Dissociative Attachment of Electrons in Iodine. III. Discussion

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The absolute cross section, $\sigma(E)$, for electron attachment in iodine is determined from the measured values of the average cross section, $\bar{\sigma}(E')$, described in parts I and II of this series. This is accomplished by solution of the integral equation relating the average cross section, the actual cross section, and the energy distribution of the electrons. The derived cross section $\sigma(E)$ exhibits a much sharper energy dependence than that of $\bar{\sigma}(E')$ given in II, decreasing from a maximum value at zero electron energy to a half-value in $\sim$0.01 ev. The maximum cross section, $\sigma(0)\sim 3\times 10^{-15}$ cm^2, is orders of magnitude larger than the values obtained by previous investigators. It is proposed that the difference in values can be attributed to deficiencies in measurements involving electron distributions of appreciable energy spread.

IN parts I and II of this series, microwave measurements of the absolute cross section at 300°K and mass spectrometric determinations of the variation of the relative cross section with energy were described for electron attachment in iodine vapor. In part III we shall combine these measurements to obtain the absolute cross section as a function of energy and shall compare these results with those of other investigators.

I. RELATION OF ABSOLUTE CROSS SECTION TO MEASURED AVERAGE CROSS SECTIONS

We wish to determine the variation with energy of the absolute cross section, $\sigma(E)$, for the attachment of electrons of energy E to iodine molecules. However, our measurements, made either with a thermal (300°K) electron distribution in the microwave experiments or with a beam of finite energy spread ($\sim$0.1 ev) in the mass spectrometer work, represent cross sections which are an appropriate average of $\sigma(E)$, i.e.,

$$\bar{\sigma}(E')=\int_0^\infty \sigma(E)n(E,E')dE, \qquad (1)$$

where $\bar{\sigma}(E')$ is the average of the cross section over the normalized electron energy distribution, $n(E,E')$, which has an average energy E'.

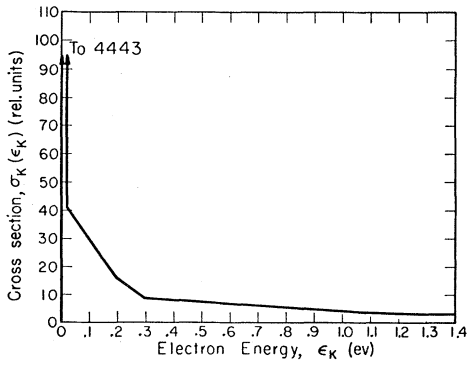

FIG. 1. Approximation of the actual cross section, $\sigma(E)$, by the piecewise linear function, $\sigma_k(\epsilon_k)$. The values ϵ_k separating the linear segments were chosen by inspection of the curve of $\bar{\sigma}(E')$ given in Fig. 2 of II.

In principle, if $n(E,E')$ is known and one measures $\bar{\sigma}(E')$ as a function of E', one can obtain $\sigma(E)$ as a function of energy. The relative values of $\bar{\sigma}(E')$ as a function of E' and the relative electron energy distribution are taken from the data for I^- and SF_6^- shown in Fig. 2 of II. As discussed in II, the SF_6^- curve represents a mirror reflection of the energy distribution of the measuring electron beam. The zero of the energy scale is taken at the maximum of the SF_6^- cross section. It is assumed that the electron energy distribution's shape is unchanged as the accelerating voltage is changed; that is, the same form of distribution is merely translated along the energy axis and thus may be represented as $n(E-E')$.

The solution of the integral equation (1) for $\sigma(E)$ is described in detail by Jeeves.[1] A brief resumé of the method will be given here:

(1) Since the measurements of $\bar{\sigma}(E')$ are in the form of a finite set of values, the integral of Eq. (1) is replaced by a finite set of integrals of the type

$$\bar{\sigma}(E_i')=\int_0^\infty n(E-E_i')\sigma(E)dE. \qquad (2)$$

(2) For $\sigma(E)$ a function was used which had the following properties:

(a) It was piecewise linear with abscissa values ϵ_k and ordinate values σ_k (see Fig. 1);

(b) It was always positive, i.e., $\sigma(E)\geqslant 0$;

(c) It was zero for negative electron energies;

(d) It permitted relatively simple curvature. Only two changes of sign on curvature were allowed. This prevented the inaccuracies in the data from causing violent oscillations in the derived $\sigma(E)$.

(3) The indicated integration was carried out numerically. The integrals (2) thus were replaced by sums. The values of the sums were:

$$\bar{\sigma}(E_i')=\sum_l A_{il}n(E_l-E_i')\sigma_l, \qquad (3)$$

where the A_{il} are suitable constants for the summation.

[1] T. A. Jeeves, Research Report 412FF142-R2, Westinghouse Research Laboratories (unpublished).

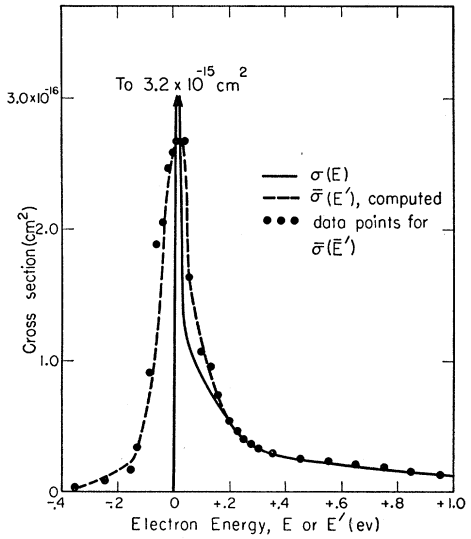

FIG. 2. The attachment cross section as a function of electron energy in iodine. The solid circles represent the measured values of $\bar{\sigma}(E')$ described in II; the solid line the derived curve of the actual cross section $\sigma(E)$ obtained by solution of the integral equation (1). The dashed line represents the fit of the data obtained with this choice of $\sigma(E)$.

(4) The values of ϵ_k were chosen by inspection of the $\bar{\sigma}(E')$ curve. The values of σ_l were determined by minimizing the sum of the squared errors between the values given by the data, and the values from Eq. (3), $\sum_i[\bar{\sigma}(E_i')-\tilde{\sigma}(E_i')]$.[2]

The problem was programmed to a Datatron[2] for solution.

The resultant curve for $\sigma(E)$ is shown by the solid curve in Figs. 1 and 2. When this derived curve is combined with the tabulated $n(E-E')$ values, the fit of the integral to the original data for $\bar{\sigma}(E')$ is that shown by the dashed curve of Fig. 2. Thus, in going from the averaged cross section $\bar{\sigma}(E')$ to the actual cross section $\sigma(E)$, we have obtained as much information about the true shape of $\sigma(E)$ as the accuracy of the original measurements combined with reasonable physical assumptions permits. The relative scale of the two curves is established by the consideration that the areas under the two curves, $\sigma(E)$ *vs* E and $\bar{\sigma}(E')$ *vs* E', must be equal. This condition was used to determine the scale for $\bar{\sigma}(E')$ in Fig. 2. It is not surprising that at higher energies, when the actual cross section varies only slightly over the energy width of the measuring electron beam, the two curves merge.

In order to obtain the absolute magnitude of $\sigma(E)$ we make use of the microwave results, which represent an absolute value of the *average* attachment rate for the particular case of electrons with a Maxwellian distribution at 300°K. For a Maxwellian distribution the fraction of electrons between E and $E+dE$ is proportional to $E^{\frac{1}{2}}\exp(-E/kT)dE$. Thus we may write

$$\frac{\nu_a(T)}{n}=\langle\sigma v\rangle_T=\text{const}\int_0^\infty\sigma(E)E\exp(-E/kT)dE, \quad (4)$$

where $\nu_a(T)$ is the average attachment rate per electron (obtained from Fig. 2 of I), n is the neutral atom density, v is the electron velocity, and the average is carried out over the thermal distribution. The indicated integration was carried out on the Datatron to establish the absolute scale of $\sigma(E)$ shown in Fig. 2.

II. DISCUSSION

The absolute cross section, $\sigma(E)$, determined from this analysis is shown on a linear scale in Fig. 2 and on a log-log scale in Fig. 3. Since the analysis was made by using linear segments to represent $\sigma(E)$, we have shown a slightly smoothed curve. Also shown in Fig. 3 are the measurements of Buchdahl[3] and of Healy.[4] Buchdahl used a total ionization tube similar to the type described in II, while Healy measured the attachment of a swarm of electrons moving through a gas under the influence of an applied electric field.[5]

In the present experiment the accuracy of the original data is not sufficient to determine the precise shape of the curve at low energies (<0.015 ev); however, it is clear that the true cross section has a much sharper energy dependence than the published "cross-section" data obtained with electron beams of ordinary energy

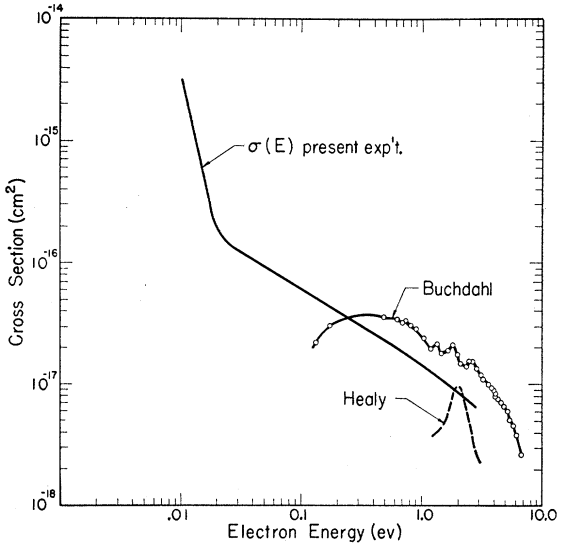

FIG. 3. A comparison of various measurements of the attachment cross section in iodine. The curves of Buchdahl and of Healy represent cross sections averaged over the particular electron energy distributions used in their measurements.

[2] Electrodata Division of the Burroughs Corporation, Pasadena, California.

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

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

[5] The energy scale for Healy's measurements is that calculated by him from measurements of D/μ, where D and μ are the electron's diffusion coefficient and mobility, respectively.

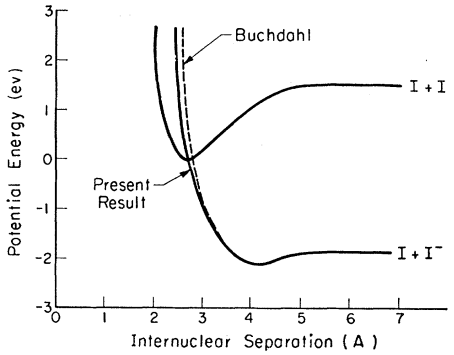

FIG. 4. Schematic representation of the potential energy curves for iodine (after Buchdahl[3]). The present results require a modification of the repulsive I_2^- curve in such a manner that it crosses the I_2 curve at its minimum.

spread, e.g., Buchdahl's measurements.[3] In fact, the actual energy dependence of the cross section is not accurately determined even with the relatively narrow energy spread of the electron beam used in the retarding potential difference (RPD) method (see Fig. 2).

The cross section falls from its maximum to its half value in $\sim$0.01 ev. It decreases monotonically, though more slowly thereafter, and merges with the $\bar{\sigma}(E')$ curve at 0.2 ev. Neither the $\sigma(E)$ nor the $\bar{\sigma}(E')$ curve shows any sign of the maximum observed by Buchdahl[3] at $\sim$0.4 ev. At higher energies ($>$0.4 ev) the values of $\sigma(E)$ are in order of magnitude agreement with the values obtained by Buchdahl and show roughly the same energy variation. Neither the present results nor those of Buchdahl give evidence for the sharp peak at $\sim$2 ev reported by Healy[4] in his swarm experiments.

Since neither the shape of the curve determined by the RPD measurements of II nor the large value at 0.039-ev energy determined from the microwave measurements of I can be reconciled with Buchdahl's reported maximum cross section at 0.4 ev, we conclude that his result is in error. Two possible experimental difficulties which could lead to an apparent maximum at 0.4 ev are (1) a change in contact potential when iodine was admitted to his tube, with a resultant shift in his energy scale, or (2) a broadening of his electron energy distribution as he went to lower electron energies, with a resultant decrease in the fraction of low-energy electrons (which exhibit a large attachment probability). Evidence for the first effect was obtained in the measurements of II in which a large change in contact potential was observed when iodine was admitted to the tube. In the mass spectrometer studies, this effect was circumvented by simultaneously measuring the attachment curves with I_2 *and* SF_6 present. The SF_6 cross section served to fix the energy scale. In a total ionization tube, where mass analysis is not possible, one can only alternately admit the I_2 and a calibrating gas with a resulting uncertainty in the energy scale. The second effect, that of a broadened energy distribution at low electron energies (low accelerating voltages), often results when it is found necessary to increase the filament temperature to maintain emission at a given value as one goes to lower accelerating voltages. It is possible that such an effect could have decreased the useful fraction of low-energy electrons to the point where the "cross section" apparently decreased as the average electron energy (accelerating voltage) was decreased.

The present observation of a maximum attachment cross section at essentially zero energy requires a modification of the potential curves suggested by Buchdahl to describe the dissociative attachment process [see Fig. 4(b) of reference 3]. From the present work, we conclude that the negative ion potential curve crosses the neutral molecule curve at its minimum as shown schematically in Fig. 4.

Finally, the present results demonstrate that, when measurements are made of a cross section which varies appreciably in an energy interval comparable to or less than the energy spread of the measuring beam, the observed cross-section *vs* energy curve differs markedly in magnitude and in shape from the actual cross-section curve. However, the techniques described in the present paper may be used to determine the actual cross section, $\sigma(E)$, from the average cross-section data, $\bar{\sigma}(E')$ *vs* E', and a knowledge of the energy distribution of the measuring beam.

It is a pleasure to acknowledge the helpful contributions of T. A. Jeeves in the machine solution of the integral equation.