intersect the intracavity photons of the dye laser, which is chopped at 100 Hz.

The ions which pass through the extraction aperture are mass selected by a quadrupole mass