PHYSICAL REVIEW VOLUME 109, NUMBER 6 MARCH 15, 1958

Dissociative Attachment of Electrons in Iodine. I. Microwave Determination of the Absolute Cross Section at 300°K

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(Received November 18, 1957)

Microwave techniques are used to study electron attachment to iodine molecules during the afterglow following a pulsed discharge in an iodine-helium mixture. The helium gas decreases the ambipolar diffusion loss of the electrons and assures that the electrons are in thermal equilibrium with the gas during the afterglow. It is shown that under the experimental conditions electron attachment is the dominant electron-loss process. The measured cross section for electron attachment to iodine at 300°K is $\sigma_a = 3.9\times10^{-16}$ cm^2.

STUDIES of the formation of negative ions in iodine vapor have been carried out by a number of investigators.[1-4] Hogness and Harkness,[2] using mass spectrometer techniques, demonstrated that the electron capture was the result of dissociative attachment, i.e.,

$$I_2 + e \rightarrow I^- + I. \tag{1}$$

Subsequent measurements, using electron swarm[3] and electron beam[4] techniques, have been made of the absolute attachment cross section as a function of energy; however, the results are in marked disagreement with each other concerning both the absolute magnitude and the energy dependence of the cross section.

In order to provide an independent measurement of the absolute cross section as well as to extend the measurements to much lower energies (~0.04 ev) than were previously attained, microwave techniques have been applied to the study of electron attachment during the afterglow following a pulsed discharge in iodine vapor.

I. THEORY

The rate of electron attachment is determined by measuring the decay of electron density from an initially ionized gas. Because of the requirement of quasi-neutrality ($n_+ \simeq n_- + n_e$) in the ionized gas, one has for a stationary state

$$\partial n_+/\partial t = \partial n_-/\partial t + \partial n_e/\partial t, \tag{2}$$

where n_+, n_-, and n_e refer to positive ion, negative ion, and electron concentrations, respectively. If we consider negative-ion formation and diffusion as the significant processes, the positive ions are governed by the equation

$$\partial n_+/\partial t = D_a \nabla^2 n_+, \tag{3}$$

where D_a is the ambipolar diffusion coefficient. The fundamental solution of this equation is

$$n_+ = n_+(0) \exp(-\nu_D t), \tag{4}$$

where $n_+(0)$ is the ion density at $t=0$ and $\nu_D = D_a/\Lambda^2$, Λ being the characteristic diffusion length of the containing vessel. It will be shown later in this section that the positive ions obey the usual ambipolar diffusion law even in the presence of electron attachment. Also, it will be shown that the negative ions diffuse much more slowly than the positive ions, with the result that the rate of change of negative ion density is given by

$$\partial n_-/\partial t = \nu_a n_e, \tag{5}$$

where

$$\nu_a = n_g \sigma_a v \tag{6}$$

is the attachment rate per electron, σ_a the attachment cross section, n_g the neutral-molecule density, and v the rms thermal velocity of the electrons. Thus,

$$\partial n_e/\partial t = -\nu_a n_e - \nu_D n_+. \tag{7}$$

If we assume that, at $t=0$, $n_-(0)=0$, i.e., $n_e(0)=n_+(0)$, the solution of Eq. (7) is

$$n_e = \frac{n_e(0)}{1-\nu_D/\nu_a}\left[\exp(-\nu_a t) - \frac{\nu_D}{\nu_a}\exp(-\nu_D t)\right]. \tag{8}$$

If the experimental conditions can be arranged so that the positive-ion diffusion rate is small compared to the attachment rate, then according to Eq. (8) the electron density decreases exponentially with time.

The effect of negative-ion formation on the ambipolar diffusion of the positive ions, negative ions, and electrons can be demonstrated by a simple extension of the theory concerning the diffusion of electrons and two species of positive ions.[5] The particle current density, Γ, for any of the three types of particles consists of a diffusion and a mobility term, i.e.,

$$\Gamma_X = -D_X \nabla n_X \pm \mu_X n_X E_s, \tag{9}$$

where the symbol X may be used to represent the electrons, positive ions, or negative ions. D is the diffusion coefficient and μ the mobility of the particle, and E_s is the space-charge field set up by a small difference in density between the positive and negative particles. The + sign in front of the mobility term refers to the positive ions and the − sign to the negative

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[1] For a discussion, see H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 270 ff.

[2] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928).

[3] R. H. Healy, Phil. Mag. **26**, 940 (1938).

[4] R. Buchdahl, J. Chem. Phys. **9**, 146 (1941).

[5] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

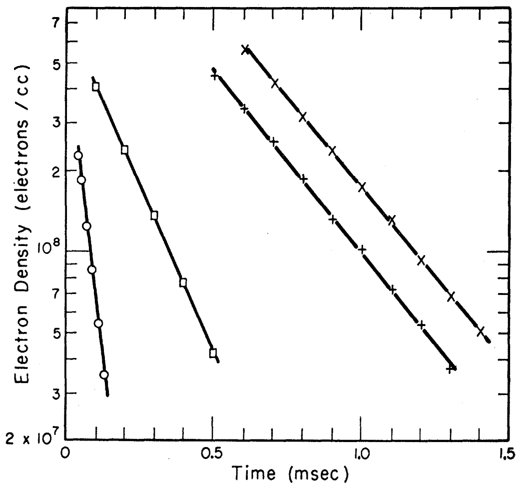

FIG. 1. Decay of electron density at 300°K in an iodine-helium mixture. The iodine vapor pressures (in mm Hg) are: ○—1.5×10^{-4}, □—2.1×10^{-5}, +—1×10^{-7}, ×—3×10^{-10}. The helium pressure is 3 mm Hg.

ions and electrons. If one solves the three equations of (9) under the conditions $\Gamma_+=\Gamma_e+\Gamma_-$, $D_e\sim1000\,D_-$ or $1000\,D_+$, and $\mu_e\sim1000\,\mu_-$ or $1000\,\mu_+$, one finds that if the negative ion to electron density ratio, $r\equiv n_-/n_e$, is less than 100, then

$$E_s\simeq-\frac{D_e}{\mu_e}\frac{\nabla n_e}{n_e}, \tag{10}$$

which is the usual ambipolar space charge field. The current equations (9) then may be simplified to the forms

$$\Gamma_+\simeq-2D_+\left(1+r\frac{\mu_-}{\mu_e}\right)\nabla n_+, \tag{11a}$$

$$\Gamma_-\simeq-2D_-\left[\frac{\mu_+}{\mu_e}(1+r)\right]\nabla n_-, \tag{11b}$$

$$\Gamma_e\simeq-2D_+(1+r)\nabla n_e. \tag{11c}$$

Thus, the ambipolar diffusion coefficient of the positive ions is given by $D_a\simeq2D_+$; i.e., in the presence of the usual ambipolar space charge field which aids the diffusion of the positive ions they move at twice the free positive ion diffusion rate. The negative ions, however, must diffuse *against* the space charge field and hence their effective diffusion rate is initially reduced to $\sim10^{-3}$ the free negative ion rate. Since $\Gamma_-\ll\Gamma_+$, the condition that $\Gamma_+=\Gamma_e+\Gamma_-$ requires that the electrons diffuse to the walls at essentially the same rate as the positive ions.

II. EXPERIMENTAL TECHNIQUE

Microwave techniques are used to measure the decay of electron density during the afterglow following a pulsed discharge in iodine vapor. These techniques are described in detail in a number of previous publications.[6,7] The gas sample to be studied is enclosed in a quartz bottle within a TM_{010}-mode microwave cavity resonant at 3000 Mc/sec. The electron density following a pulsed discharge in the bottle is determined from measurements of the change of resonant frequency of the cavity with time.

In order to obtain absolute cross sections from the measurement of the decay of electron density, it is necessary to know the electron energy distribution. During the discharge the average electron energy is the order of 1 ev. In the afterglow the electron energy decreases with time as a result of elastic recoil collisions and diffusion cooling.[8] In pure iodine this energy decay occurs on a time scale comparable to the measuring interval, and hence the electron energy is both unknown and time varying. In order to bring the electrons rapidly into thermal equilibrium with the gas at the start of the afterglow and at the same time reduce the diffusion of the electrons to the walls, helium gas at a pressure of 3 mm Hg was added to the iodine. The excitation potentials of helium are sufficiently large to assure that the helium atoms are not excited or ionized in these experiments. The resulting time for the electrons to reach thermal equilibrium with the gas is less than 50 μsec.

The iodine-helium mixture is contained in a sealed-off quartz cylindrical bottle with a tip projecting from one of the plane ends. The bottle was first evacuated and baked out at 450°C on an ultrahigh-vacuum system.[9] Crystals of chemically pure iodine were then triply distilled into the bottle and 3 mm Hg pressure of helium added before seal-off of the projecting tip.

The cylindrical bottle is enclosed in a special microwave cavity which is kept at room temperature while the projecting tip extends out of the cavity into an "oven" whose temperature can be varied from 160°K to 230°K to give vapor pressures in the range 10^{-10}–10^{-4} mm Hg of iodine. The "oven" consists of a copper cylinder containing a heating element which surrounds the projecting tip. The copper is connected by a stainless steel tube to a dry ice-alcohol or liquid nitrogen bath. By varying the power to the heater, the desired temperature, as monitored by thermocouples, is obtained at the projecting tip.

III. MEASUREMENTS

In order to avoid substantial negative ion formation during the discharge, a short pulse length ($\sim$10 μsec) is used. To simplify the analysis of the data, measurements are carried out under conditions where the attachment outweighs the diffusion loss of electrons and consequently only the first term of Eq. (8) is important. This requires that the afterglow measurements be limited to ranges where the negative-ion

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[6] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).
[7] M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).
[8] M. A. Biondi, Phys. Rev. **93**, 1136 (1954).
[9] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

concentration is less than 10–100 times the electron concentration.

Some of the measured electron decay curves are shown in Fig. 1. At the highest iodine pressure, 1.5×10^{-4} mm Hg, the decay is most rapid; as the iodine pressure is decreased the rate of attachment decreases. However, at pressures of iodine of 10^{-7} mm Hg and less, the decay rate does not decrease to the value appropriate for the ambipolar diffusion of iodine positive ions and electrons in 3 mm Hg of helium gas; instead a much larger constant decay rate is found. Mass spectrometric studies of attachment in iodine vapor[10] have shown that hydrogen iodide is formed in the measuring tube. This suggests that our observed background decay rate is the result of electron attachment to a fixed pressure of HI, presumably formed during the sealing-off of the quartz bottle. Since the vapor pressure of HI over the range 160° to 230°K is much greater than the inferred pressure of HI in the bottle,[11] varying the temperature of the projecting tip over this range does not alter the pressure of the HI in the quartz bottle.

The observed variation of the decay rate, ν_a', with iodine pressure is shown in Fig. 2. The derived rate of attachment to iodine molecules, ν_a, is obtained by subtracting the constant background value $\nu=3.0\times10^3$ sec^{-1} from the data. The slope of the line drawn through the resulting points is unity, in agreement with the expected linear dependence of the attachment rate on iodine vapor density. From Eq. (6) we find that the attachment cross section at 300°K is $\sigma_a=3.9\times10^{-16}$ cm^2. This value, obtained for an average electron energy of 0.039 ev, is an order of magnitude larger than the maximum cross section which Buchdahl[4] found to occur at ~0.4 ev. A discussion of possible origins of this discrepancy is given in part III of these articles. In addition the microwave measurements are combined with the results of mass spectrographic studies[10] to obtain the absolute cross section as a function of electron energy.

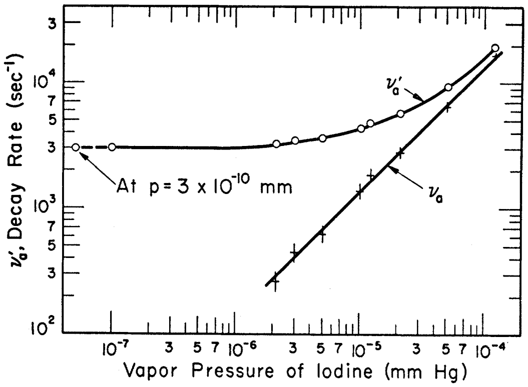

FIG. 2. The measured electron decay rate, ν_a', at 300°K as a function of the vapor pressure of iodine. The derived iodine attachment rate, ν_a, is obtained by subtracting the constant background rate determined at $p<10^{-7}$ mm Hg from the measured values of ν_a'.

The author wishes to thank various members of the Physics Department, in particular A. V. Phelps, for stimulating discussions of this work.

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[10] See R. E. Fox, following paper [Phys. Rev. **109**, 2008 (1958)], hereafter denoted as II.

[11] The mass spectrographic studies indicate that the attachment cross section is the same order of magnitude for HI as for I_2; therefore, the inferred pressure of HI in the bottle is $\sim10^{-5}$ mm Hg.