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LARGE ISOTOPE EFFECT IN THE FORMATION OF H^- OR D^- BY ELECTRON IMPACT ON H_2, HD, AND D_2

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A large isotope effect has been experimentally observed in dissociative attachment of electrons ($H_2+e \rightarrow H+H^-$)[1,2] in H_2, HD, and D_2. The cross section for production of H^- from H_2 exceeds the sum of the cross sections for H^- and D^- from HD, which in turns exceeds that for D^- from D_2.

The apparatus, a total-ionization tube similar to the device of Tate and Smith,[3] has been described previously.[4] The electron beam was obtained from an indirectly heated oxide-coated cathode and collimated by an axial magnetic field of 500 gauss. Complete collection of all the ions formed in a fixed path length of the electron beam was achieved by increasing the ion draw-out field until there was no further increase in current to the ion collector plate. Typical saturation curves for the negative ions are shown in Fig. 1, in which $V_{\|}$ is the ion draw-out field in V/cm. It is found that the H^- ions produced in H_2 may be described in terms of two different categories according to their kinetic energy.[2] The H^- ions produced by electrons between about 8 and 12.5 eV have ~3.5 eV of initial kinetic energy, whereas the H^- ions produced near 14.0 eV have almost no initial kinetic energy. It is apparent that a higher ion draw-out field is required for complete collection of the energetic H^- ions. The saturation is not completely flat at high $V_{\|}$ for 14-eV electrons because the energy spread introduced by the ion draw-out field (~±0.05 eV per 10-V/cm field) reduces the apparent cross section due to the sharp resonance energy dependence of the cross section. It was found that by using an ion draw-out field of 24 V/cm between 7 and ~12.8 eV, and 10 V/cm above ~12.8 eV, nearly complete collection could be achieved over the entire energy range. At about 12.8 eV, the ion current was essentially the same for either field. A discussion of other consistency checks is given in reference 4. The energy spread of the electron beam used in taking the data shown in Fig. 2 was 0.30 eV full width at half-height.[5] However, in a single run taken in H_2 with an electron energy distribution width of 0.15 eV, the cross section was essentially the same. Since the electron current had a smaller absolute value with the narrower distribution, the weaker ion currents were somewhat more noisy, and the results are not presented here.[5] The absolute energy scale was established in two ways. The linearly extrapolated onset of positive ions was found to be 15.4 eV[4,6] by comparison with positive ions in He, Ne, and Ar in the "total-collection mass-spectrometer" version of the total-ionization tube. Reversal of the ion draw-out field and study of the positive ions establishes the energy scale. Alter-

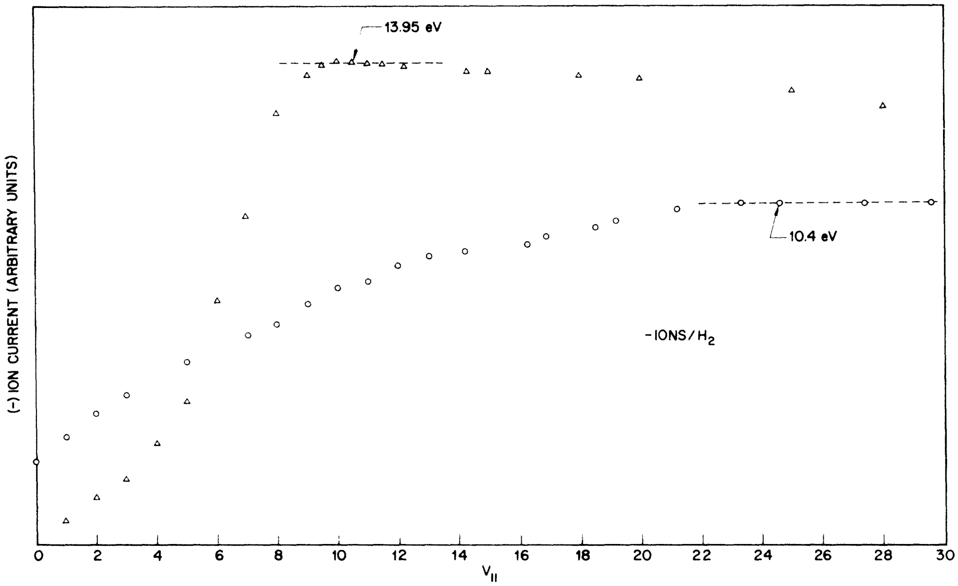

FIG. 1. Negative-ion current as a function of ion draw-out field for 10.4- and 13.95-eV electrons in H_2.

natively, by plotting electron current versus electron energy, and extrapolating the electron current to zero, one finds that the energy intercept is the contact potential. This was verified in a large number of gases. Thus, the energy scale could be established by either method, both methods agreeing to within ±0.05 eV. The ion current was automatically divided by the electron current and plotted versus electron energy on an X-Y plotter.[7] Absolute cross sections were obtained by comparison with known total cross sections for positive

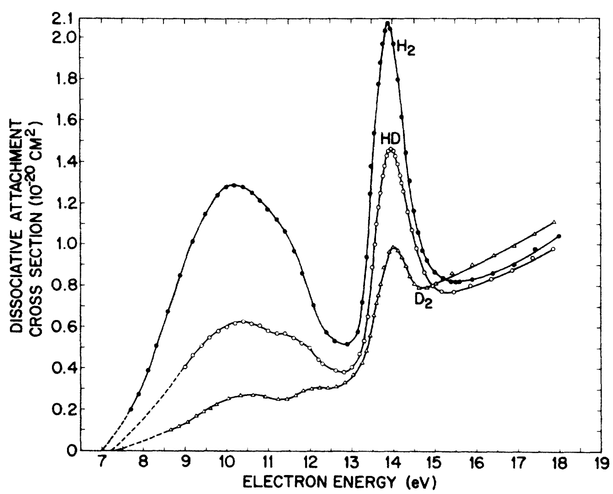

FIG. 2. Measured total cross sections for negative-ion formation in H_2, HD, and D_2 as functions of electron energy in a total-ionization tube.

ionization.[8,3]

The total cross sections for production of negative ions are shown in Fig. 2 as functions of electron energy. There are three main resonance peaks that overlap somewhat, corresponding to potential curves[9,2,10] of H_2^-. The two lower peaks correspond to states asymptotic to $H(1s)+H^-$, whereas the peak near 14 eV corresponds to an excited state asymptotic to $H(n=2)+H^-$ because the H^- ions from this state have very low kinetic energy.[2,4] The shift of the maximum of the resonance near 14 eV to higher energies with increasing mass of the isotopes is small but probably real. The shift is expected for two reasons. First, the ground-state vibrational levels lie at lower energies as the mass is increased. Second, the equilibrium internuclear distance decreases with increasing mass, leading to transitions to higher energy portions of the repulsive H_2^- potential-energy curve. The rising portion of the cross section above the 14-eV peak was originally attributed[1] to ion-pair formation ($H_2+e\rightarrow H^+ + H^- + e$). However, our results indicate that the rising portion of the cross section starts at least 1.5 eV below the minimum energy for ion-pair formation, 17.2 eV. The energy scale of reference 1 is probably too high by ~0.6 eV (see footnote 3 of reference 2), and this, coupled with the large electron-energy spread in reference 1, may have caused the authors to interpret the rising portion of the cross section as beginning at 17.2 eV. One possibility is that scattered electrons may be contributing to the negative "ion current" since the present work, as well as that of Schulz,[2] does not provide for mass analysis.[11] This may partially explain the very large discrepancy between the absolute magnitudes of the cross-section peaks near 14 eV as reported by Schulz[2] and as given herein. Electrons ejected from H_2 by positive ionization near threshold have very low kinetic energy, and may possibly reach the ion collector plate if they have the proper initial orientation. It is not certain what process produces negative ions above the third resonance peak at 14 eV, and the role of ion-pair production is unclear. It should be noted that ion-pair production may have an onset considerably above 17.2 eV if the H_2 curve that dissociates into $H^+ + H^-$ is strongly repulsive in the Franck-Condon region.

The observed isotope effect can be crudely rationalized in terms of competition between dissociation and electron ejection. When the intermediate state H_2^- is formed, it takes roughly 10^{-13} sec to dissociate. If the H_2^- has a finite probability for emission of an electron, the observed cross section for production of H^- will be depleted by this latter process. The probability of electron emission per unit time is expected to depend only upon internuclear separation and to be independent of mass. Since the dissociation process requires more time for the heavier isotopes, relatively more ejection of electrons will occur, and the yield of negative atomic ions should be lower in the heavier isotopes.

It is believed that the present results should be of significance in the theory of attachment of electrons to molecules, although it is difficult to relate our results to existing calculations.[12,13] Since it is currently believed that intermediate negative-ion formation may be responsible[14] for observed resonances in elastic scattering of electrons, one might expect to find an isotope effect in elastic-scattering resonances from the H_2 molecule.

[1] N. I. Khvostenko and V. M. Dukel'skii, Zh. Eksperim. i Teor. Fiz. 33, 851 (1957) [translation: Soviet Phys.—JETP 6, 657 (1958)].

[2] G. J. Schulz, Phys. Rev. 113, 816 (1959).

[3] J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).

[4] D. Rapp and D. D. Briglia, Lockheed Missiles and Space Company Technical Report No. 6-74-64-40 (unpublished); Bull. Am. Phys. Soc. 10, 180 (1965); "Ionization of H_2 Near Threshold by Electron Impact" (to be published).

[5] The distributions quoted were measured by retarding techniques as reported in reference 4 (to be published). The absolute ion currents with the narrow distribution were in the 10^{-14}-A range, whereas they were in the 10^{-13}-A range with the broader distribution.

[6] Note that Schulz uses the onset of H_2^+ as 15.56 eV as his standard to determine his energy scale. We believe that his energy scale may therefore be too high by ~0.15 eV, since the proper value is 15.4 eV [D. D. Briglia and D. Rapp, Phys. Rev. Letters 14, 245 (1965)].

[7] D. D. Briglia and D. Rapp, "Electron Collision Cross Section Plotter" (to be published).

[8] D. Rapp, P. E. Golden, and D. D. Briglia, Bull. Am. Phys. Soc. 10, 180 (1965).

[9] D. Rapp, T. E. Sharp, and D. D. Briglia, Lockheed Missiles and Space Company Technical Report No. 6-74-64-45 (unpublished).

[10] A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. (London) A69, 615 (1956).

[11] For example, see Fig. 2 of G. J. Schulz, Phys. Rev. 128, 178 (1962). Although the ionization tube used by Schulz is excellent for energetic negative ions, he requires a large draw-out field for low-energy ions. But at high draw-out fields, he collects scattered electrons. Thus, the low-energy H^- ions from the 14-eV resonance peak would be difficult to collect properly in his apparatus due to scattered electrons. In our apparatus, it is difficult to assess how much of a problem scattered electrons were. However, our higher magnetic field may have helped to reduce this somewhat.

[12] J. C. Y. Chen, Phys. Rev. 129, 202 (1963).

[13] J. N. Bardsley, A. Herzenberg, and F. Mandl, Atomic Collision Processes, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), pp. 415-427.

[14] C. E. Kuyatt and J. A. Simpson, Bull. Am. Phys. Soc. 10, 184 (1964).