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Temperature dependence of the electron attachment coefficient in iodine[a)]

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The attachment coefficient for iodine in a (1% I_2 + 99% N_2) mixture, 50 Torr total pressure, has been measured in an electron swarm experiment from 1 to 50 Townsends (1 Townsend = 1Td = 10^{-17} V cm^2). As the temperature was increased from 35 to 110°C, the attachment coefficient increased for any E/N (electric field intensity/gas number density) values greater than 7 Td. These results are compared to other experimental data and an explanation for the temperature dependence, based on the population of upper vibrational states, is presented.

I. INTRODUCTION

Many researchers[1-6] have studied dissociative attachment in iodine as it occurs in the process

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

However, only Healey[1] performed an electron swarm experiment, and Truby[2] was the only one to investigate the temperature dependence of the process.

Using an electron swarm experiment and the analysis technique developed by Grünberg,[7] this paper presents an experimental determination of the attachment coefficient for I_2 from 1 to 50 Td at 35 °C, 50 °C, and 110 °C. The results of Healey are questionable because of his use of the "method of mixtures"[8] to determine the attachment coefficient. Thus it was important that a new swarm experiment be performed to gather data for measuring the attachment coefficient directly. Recent theoretical studies[9,10] attempted to explain the temperature dependence reported by Truby, and it was hoped that the swarm experiment might support one of these theories.

The first section of the paper develops the theory of the experiment, and the second part describes the apparatus and procedure used to collect the data. The third section presents the experimental results, compares them to previous work, and offers an explanation for the temperature dependence.

II. THEORY

Analysis of the motion of an electron swarm is complicated by the diffusion of the swarm as it drifts through the gas. This experiment, however, was conducted under conditions where the diffusion of the swarm is not significant and can be ignored in the development of the theory.

The energy given to a collection of charged particles moving under the influence of an electric field E is

$$\epsilon = \int\int \rho E W d\tau\, dt , \tag{2}$$

where ρ is the charge density of the particles and W the drift velocity. Further, $d\tau$ and dt are volume and time differentials, respectively.

Consider a volume of gas in a uniform electric field between two parallel plates separated by a distance d. If n_0 electrons are placed at a point on the surface of the cathode, the charge density can be written

$$\rho_e(z,t) = e n_0 \exp[(\alpha - \eta) W t]\, \delta(x)\, \delta(y)\, \delta(z - Wt) , \tag{3}$$

with e as the charge of the electron and α and η being the ionization and attachment probabilities per unit length.

Let T_e be the transit time for the electrons to move across the gap; then the energy given to the swarm is

$$\epsilon_e = \int_0^{T_e}\int E n_0 e \exp[(\alpha - \eta) W t]\, \delta(x)\, \delta(y)\, \delta(z - Wt) d\tau\, dt$$

$$= \frac{E n_0 e}{(\alpha - \eta)} \{\exp[(\alpha - \eta) d] - 1\} . \tag{4}$$

As the electrons travel through the gas, ions will be produced. The rate of negative ion production is

$$dn_-/dt = \eta W n_e , \tag{5}$$

and the number of negative ions at a distance z from the cathode is

$$n_-(z) = \eta n_0 \exp[(\alpha - \eta) z]\, \delta(x)\, \delta(y) . \tag{6}$$

Let W_- be the drift velocity for the negative ions; the number of ions remaining in the gap after time t is then

$$n_-(t) = \frac{\eta n_0}{(\alpha - \eta)} \{\exp[(\alpha - \eta)(d - W_- t)] - 1\} . \tag{7}$$

The energy given to the negative ions during their transit time T_- is

$$\epsilon_- = \frac{e E n_0}{(\alpha - \eta)^2} \{\exp[(\alpha - \eta) d] - [1 + (\alpha - \eta) d]\} . \tag{8}$$

It has been shown by Fox[6] that, over the electron energy range studied in this experiment, no positive ions are produced from iodine. Up to 50 Td, the ionization coefficient is so small for nitrogen that it can be assumed that no positive nitrogen ions are produced. Therefore, the ionization coefficient α can be set equal to zero.

From the conservation of energy, the energy given to

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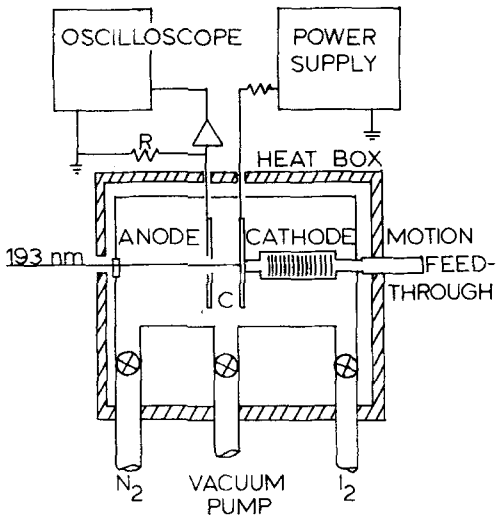

FIG. 1. Block diagram of apparatus used to study electron attachment in I_2. An ArF laser was used to provide a burst of photoelectrons at the cathode. The heat box, containing the drift region, determined the temperature at which the experiment was performed. The N_2 supply also contained the pressure gauge. The iodine was immersed in a constant temperature bath. A micrometer screw motion feedthrough can move the cathode.

the electrons and the ions must come from that initially stored in the capacitor C (the parallel electrodes). Since $W \gg W_-$, the electrons move through the gap before the ions begin to move appreciably. Thus, the energy taken from the capacitor can be split into two parts,

$$\tfrac{1}{2}C(V_e^2 - V_i^2) = \epsilon_e \,, \tag{9}$$

and

$$\tfrac{1}{2}C(V_f^2 - V_e^2) = \epsilon_- \,, \tag{10}$$

where V_i is the initial voltage across the plates, V_e is the voltage after the arrival of the electrons, and V_f is the final voltage after the arrival of all charged particles at the anode. Let $V_e = V_i + \delta v_e$ and $V_f = V_e + \delta v_-$, where δv_e and δv_- are very small compared to the applied voltage V_i. Keeping only first order terms in δv_e and δv_-, it is found that

$$\delta v_e = \frac{en_0}{C\eta d}[\exp(-\eta d) - 1] \tag{11}$$

and

$$\delta v_- = -\frac{en_0}{C\eta d}[\exp(-\eta d) - 1 + \eta d] \,. \tag{12}$$

The ratio of the total voltage change to the change due to the electrons[7] yields an expression containing the attachment coefficient,

$$R = (\delta v_e + \delta v_-)/\delta v_e = \eta d/[1 - \exp(-\eta d)] \,. \tag{13}$$

III. EXPERIMENTAL APPARATUS AND TECHNIQUES

The principle of the experimental method[11] is to produce a burst of photoelectrons at a cathode by means of light from an ArF laser. The laser operated at 193 nm with a pulse width of 17 nsec. The beam was steered and focused to a 0.1 cm diam spot on the cathode.

The measurement of the temperature dependence of the attachment coefficient required the ability to control the temperature inside the drift region apparatus. To accomplish this, the major portion of the vacuum system was placed inside a thermally insulated box whose temperature could be varied from room temperature to 150 °C through the use of a controlled heating element.

A schematic diagram of the apparatus is shown in Fig. 1. The electrodes used in the drift region were each 2.5 cm in diameter. The gap between the electrodes was adjustable from zero to 1.250 cm, with an accuracy of ±0.0025 cm.

To accurately measure the pressure in the apparatus, a Texas Instruments Fused Quartz Precision Pressure Gauge was connected to the system through the nitrogen supply line. The iodine vapor pressure[12] was fixed by placing 50 g certified grade iodine inside a stainless steel cylinder that was immersed in a constant temperature bath located next to the insulated box. The supply line from the cylinder to the box was wrapped in a heat tape that kept the temperature of the line the same as that inside the box. The temperature of the bath could be set from 0 °C to 70 °C with a stability of ±0.1 °C, and was always kept below that of the drift region.

The 10^{10} Ω resistor connected to the anode produced a large RC time constant that gave a long, flat top to the voltage waveform displayed on the oscilloscope. In Fig. 2 a set of typical oscilloscope traces are shown. The discontinuity in the slope at the arrival of the electrons defines δv_e and δv_- which can be used in Eq. (13) to solve for η. It is important to note that fluctuations in the laser intensity do not affect the value obtained for the attachment coefficient.

IV. RESULTS AND DISCUSSION

A. Experimental results

The data obtained for the attachment cross section η/N' as a function of E/N are shown in Fig. 3. Each

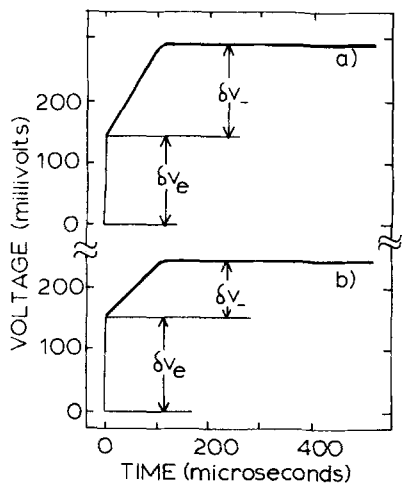

FIG. 2. Oscilloscope traces showing electron attachment in (I_2+N_2) at 10 Td. Trace (a) was taken at 110 °C, and (b) was recorded at 35 °C. δv_e and δv_- have been identified for each trace.

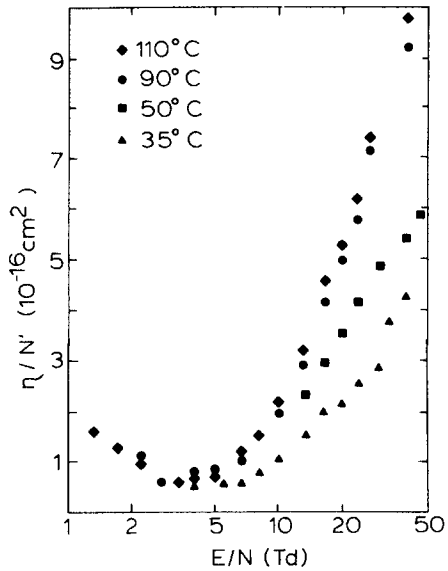

FIG. 3. Temperature dependence of the attachment coefficient of 1.0% I_2 in approximately 50 Torr of nitrogen as a function of E/N. N' is the number density for I_2 and N is the total gas number density.

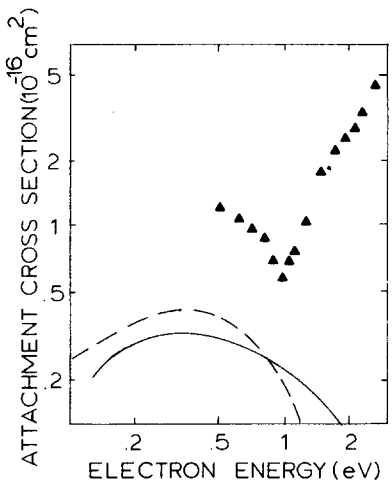

FIG. 4. Effective electron attachemtn cross section for I_2 as a function of electron energy. The electron energy for the present results ( ) is the mean swarm energy while the results of Buchdahl (——) and of Frost and McDowell (— —) are plotted against the electron beam energy.

point represents an average of at least five individual measurements. These values are relatively accurate to ±5% with an absolute accuracy of ±15%. The relative accuracy is determined from the spread in the data and the absolute accuracy is limited by the knowledge of the iodine concentration and the exact temperature in the drift region. The most noticeable feature of the attachment cross section is its increase with temperature at higher E/N values.

The only other swarm data available are those of Healey[1] taken at 15 °C. Using his "method of mixtures," he combined data for iodine in helium, iodine in carbon dioxide, and pure iodine. The combined result for η/N' is about an order of magnitude below the present results shown in Fig. 3 over the range of 35–50 Td.

The attachment cross section in iodine has also been measured by Buchdahl[3] and by Frost and McDowell[4] using electron beam techniques. In order to compare directly with their data, it is assumed that small quantities of iodine do not greatly change the electron energy distribution from that of pure nitrogen. With this assumption, it is possible to plot the new results against $(3/2)D_T/\mu$ (transverse diffusion/electron mobility), where the D_T/μ values for nitrogen were those obtained by Crompton.[13] Figure 4 shows all three sets of data. A value of 3.9×10^{-16} cm^2 has been obtained for an electron energy of 0.04 eV by Biondi,[5] who used microwaves to study the rate of electron decay in a stationary afterglow of (I_2 + He) mixtures.

B. Temperature dependence

When Truby first reported the temperature dependence of the attachment coefficient in iodine, he suggested that the increase in the coefficient might be caused by increased populations in upper vibrational levels of I_2 at higher temperatures.[2] The vibrational levels are closely spaced in I_2 (about 215 cm^{-1}) and the first five or six levels can be populated over the temperature range studied. Using the equation developed by Herzberg,[14] the fractional populations for the $v=0$ to $v=5$ vibrational states were calculated and are listed in Table I. The rotational levels are also very tightly spaced, making it almost impossible to populate rotational levels of lower vibrational state that have more energy than the next highest vibrational state.

To explain the temperature dependence of η/N', it must be assumed that dissociative attachment takes place in two steps[15]:

$$e + I_2 \rightarrow I_2^{-*} \rightarrow I + I^- . \qquad (14)$$

TABLE I. Fractional populations of the lower vibrational state of I_2 at different temperatures (Ref. 14).

Temp(°C) \ Vibrational state	0	1	2	3	4	5
Energy (cm^{-1})	107	322	536	751	966	1180
35	0.632	0.234	0.086	0.032	0.012	0.004
50	0.614	0.238	0.093	0.036	0.014	0.005
90	0.573	0.246	0.107	0.046	0.020	0.008
110	0.554	0.249	0.112	0.051	0.023	0.011

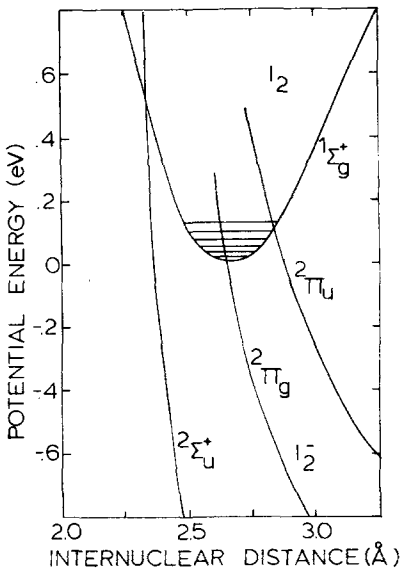

FIG. 5. Relevant parts of potential energy curves for I_2 and I_2^- as a function of internuclear distance. $^2\Sigma_u^+$, $^2\Pi_g$, $^2\Pi_u$ are I_2^- curves. The vibrational levels ($v = 0$ to $v = 5$) for I_2 are drawn to scale and the locations of the curve crossings for $^2\Pi_u$ and $^2\Pi_g$ are approximately correct.

Figure 5 shows the potential energies involved in these processes. It has been proposed by Person[16] and Matsuzawa[17] that two $^2\Pi$ states of I_2^{-*} cross the I_2 potential curve near its minimum. A displacement of the crossing from the minimum coupled with the changed populations of the vibrational states could explain the increase in the attachment coefficient as the temperature increased.

Shipsey,[9] using the theory of O'Malley for dissociative attachment, attempted to fit Truby's data and the best fit placed the $^2\Pi_u$ crossing at 0.066 eV above the I_2 ground state minimum; this corresponds to crossing the I_2 curve at $v = 2$. The present results from the swarm experiment appear to be better fit by Shipsey's $^2\Pi_u$ curve that crosses at $v = 4$. Recently, Birtwistle and Modinos,[10] using their own theory, tried to find the curve crossing point for $^2\Pi_u$ on the I_2 curve. Their calculations, with Truby's data, predicted the crossing to be at 0.14 eV above the I_2 minimum, which is between the $v = 4$ and $v = 5$ states.

From Table I, it can be seen that the fractional population of the $v = 4$ state nearly doubled over the temperature range studied, while the fraction in $v = 2$ increased by only 30%. Calculations of the fraction in rotational states[16] of the $v = 4$ level above 0.14 eV show a fourfold increase from 35 to 110 °C. These dramatic changes in populations of the $v = 4$ state could explain the significant increases in the attachment coefficient, since more of the I_2 molecules would be in a favorable position for electron attachment if the predicted curve crossing of Birtwistle and Modinos is correct.

Neither Shipsey's work nor that of Birtwistle and Modinos was able to simultaneously calculate two distinct I_2^{-*} curves crossing the I_2 ground state as were predicted by Person[16] and Matsuzawa.[17] However, the data presented in Figs. 3 and 4 seem to show two distinct processes, one at mean electron swarm energies above 0.9 eV. It appears that the low energy process could move through the $^2\Pi_g$ state of I_2^{-*} while the higher energy process follows the $^2\Pi_u$ curve. The location of the $^2\Pi_g$ crossing near the I_2 minimum would make this process less temperature dependent, but the present data are insufficient to verify any temperature effects.

Although Shipsey's predicted curve crossing[9] could be correct, these results give better support to the theoretical predictions of Birtwistle and Modinos.[10] Therefore, it appears that dissociative attachment is a two step process[15] with the $^2\Pi_u$ potential energy curve crossing the I_2 ground state curve at 0.14 above the ground state minimum. Further experimental and theoretical studies are needed to determine the exact location of the $^2\Pi_g$ curves.

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