Physics Faculty Research & Creative Works   Physics

01 Jan 1979

Negative Ion Production Rates In Rare Gas-Halide Lasers

Kaare J. Nygaard
Missouri University of Science and Technology

Howard L. Brooks

Scott R. Hunter

Negative Ion Production Rates in Rare Gas–Halide Lasers

KAARE J. NYGAARD, SENIOR MEMBER, IEEE, HOWARD L. BROOKS, AND SCOTT R. HUNTER

(*Invited Paper*)

Abstract—This paper reports on dissociative electron attachment in F_2, NF_3, Cl_2, and I_2. The principle of the method is to produce a short burst of photoelectrons from a photocathode by means of light from an argon-fluoride laser. Subsequently, by studying the motion of electrons and negative ions in a constant electric field (E) region, information is obtained about drift velocities and effective attachment cross sections. Helium, argon, and nitrogen were used as buffer gases. Of particular interest is a very strong temperature dependence of the attachment coefficient in I_2. Measurements were taken from 35 to 110°C, covering an E/N range of 1-50 Townsend. An explanation based on vibrational excitation is presented.

I. INTRODUCTION

THE MAJOR purpose of this paper is to discuss properties of electrophilic molecules of importance in rare gas-halogen lasers. The characteristics and modeling of this type of lasers have recently been reviewed by other workers [1]-[3] and will not be reiterated here. The emphasis will be on the *gaseous* electronics aspects of the problem, and *not* on the *quantum* electronics. The amount of data available on negative ion production in general is sizeable [4], but when it comes to special cases like F_2, NF_3, and Cl_2 at energies of a few electron volts, very little information was available until recently, mostly due to experimental difficulties.

In this paper, results are presented pertaining to the attachment coefficient $\eta(cm^{-1})$ and the rate coefficient $k(cm^3/s)$. If the density of attaching molecules is $N'(cm^{-3})$, the quantity η/N' represents an *effective* cross section for attachment averaged over the electron energy distribution in the discharge. A determination of the average energy would be very important when speculating on the properties of novel laser systems. One significant step in that direction is to measure the electron drift velocity W in laser gas mixtures [5]. Once the drift velocity is known, the rate coefficient for two-body reactions can be determined from

$$k = \frac{\eta}{N'} W. \tag{1}$$

In cases where simultaneous measurements of electron drift velocities and attachment coefficients in gas mixtures were made, results for the rate coefficient are reported. If data on the actual drift velocity are not available, great care should be exercised when using values obtained in the pure buffer gas at certain N and E/N values to obtain the rate coefficient. (N is the number density and E is the applied electric field. E/N will be expressed with the unit of 1 Townsend $\equiv$ 1 Td $\equiv 10^{-17}$ V · cm^2.)

It would be ideal to report data on the attachment rate as a function of average electron energy $\langle \epsilon \rangle$. Unfortunately, the experimental method is not able to measure $\langle \epsilon \rangle$ and, therefore, this paper will use

$$\langle \epsilon \rangle = \frac{3}{2} \frac{D}{\mu} \tag{2}$$

in the pure buffer gas where D and μ are the electron diffusivity and mobility, respectively. This is true only for a Maxwellian distribution. In a laser discharge supporting a high number of inelastic processes, the actual distribution is strongly *non-Maxwellian*, and (2) may, not be used. It does, however, give an upper bound on the energy. In most of the data presented in this paper, η/N' (or k) is plotted as a function of the well-defined parameter E/N to avoid the ambiguity in the average electron energy.

The material in this paper is organized as follows: in Section II the theoretical background for the method is discussed and the apparatus is described in Section III. In Section IV results are presented in F_2, NF_3, Cl_2, and I_2 with comparisons to other workers. Finally, in Section V recommendations are given for future research on electron transport coefficients that are needed for modeling of rare gas-halide and mercury-halide laser systems.

II. METHOD

If the cross section $\sigma(\epsilon)$ for attachment in a reaction such as

$$F_2 + e^- \rightarrow F + F^- \tag{3}$$

were known, the corresponding rate coefficient as a function of average energy $\langle \epsilon \rangle$ could be calculated from

$$k(\langle \epsilon \rangle) = \sqrt{2/m} \int \sqrt{\epsilon}\, \sigma(\epsilon) f(\epsilon)\, d\epsilon \tag{4}$$

requiring the electron energy distribution $f(\epsilon)$ to be known.

Chantry [6] has recently succeeded in measuring the cross section for reaction (3) in a beam experiment, and he obtained results for k that are in good agreement with those from plasma and swarm experiments. Beam experiments are "cleaner" in that often one process can be studied at a time, but a practical difficulty is that the spread in beam energy may equal the energy itself below 0.1 or 0.2 eV. On the other hand, in a swarm experiment the effect of the low energy electrons is automatically and correctly taken into account when the attachment coefficient is measured. However, information about specific processes may be lost in practical situations characterized by several inelastic collisions. For these reasons, it is important that beam and swarm experiments develop along parallel avenues of research.

In these experiments, the following method [7] has been used to determine the attachment coefficient η. At time $t = 0$, n_0 photoelectrons are generated at a photocathode by means of light from a pulsed laser, as illustrated in Fig. 1. The resulting group of electrons will drift against the electric field $\vec{E}$ toward the anode. As some of the electrons are lost in negative ion production and new electrons are produced by Townsend ionization, the measured current transient will change, which is the principle of the method.

The continuity equation governing the motion of the electrons is given by

$$\frac{\partial n_e}{\partial t} + W \frac{\partial n_e}{\partial z} - D_T \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial n_e}{\partial r} \right) - D_L \frac{\partial^2 n_e}{\partial z^2}$$
$$= -(\eta - \alpha) W n_e \qquad (5)$$

where $n_e = n_e(z, r, t)$ is the electron number density as a function of position and time and D_T and D_L are the *transverse* and *longitudinal* electron diffusivities, respectively. Furthermore, α represents Townsend's first ionization coefficient. If the initially produced photoelectrons can be described as δ-functions in space and time, the solution to (5) may be written as

$$n_e(r, z, t) = \frac{n_0}{4\pi D_T t} \exp\left[-(\eta - \alpha) W t\right] \exp\left[-\frac{r^2}{4D_T t}\right]$$
$$\cdot \left\{ \frac{z}{Wt} \exp\left[-\frac{(z - Wt)^2}{4D_L t}\right] \frac{1}{(4\pi D_L t)^{1/2}} \right.$$
$$- \frac{(2d - z)}{Wt(4\pi D_L t)^{1/2}} \exp\left[-\frac{(z - 2d - Wt)^2}{4D_L t}\right]$$
$$\left. \cdot \exp\left[2\lambda_L d\right] \right\}. \qquad (6)$$

Equation (6) is the solution to (5) with boundary conditions $n = 0$ at $z = d$ and $n \simeq 0$ at $z = 0$, where λ_L is defined as

$$\lambda_L \equiv \frac{W}{2D_L}. \qquad (7)$$

Neglecting diffusion, the following expressions for the currents of electrons and negative and positive ions are obtained:

$$I_e(t) = \frac{n_0 e}{T_e} \exp\left[(\alpha - \eta) W t\right] \qquad (8)$$

for

$$0 \leqslant t \leqslant T_e,$$

$$I_n(t) = \frac{n_0 e}{T_n} \frac{\eta}{(\alpha - \eta)} \{\exp\left[(\alpha - \eta)(d - W_n t)\right] - 1\} \qquad (9)$$

for

$$T_e \leqslant t \leqslant T_n + T_e$$

and

$$I_+(t) = \frac{n_0 e}{T_+} \frac{\alpha}{(\alpha - \eta)} \{\exp\left[(\alpha - \eta)d\right] - \exp\left[(\alpha - \eta) W_+ t\right]\} \qquad (10)$$

for

$$T_e \leqslant t \leqslant T_+ + T_e.$$

In (8)–(10) subscripts e, n, and $+$ have been used to identify transit times T and drift velocities. (Conventionally, W is used for the electron drift velocity.)

A practical way to perform an experiment to determine attachment and ionization coefficients is to integrate the electron current form 0 to T_e and then to measure the corresponding voltage drop over the load resistor R as

$$V_R(T_e) = \frac{n_0 e}{C} \{1 - \exp\left[(\alpha - \eta)d\right]\}. \qquad (11)$$

Subsequently, by waiting until *all* charge carriers have left the gap, a voltage drop could be measured as

$$V_R(\infty) = \frac{n_0 e}{C} \eta d \left\{1 - \frac{\alpha}{\eta} \exp\left[(\alpha - \eta)d\right]\right\}. \qquad (12)$$

Taking the ratio of (11) and (12) yields

$$\frac{V_R(T_e)}{V_R(\infty)} = \frac{1}{\eta d} \frac{\{1 - \exp\left[(\alpha - \eta)d\right]\}}{\left\{1 - \frac{\alpha}{\eta} \exp\left[(\alpha - \eta)d\right]\right\}}. \qquad (13)$$

Notice that both α and η can be determined from (13) by measuring the voltage ratio as a function of electrode separation d while keeping E/N constant. If $\eta \gg \alpha$, then (13) simplifies to

$$\frac{V_R(T_e)}{V_R(\infty)} = \frac{1 - \exp(-\eta d)}{\eta d}, \qquad (14)$$

which is identical to Grünberg's result [8]. Since η is determined from voltages read from the same transient, there is no need to worry about fluctuations in laser energy from pulse to pulse.

III. EXPERIMENTAL

In cases where $\alpha - \eta \approx -\eta$, i.e., at sufficiently low values of E/N, (14) has been used to determine the attachment coefficient η. The main features of the apparatus are shown in Fig. 1. The vacuum chamber is made from stainless steel and is pumped by two 25 1/s ion pumps to an end vacuum of about 10^{-7} torr. A mechanical forepump is separated from
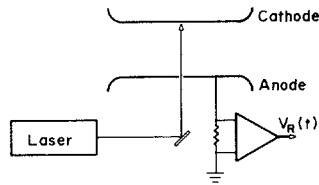
Fig. 1. Schematic diagram of the apparatus. Light from an ArF laser (193 nm) is focused onto the cathode of a drift gap producing a burst of photoelectrons. The integrated voltage drop across the anode load resistor contains information about the electron drift velocity and attachment and ionization coefficients.
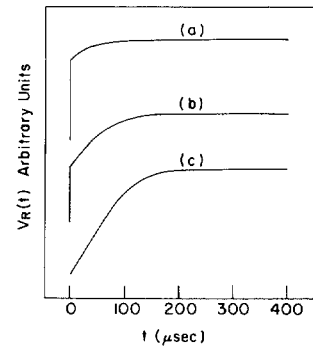

Fig. 2. Typical retraced oscillograms of integrated voltage transients (displaced in the vertical direction) chosen to demonstrate the cases of (a) weak, (b) intermediate, and (c) strong attenuation due to dissociative attachment.

the high vacuum volume by zeolite and active carbon traps. The system is usually baked out overnight at about 100°C.

Typical gas mixtures consisted of 0.1-1 percent of the attaching gas with argon, helium, or nitrogen as buffer gases. All partial and total gas pressures were measured to an accuracy of 1 percent with an array of MKS Baratrons with full pressure ranges of 1, 10, 100, 1000, and 10 000 torr. With fluorine great care was exercised to ensure proper passivation of the apparatus [9].

The electrodes are either aluminum or stainless steel with a diameter of 20 cm. The electrode separation was adjusted between 0.5 and 4 cm by a micrometer screw.

The salient feature of the experiment is to use light from pulsed ultraviolet lasers to produce photoelectrons at the cathode (upper electrode in Fig. 1). What is needed is about 10^6 photoelectrons emitted from the cathode surface to form a "measurable" swarm. The photoelectric efficiency of the cathode depends very strongly on layers of fluorides and possibly on layers of adsorbed HF formed when fluorine reacts with the small amount of water present on the surface, even after a vacuum bakeout. Due to these difficulties, it was necessary to use photoelectric efficiencies (defined as number of photoelectrons emitted into the gap divided by the total number of photons incident per laser pulse) as low as 10^{-10}.

In the first experiments [5], [9], light from a xenon ion laser [10] characterized by a wavelength of 2315 Å and a pulse halfwidth of about 100 ns was used. This pulse duration is sufficiently short to study attachment, but is too long to measure electron transit times of a few hundred nanoseconds.

There were difficulties in operating the xenon ion laser reliably over a long period of time, and it was decided instead to use an argon-fluoride laser producing 200 kW at 1930 Å with a pulsewidth of about 17 ns. Basically, the design is that of a modified Tachisto Tac II CO_2 laser [11] in which the transverse discharge is preionized by a flashboard and driven by an LC inversion circuit. The Rogowski profile electrodes are 60 cm long and are separated by 2 cm; the discharge itself is approximately 3 mm wide, giving a discharge volume of 36 cm^3. CaF_2 windows are used at normal incidence to contain the mixture. The 1 m optical cavity consists of a 5 m radius full reflector and a flat 40 percent transmitting output coupler. With this laser, there were few difficulties in producing 10^6-10^7 photoelectrons per laser pulse. The light was focused through a small hole in the anode onto a 1 mm diameter spot on the cathode. In another geometry, a 1 cm diameter area on the cathode was illuminated. The results obtained are indepen-

dent of light intensity and total number of photons per laser pulse. On the underside of the anode (not shown), a Teflon collimator was installed in order to eliminate the effect of stray light in the apparatus.

The integrated voltage transient due to the motion of electrons and negative ions [see (11), (12)] is measured across the load resistor R (10^{10}-10^{11} Ω) via a unitary gain impedance converter. The RC time constant of the circuit is about 1 s, which is much longer than a negative ion transit times of about 200 μs.

Fig. 2 shows typical data. Curve (a) shows the case of "weak" attenuation, i.e., most of the electrons drift to the anode and contribute to the almost instantaneous rise in collected charge. In curve (b), an increased attachment rate is shown, where about half of the electrons are lost in negative ion production. The slowly increasing part of the curve shows the integrated negative ion current and is of the form

$$Q_n(t) = \int_0^t I_n(t)\,dt = \frac{en_0}{T_n}\left[t - \frac{\exp(-\eta d)}{\eta W_n}\right]$$

$$\cdot [\exp(\eta W_n t) - 1]. \tag{15}$$

In curve (c) most of the electrons are absorbed close to the cathode, and all that is left is a cloud of negative ions drifting across the gap in about 200 μs. The method can be used to determine the attachment coefficient η when the voltage ratio $V_R(T_-)/V_R(T_n)$ falls in the range from 0.1 to 0.9. The overall accuracy in η/N' is ±12 percent.

IV. RESULTS AND DISCUSSION

A. Fluorine (F_2)

Starting out with a mixture of 1 percent F_2 in 10 torr of helium, the results for η/N' are shown in Fig. 3. The data for η/N' are absolute since the density of fluorine molecules was measured absolutely. After careful bakeout and replenishing the gas mix every half hour, reproducibility on a day-to-day basis was easily obtained. The fluorine gas was 98 percent pure [12].

By expanding the time scale in Fig. 2, the electron transit time T_e can be observed and the electron drift velocity is found from $W = d/T_e$ [5]. Fig. 4 shows drift velocity measurements in pure helium as well as with 0.2 and 1 percent F_2
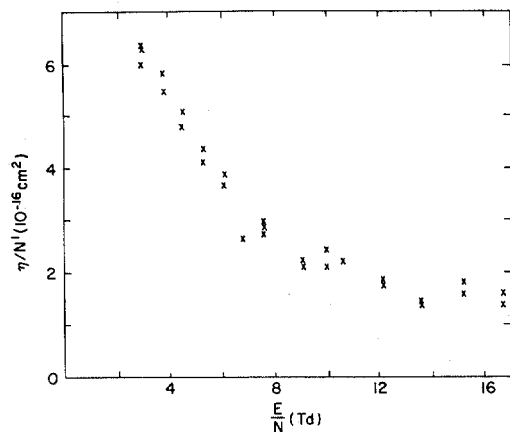
Fig. 3. Attachment coefficient divided by fluorine density as a function of E/N with a fluorine concentration of 1.0 percent in 10 torr helium.
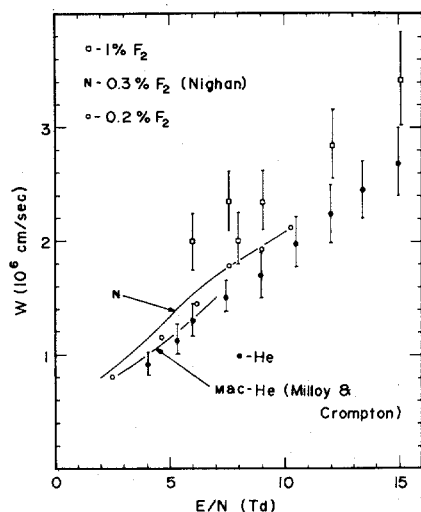

Fig. 4. Electron drift velocities in He-F_2 mixtures as a function of E/N. All data points are present results. The full-drawn curve marked N is due to Nighan [14] and pertains to a calculation in (0.3 percent F_2 + 99.7 percent He). The curve marked M & C depicts measurements in pure helium by Milloy and Crompton [13].

Fig. 5. Reaction rate coefficient for electron dissociative attachment in fluorine as a function of average electron energy. *References*: Hall [20]; Chantry [6]; Sides *et al.* [15]; Chen *et al.* [16]; Nygaard *et al.* [9]; Schneider and Brau [18].

Fig. 6. Attachment cross sections as a function of electron energy. Curve a is the relative cross section of Tam and Wong [21] for F_2, with the magnitude arbitrarily selected. Curve b is the cross section determined by Hall [20] for F_2. Curves c and d are the results of Chantry [6] for F_2 and NF_3, respectively.

added. As a check, in pure He there is good agreement between these results and those of Milloy and Crompton [13] in the region of overlap. In the region of E/N from 5-15 Td, there is a dramatic increase in W when 1 percent F_2 is added to the He buffer gas. The systematic trend showing an increase in electron drift velocity with increasing fluorine concentration has been supported by Nighan [14] in a recent calculation for a (0.3 percent F_2 + 99.7 percent He) mixture (see curve marked N in Fig. 4). His model includes vibrational excitation, dissociative attachment, and dissociation of the F_2 molecule, and the results are consistent with the experimental data.

Multiplying the η/N' values in Fig. 3 with the W values in Fig. 4 yields the results shown as open triangles in Fig. 5 with an accuracy of about ±20 percent. In order to make comparisons with other workers, the true E/N abscissa used in Figs. 3 and 4 has been converted to $(3/2)D/\mu$ in pure helium. The validity of this procedure was discussed in the Introduction. The other experimental points in Fig. 5 are identified in the caption.
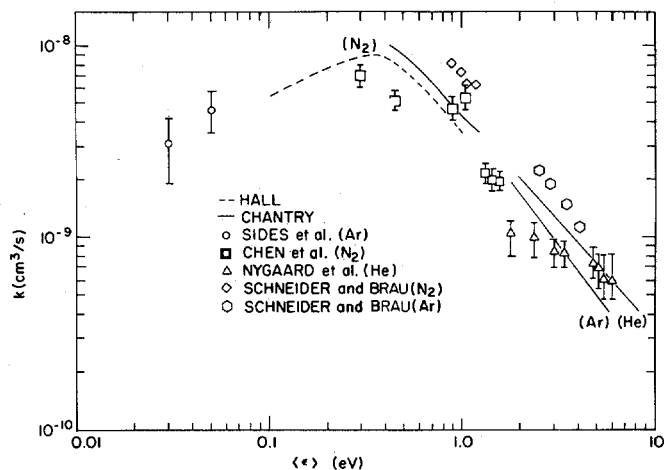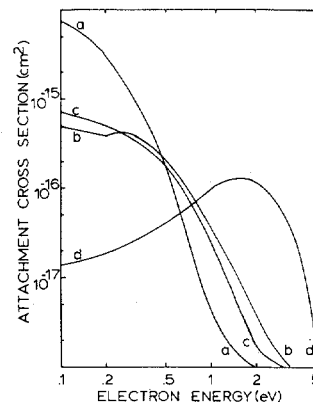
As mentioned previously, the cross section for dissociative attachment in fluorine has been measured by Chantry [6] and is shown in Fig. 6. By using his own cross-section values in (4), Chantry (in cooperation with Mitchell and Kline) obtained the full-drawn curves shown in Fig. 5 with N_2, Ar, and He as buffer gases. The theoretical curves follow the trend of three different experiments for energies above 0.5 eV.

A number of different experimental methods have been used to cover an electron energy range of more than two decades. The open circles at about 0.03 and 0.05 eV were obtained by Sides *et al.* [15] in a flowing afterglow experiment. They used argon as a buffer gas, and measured the F^- ion signal with a quadrupole mass spectrometer. The quoted uncertainty is from 25 to 50 percent.

In the energy region from 0.2 to 1 eV, an important contribution has been made by Chen *et al.* [16]. The principle of their experiment was to send a 100 keV electron beam into an electrical discharge and to measure the discharge currents in pure N_2 and in (N_2 + F_2). The fluorine concentration was always less than 0.3 percent, so they assumed, probably

to within 10 percent, that the electron drift velocity did not change when fluorine was added to the nitrogen gas. (It is speculated that the change in W is less in a molecular gas than in a noble gas.) Their data are put on an absolute scale by normalizing to the $(N_4^+ + e)$-recombination coefficient [17]. In Fig. 5 their energy scale has been corrected by a factor of 3/2 to bring their data in line with a mean energy equal to $(3/2)D/\mu$. This brings their results closer to the curve calculated by Chantry for $(F_2 + N_2)$.

As discussed in the previous paragraph, Chen *et al.* used a very long ($\simeq 100$ μs) electron beam pulse to set up a steady-state condition in the discharge volume, while Schneider and Brau [18] used a very short pulse ($\simeq 7$ ns) and studied the decay rate of the electron density in a region of constant E/N. With nitrogen and argon as buffer gases, their results covered an electron mean energy range from 0.4 to 4 eV. The mean energies were obtained from a Boltzmann code, *not* simply the $(3/2)D/\mu$ values pertaining to the pure buffer gas. Great care was taken in passivating the gas sample cylinder, and the discharge cell was refilled before each shot, with time between shots a few minutes. They also used very low fluorine concentrations ($\approx 10^{-2}$ percent), and found the electron density decay rate to be proportional to the F_2 concentration over a range of a factor of 3. Their results are above the curves based on Chantry's cross section [6] by a factor of 1.75. The discrepancy between Schneider and Brau's and the results [9] obtained in the swarm experiment can probably be ascribed to the 100 times higher F_2 concentration used in the swarm experiment as well as uncertainties in the electron drift velocities. In order to obtain an absolute number for k it was necessary to measure the *three* quantities η, W, and N', whereas Schneider and Brau had to determine only a decay time constant and N'.

As a byproduct of their work on a plasma return discharge, Mangano *et al.* [19] found approximate values of k between 2 and 1×10^{-9} cm^3/s, at the high-energy end, shown in Fig. 5, by studying a discharge in (1 percent F_2 + 5 percent Kr + 94 percent He). Their points are not included in Fig. 5, but are in good agreement with the other experimental data.

In addition to the attachment rates based on Chantry's cross section, Hall's non-Maxwellian computation [20] in nitrogen has been included in Fig. 5. The broken curve is the best fit of his resonance theory to the experimental data of Sides *et al.* [15] and Chen *et al.* [16]. Hall has also calculated the attachment rate in vibrationally excited F_2, and found a strong increase from $v = 0$ to $v = 1$.

For completeness, it should be noted that Tam and Wong [21] have measured *relative* cross sections for dissociative attachment in all of the halogen molecules and their results for F_2 are shown in Fig. 6. These values could, in principle, be put on an absolute scale by deconvoluting attachment rate data.

B. Nitrogen Trifluoride (NF_3)

In spite of its extensive use as a halogen donor in rare gas-halide lasers, little information has been available, until recently, on cross sections and attachment rates in NF_3. There are significant differences between previous measurements
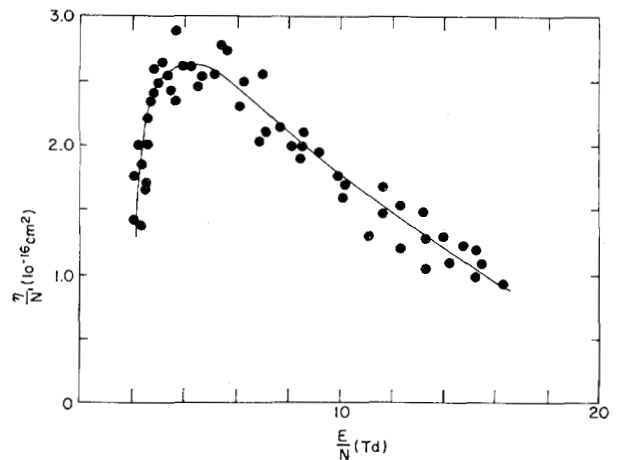

Fig. 7. Effective attachment cross section in 0.5 percent NF_3 in 20 torr He at 23°C.

done at electron temperatures of 300–350 K: Sides and Tiernan [22] found a value of $(2.1 \pm 0.8) \times 10^{-11}$ cm^3/s with an argon buffer gas at a pressure of 0.8 torr. This is in close agreement with the value of 2.4×10^{-11} cm^3/s obtained by Mothes *et al.* [23], also in a flowing gas system. The value of $(1.6 \pm 0.6) \times 10^{-9}$ cm^3/s determined by Shaw and Jones [24], using similar experimental techniques, appears to be too high.

The above results are interesting in themselves, but do not apply to rare gas-halide lasers where electron energies of several electron volts are prevalent. An important result was obtained by Harland and Franklin [25], who, in a time-of-flight mass spectrometer, detected predominantly F^--ions and found a maximum cross section of 6×10^{-17} cm^2 at an electron energy of 1.7 eV. This agrees reasonably well with the cross section measured by Chantry [6], which shows a maximum of about 1.4×10^{-16} cm^2 at 2 eV.

In this experiment, the attachment coefficient η was measured in a gas mixture consisting of 0.5 percent NF_3 in 20 torr helium, and the data are shown in Fig. 7. It is interesting to note an "onset" at about 2 Td and a maximum value of 2.6×10^{-16} cm^2 at about 4 Td. Each point in the illustration is an average over three–five separate observations. Measurements were taken at electrode separations of 2 and 3 cm. All points fall within ± 20 percent of the line drawn in Fig. 7, with no systematic distance effect. The uncertainty in NF_3 gas number density N' is less than ± 5 percent. Working under prepassivated conditions, there were no observable pressure decreases due to loss of NF_3 to the walls.

No measurements of the electron drift velocity in the $(NF_3 + He)$-gas mixture were taken; instead, the values of Crompton *et al.* [26] up to 4 Td and those of Anderson [27] and Phelps *et al.* [28] above 13 Td were used. Speculatively, the electron mean energy was set equal to $(3/2)D/\mu$, based on the data of Milloy and Crompton [13] and of Townsend and Bailey [29]. With these approximations, the results obtained for the attachment rate are shown in Fig. 8. The rate exhibits a broad maximum of 4×10^{-9} cm^3/s at about 5.5 eV. The rate coefficient calculated by Chantry [6] based on his experimental cross section shows a maximum value of 5.4×10^{-9} cm^3/s at about 2 eV. In view of the many assumptions made, it is not surprising that the positions of the maxima do not
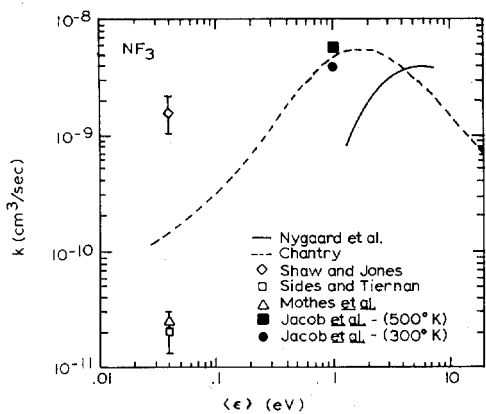
Fig. 8. Attachment rate coefficient in NF_3 as a function "mean" energy. *References*: Nygaard et al. (present results); Chantry [6]; Shaw and Jones [24]; Sides and Tiernan [22]; Mothes et al. [23]; Jacob et al. [30].

coincide. At an average evergy of 1 eV, the group at AVCO [30] has found $k = 4 \times 10^{-9}$ cm³/s at 300 K and $k = 6 \times 10^{-9}$ cm³/s at 500 K.

In order to demonstrate the large spread in data, Fig. 8 also shows the results from the flowing afterglow experiments.

C. Chlorine (Cl_2)

Chlorine has been used as a halogen donor in rare gas–halide and mercury–halide lasers, and the attachment rate for average energies around 1 eV has recently been reported by Rokni et al. [31]. The principle of their experiment was to observe the exponential decay of the electron density in an electron-beam controlled ($Cl_2 + N_2$) discharge. The Cl_2 density was carefully monitored by absorption of the Hg 366 nm line. As a very important consistency check, they varied the Cl_2 density by a factor of 5 and found the attachment rate to be proportional to the density over this range.

Their results are shown in Fig. 9 with open circles representing room temperature and filled circles 250°C data. It is interesting to notice that the attachment rate coefficient increases by about a factor of two due to the change in temperature. The single point at 3.1×10^{-10} cm³/s is due to Christodoulides et al. [32] and was measured at an electron temperature at 300 K. The full-drawn curve in Fig. 9 is the result of a Boltzmann code calculation using the *relative* cross-section values of Tam and Wong [21] normalized to the attachment rate of Rokni et al. [31]. The latter authors also measured the attachment rate coefficient in a mixture of ($Ar + Cl_2$), and at an average energy of 5.2 eV found values of 2.04×10^{-10} and 2.9×10^{-10} cm³/s at room temperature and 250°C, respectively.

Using the swarm experiment, tentative measurements of the rate coefficients in ($Cl_2 + N_2$)- and ($Cl_2 + Ar$)-gas mixtures have been made over a wide range of E/N. Within a factor of two, there is agreement with Rokni et al. [32]. These results will be published elsewhere when the Cl_2 density has been determined accurately.

D. Iodine (I_2)

In the previous paragraph a good demonstration of the effect of gas temperature on the attachment coefficient in Cl_2
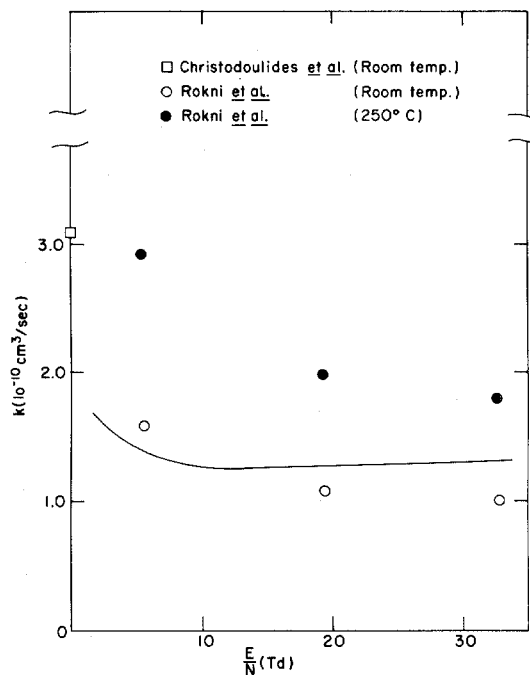

Fig. 9. Attachment rate coefficient in Cl_2. The full-drawn curve is the result of a Boltzmann calculation using the cross-section values of Tam and Wong [21]. *Other references:* Christodoulides et al. [32]; Rokni et al. [31].
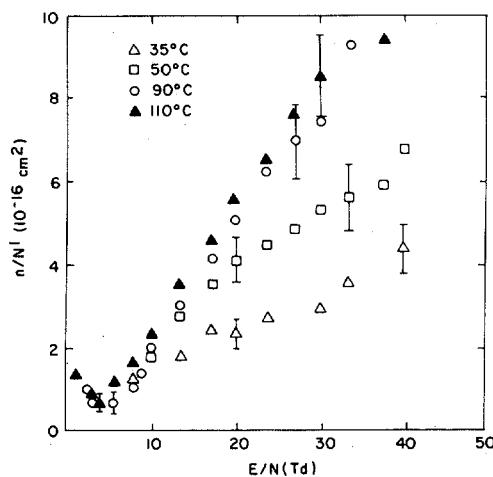

Fig. 10. Temperature dependence of the effective attachment cross section of 1 percent I_2 in approximately 50 torr of nitrogen as a function of E/N.

was shown. Recently, using the swarm techniques, a completed set of measurements in I_2 using nitrogen as a buffer gas have been obtained, and they show effective attachment cross sections that depend very strongly on gas *and* electron temperature.

The principle of the experiment was the same as in F_2 and NF_3, but a vacuum chamber was used in which the temperature could be varied from room temperature to 130°C. Details of the experimental procedure have been reported elsewhere [33].

The data obtained for η/N' are shown in Fig. 10; these values are relatively accurate to ± 5 percent with an absolute accuracy of ± 15 percent. The most noticeable feature of the attach-
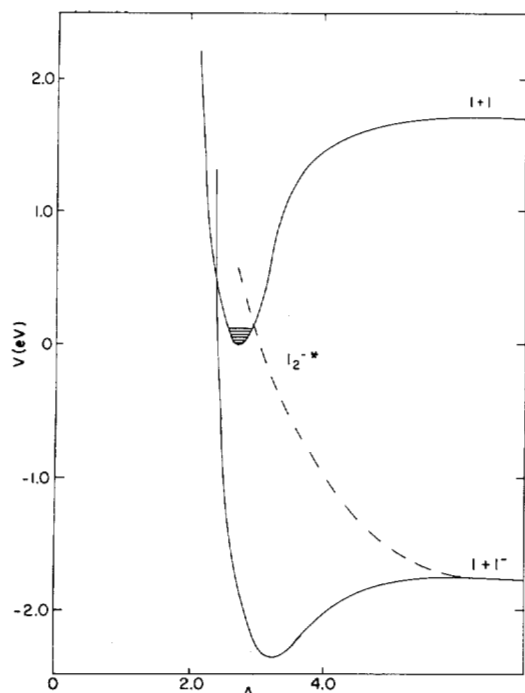
Fig. 11. Potential energy versus internuclear distance for I_2. (The vibrational energies are not to scale.)

TABLE I
FRACTIONAL POPULATIONS OF THE LOWER VIBRATIONAL STATES OF I_2 AT DIFFERENT TEMPERATURES

Vibrational State		0	1	2	3	4	5
Energy (cm^{-1})		107	322	536	751	966	1180
T E M P E R A T U R E	35°C	.632	.234	.086	.032	.012	.044
	50°C	.614	.238	.093	.036	.014	.005
	90°C	.573	.246	.107	.046	.020	.008
	110°C	.554	.249	.112	.051	.023	.011

the higher vibrational states similar to those presented by Hall [20] for F_2.

V. CONCLUDING REMARKS

This paper has presented the principle, method, and results obtained using an electron swarm experiment to investigate dissociative electron attachment in F_2, NF_3, Cl_2, and I_2. These results have shown good agreement with the data obtained by other researchers.

The techniques used to collect these data could be extended to other gas mixtures that have been previously investigated, including Br_2 and HBr [41], and CCl_4 [42], [43]. It should also be possible to study $HgBr_2$, HgI_2, and $HgCl_2$ which can serve as halogen donors to the mercury-halide lasers.

Slight modifications to the experimental apparatus would permit direct measurement of the characteristic energy D/μ in the gas mixtures. These results would remove the ambiguities discussed previously in defining the average electron energy.

With the rapid development of rare gas–halide and mercury halide lasers, the number of gas mixtures needing further investigation continues to grow. Accurate determination of the electron transport coefficients in the new mixtures is essential to the theoretical modeling of these laser systems.

ment coefficient is its increase with increasing gas temperature at high E/N values. At all four temperatures, η/N' shows a minimum of 6×10^{-17} cm^2 at 4 Td. The increase in the effective attachment cross section with increasing E/N does not follow the trend of the attachment rate seen in the other halogenated molecules. This increase may be caused by the electron energy distribution in the nitrogen buffer gas [44], [45], and cannot be considered significant until new data are collected for iodine using other buffer gases.

Previous experiments using electron beam techniques are considered unreliable and are not included in this study. On the other hand, Biondi [35] found a value of $\eta/N' = 3.9 \times 10^{-16}$ cm^2 at an average electron energy of 0.04 eV in an (I_2 + He)-afterglow experiment. His value agrees with these swarm measurements at low E/N.

To explain the temperature dependence of η/N', it must be assumed that dissociative attachment takes place in two steps [35]:

$$e + I_2 \rightarrow I_2^{-*}$$

$$I_2^{-*} \rightarrow I + I^-. \tag{16}$$

Fig. 11 shows the potential energy curves involved in these processes. It has been proposed by Person [37] and Matsuzawa [38] that the two $^2\pi$-states of I_2^- cross the I_2 potential curve near its minimum. A slight displacement from the minimum becomes critical when the close spacing (≈ 200 cm^{-1}) of the vibrational levels of I_2 are considered. We have calculated [39] the fractional populations of the vibrational states and these values are listed in Table I. The dramatic changes on the populations of the $v = 4$ state and the data presented in Fig. 10 support a crossing at 0.14 eV [40] or just above the $v = 4$ state. These results indicate increasing cross sections in

REFERENCES

[1] M. Rokni, J. A. Mangano, J. H. Jacob, and J. C. Hsia, "Rare gas fluoride lasers," *IEEE J. Quantum Electron.*, vol. QE-14, pp. 464–481, July 1978.
[2] W. L. Nighan, "Plasma processes in electron-beam controlled rare-gas halide lasers," *IEEE J. Quantum Electron.*, vol. QE-14, pp. 714–726, Oct. 1978.
[3] C. A. Brau, "Rare gas halide laser," Los Alamos Scientific Lab., Los Alamos, NM, LA-UR-78-311; also submitted to Springer-Verlag.
[4] J. Dutton, "A survey of electron swarm data," *J. Phys. and Chem. Reference Data*, vol. 4, pp. 577–856, 1975. (Electron attachment is discussed on pp. 673–687 and pp. 791–797.)
[5] K. J. Nygaard, J. Fletcher, S. R. Hunter, and S. R. Foltyn, "Electron drift velocities in helium-fluorine gas mixtures," *Appl. Phys. Lett.*, vol. 32, pp. 612–613, May 1978.

[6] P. J. Chantry, "Attachment measurements in halogen bearing molecules," ARPA Order No. 3342, Final Tech. Rep., Mar. 1978.

[7] L. G. H. Huxley and R. W. Crompton, *The Diffusion and Drift of Electrons in Gases.* New York: Wiley, 1974.

[8] R. Grünberg, "Messungen der Anlagerungskoeffizienten von Elektronen in Sauerstoff," *Z. Naturforsch.*, vol. 24a, pp. 1039–1048, 1969.

[9] K. J. Nygaard, S. R. Hunter, J. Fletcher, and S. R. Foltyn, "Electron attachment in dilute fluorine-helium mixtures," *Appl. Phys. Lett.*, vol. 32, pp. 351–353, Mar. 1978.

[10] L. D. Schearer, "A high-power pulsed xenon ion laser as a pump source for a tunable dye laser," *IEEE J. Quantum Electron.*, vol. QE-11, pp. 935–937, Dec. 1975.

[11] R. Burnham and N. Djeu, "Ultraviolet-preionized discharge-pumped lasers in XeF, KrF, and ArF," *Appl. Phys. Lett.*, vol. 29, pp. 707–709, Dec. 1976.

[12] Supplied by the Matheson Gas Company.

[13] H. B. Milloy and R. W. Crompton, "Momentum-transfer cross section for electron-helium collisions in the range 4–12 eV," *Phys. Rev. A*, vol. 15, pp. 1847–1850, May 1977.

[14] W. L. Nighan, private communication. (See also [2].)

[15] G. D. Sides, T. O. Tiernan, and R. J. Hanrahan, "Measurements of thermal electron dissociative attachment rate constants for halogen gases using a flowing afterglow technique," *J. Chem. Phys.*, vol. 65, pp. 1966–1975, Sept. 1976.

[16] H. L. Chen, R. E. Center, D. W. Trainor, and W. I. Fyfe, "Dissociative attachment of electrons to F_2," *Appl. Phys. Lett.*, vol. 30, pp. 99–101, Jan. 1977.

[17] D. H. Douglas-Hamilton, "Recombination rate measurement in nitrogen," *J. Chem. Phys.*, vol. 58, pp. 4820–4823, June 1973.

[18] B. I. Schneider and C. A. Brau, "Dissociative attachment of electrons to F_2," *Appl. Phys. Lett.*, vol. 33, pp. 569–571, Oct. 1978.

[19] J. A. Mangano, J. Hsia, J. H. Jacob, and B. N. Srivastava, "Plasma return current discharge," *Appl. Phys. Lett.*, vol. 33, pp. 487–489, Sept. 1978.

[20] R. J. Hall, "Dissociative attachment and vibrational excitation of F_2 by slow electrons," *J. Chem. Phys.*, vol. 68, pp. 1803–1807, Feb. 1978.

[21] W. C. Tam and S. F. Wong, "Dissociative attachment of halogen molecules by 0–8 eV electrons," *J. Chem. Phys.*, vol. 68, pp. 5626–5630, June 1978.

[22] G. D. Sides and T. O. Tiernan, "Dissociative electron attachment in nitrogen trifluoride," *J. Chem. Phys.*, vol. 67, pp. 2382–2384, Sept. 1977.

[23] K. G. Mothes, E. Schultes, and R. N. Schindler, "Application of electron cyclotron resonance technique in studies of electron capture processes in the thermal energy range," *J. Phys. Chem.*, vol. 76, pp. 3758–3764, 1972.

[24] M. J. Shaw and J. D. C. Jones, "Measurements of some reaction rates of importance in KrF lasers," *Appl. Phys.*, vol. 14, pp. 393–398, 1977.

[25] P. W. Harland and J. L. Franklin, "Partitioning of excess energy is dissociative resonance capture processes," *J. Chem. Phys.*, vol. 61, pp. 1621–1636, Sept. 1974.

[26] R. W. Crompton, M. T. Elford, and R. L. Jory, "The momentum transfer cross section for electrons in helium," *Australian J. Phys.*, vol. 20, pp. 369–400, 1967.

[27] J. M. Anderson, "Hall effect and electron drift velocities in the plasma of a positive column," *Phys. Fluids*, vol. 7, pp. 1517–1526, 1964.

[28] A. V. Phelps, J. L. Pack, and L. S. Frost, "Drift velocity of electrons in helium," *Phys. Rev.*, vol. 117, pp. 470–474, 1960.

[29] J. S. Townsend and V. A. Bailey, "Motion of electrons in helium," *Phil. Mag.*, vol. 46, pp. 657–665, 1923.

[30] J. H. Jacob, private communication.

[31] M. Rokni, J. H. Jacob, and J. A. Mangano, "Electron-attachment rate constant for Cl_2 at room temperature and 250°C," *Appl. Phys. Lett.*, vol. 34, pp. 187–189, Feb. 1979.

[32] A. A. Christodoulides, R. Schumaker, and R. N. Schindler, "Studies by electron cyclotron resonance technique. X. Interactions of thermal energy electrons with molecules of chlorine, hydrogen chloride, and methyl chloride," *J. Chem. Phys.*, vol. 79, pp. 1904–1911, 1975.

[33] H. L. Brooks, S. R. Hunter, and K. J. Nygaard, "Temperature dependence of the electron attachment coefficient in Iodine," *J. Chem. Phys.*, vol. 71, pp. 1870–1873, Aug. 1979.

[34] G. P. Baxter, C. H. Hockey, and W. C. Holmes, "The vapor pressure of iodine," *J. Amer. Chem. Soc.*, vol. 29, pp. 127–136, Feb. 1907.

[35] M. A. Biondi, "Dissociative attachment of electrons in iodine. I. Microwave determination of the absolute cross section at 300°K," *Phys. Rev.*, vol. 109, pp. 2004–2007, Mar. 1958.

[36] G. E. Caledonia, "A survey of the gas-phase negative ion kinetics of inorganic molecules. Electron attachment reactions," *Chem. Rev.*, vol. 75, pp. 333–351, 1975.

[37] W. B. Person, "Electron affinities of some halogen molecules and the charge-transfer frequency," *J. Chem. Phys.*, vol. 38, pp. 109–116, Jan. 1963.

[38] M. Matsuzawa, "Reactions of highly excited atoms with molecules $A^{**} + BC \rightarrow A^+ + B + C^-$," *J. Phys. Soc. Japan*, vol. 33, pp. 1108–1119, Oct. 1972.

[39] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. I–Spectra of Diatomic Molecules*, 2nd. New York: Van Nostrand, 1950, pp. 122–124.

[40] D. T. Birtwistle and A. Modinos, "Dissociative attachment in iodine," *J. Phys. B*, vol. 11, pp. 2949–2955, 1978.

[41] D. W. Trainor and M. J. W. Boness, "Dissociative attachment of electrons to Br_2 and HBr," *Appl. Phys. Lett.*, vol. 32, pp. 604–606, May 1978.

[42] A. A. Christodoulides and L. G. Christophuorou, "Electron attachment to brominated aliphatic hydrocarbons of the form n-$C_N H_{2N+1}$Br (N = 1–6, 8, and 10). I. An electron swarm study," *J. Chem. Phys.*, vol. 54, pp. 4691–4705, June 1971.

[43] J. Fischer and S. Shibata, "Electron attachment of CCl_4 in He using pulsed spark chamber efficiency as a sensitive electron indicator," presented at the 9th Int. Conf. on Phenomena in Ionized Gases, Bucharest, Romania, Sept. 1–6, 1969.

[44] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, "Determination of momentum transfer and inelastic collision cross sections for electrons in nitrogen using transport coefficients," *Phys. Rev.*, vol. 135, pp. A 1566–A 1574, 1964.

[45] W. L. Nighan, "Electron energy distribution and collision rates in electrically excited N_2, CO, and CO_2," *Phys. Rev. A*, vol. 2, pp. 1989–2000, 1970.