Recombination Coefficient of Molecular Rare-Gas Ions*

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The coefficients relating to the recombination of molecular rare-gas ions with electrons are determined from the slope of the straight part of the curve representing the reciprocal of the electron density as a function of time during the afterglow period of plasmas produced in helium, neon, argon, krypton, and xenon. The results are compared with the machine computation of Gray and Kerr. The influence on the measurements of the magnitude and duration of the plasma excitation pulse was studied. The values of the recombination coefficients obtained are $\alpha_r(He_2^+)\leqslant 4\times 10^{-9}$, $\alpha_r(Ne_2^+)=(2.2\pm 0.2)\times 10^{-7}$, $\alpha_r(Ar_2^+)=(6.7\pm 0.5)\times 10^{-7}$, $\alpha_r(Kr_2^+)=(1.2+0.1)\times 10^{-6}$, and $\alpha_r(Xe_2^+)=(1.4\pm 0.1)\times 10^{-6}$ cm^3 sec^{-1}. The values were independent of gas pressure over the pressure ranges studied. The influence on the measuring technique of the collision frequency for momentum transfer of electrons with gas atoms caused an apparent pressure dependence of the measured recombination coefficient of Xe_2^+ ions.

I. INTRODUCTION

SHORTLY after World War II, a microwave method was introduced which made it possible to measure rather accurately the electron number density as a function of time during the plasma decay period (afterglow) of a pulsed discharge.[1,2] The application of this technique resulted in the measurement of coefficients for electron-ion recombination which were approximately two orders of magnitude larger than those obtained with Langmuir probe methods.[3,4] In order to explain the magnitude of the measured values, Bates[5] postulated that the neutralization process involved was that of a collision of an electron with a diatomic positive ion and named it the dissociative recombination process.

Biondi[6] and Oskam[7] observed that, when adding small concentrations of argon atoms to helium or neon, the electrons disappear from the plasma exclusively by the ambipolar diffusion process. The values of the mobility calculated from the measured ambipolar diffusion coefficients were in close agreement with those expected for Ar^+ ions moving in helium and neon, respectively. The Ar^+ ions were produced very efficiently in these Penning mixtures (gas mixtures in which metastable excited atoms of type X can ionize atoms of type Y), and the argon atom concentrations were small enough to ensure that the influence of Ar_2^+ ions on the rate of electron disappearance was small. These studies, therefore, indicated that the large values of the recombination coefficients are measured only when molecular ions are present during the afterglow period. This is in agreement with the recombination process postulated by Bates. It should be mentioned that very recent studies carried out by means of mass-spectrometer techniques seem to indicate the possible production of $(NeAr)^+$ ions in the neon-argon mixtures used by Biondi and Oskam.[8,9]

When it is assumed that the only process by which electrons disappear from the plasma during the afterglow period is the volume recombination process, the rate of change of the electron density $n_e(t)$ is given by

$$dn_e(t)/dt=-\alpha_r n_e(t)n_+(t)\,, \qquad (1)$$

provided that only one type of ion is present, and that all electron production processes can be neglected. Here, α_r is the recombination coefficient and $n_+(t)$ is the positive ion density.

For a quasineutral plasma $[n_e(t)\simeq n_+(t)]$ the solution of Eq. (1) is

$$1/n_e(t)=[1/n_e(t_0)]+\alpha_r(t-t_0)\,. \qquad (2)$$

The curve representing the reciprocal of the electron density as a function of time during the afterglow period should be a straight line as long as the assumptions leading to the expression (2) are valid. The slope of this line gives the value of the recombination coefficient.

Gray and Kerr[10,11] have examined by machine computation the reliability of values of the recombination coefficient calculated from the $1/n_e(t)$ versus time curves obtained with the microwave cavity method. This method consists of measuring the change in the resonant frequency of a microwave cavity due to the presence of a plasma inside the cavity. The authors found that the two related quantities which mainly determine the reliability and accuracy of the measured value α_m are (a) the factor f by which the electron density $n_e(t)$ changes over the region in which the $1/n_e(t)$ versus time curve is within 2% of a straight line

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and (b) the quantity

$$\beta=\frac{\alpha_r n_e^2(t_0)}{D_a n_e(t_0)/\Lambda^2}, \tag{3}$$

which is the ratio at $t=t_0$ of the axial (or central) electron loss rate that would prevail in the absence of diffusion to the corresponding loss rate from only diffusion in the fundamental mode. Thus, β is a measure of degree to which the plasma is initially recombination-controlled ($\beta \gg 1$) or diffusion-controlled ($\beta \ll 1$). The plasma container was assumed to be an infinite cylinder or a sphere. In the definition (3), D_a is the ambipolar diffusion coefficient of the plasma electrons, Λ is the characteristic diffusion length of the plasma container, and $n_e(t_0)$ is the electron density on the axis (or in the center) at time t_0.

Gray and Kerr give the relations between the quantities f and β for both diffusion and recombination initial electron density distributions. The TM_{01} mode of the infinite cylinder which has the same spatial dependence as the corresponding TM_{010} cavity mode, was used for the microwave probing field during the calculations. The value of the recombination coefficient α_r determines, for given gas, pressure, and configuration, the value of β according to relation (3). The value of β, calculated in this way, yields the quantity f, which indicates the ratio of the electron density over which the measured $1/n_e(t)$ versus time curve should be a straight line within an accuracy of about 2%. This procedure makes it possible to obtain an indication about the reliability of the measured value α_m. The authors also give the relation between the value of f (or β) and the accuracy of measurement of α_r. Obviously, the accuracy increases with increasing values of these quantities. The influence of the production of charge carriers by metastable atom—metastable atom interactions was neglected. When the rate of electron production by this process is not small compared to the rate of loss, the measured $1/n_e(t)$ versus time curves may deviate appreciably from the theoretical curves.

The plasma containers used during both the present and previous studies were cylinders. The ratio of the diameter and length determines whether the experimental conditions relate more closely to the theoretical analysis of the infinite cylinder or to that of the sphere. The measured value α_m and the subsequent calculation of β then makes it possible to obtain an estimate of the expected theoretical value of the quantity f. An inspection of the measurements as reported in the literature shows that only a small fraction of the studies satisfies the conditions as given by Gray and Kerr.

The recombination coefficient related to the postulated dissociative recombination process should be independent of gas pressure, since only an electron and ion are involved in the collision process. The dependence of α_m on gas pressure, as reported for instance for Xe_2^+ ions, is either due to a different type of recombination process or is of experimental origin.

Various authors, when studying the electron-ion recombination process, report a dependence of the measured α_m on the magnitude and duration of the plasma excitation pulse.[12–15] It is evident that the value of α_r should be independent of these variables, so that the origin of the measured dependences must be due to other phenomena. The type of excitation pulse may influence the initial spatial density distribution of the charge particles or, when impurity atoms are present, may influence the number of impurity ions produced during the excitation pulse.

The present paper reports results obtained for the values of α_r during studies of the physics of decaying plasmas produced in helium, neon, argon, krypton, and xenon. The values presented for α_r are calculated from curves satisfying the f-β relationship given by Gray and Kerr. The dependence of the measured value α_m on the gas pressure was determined and the influence of the plasma excitation pulse was investigated.

Two different types of microwave cavities (TM_{010} and TE_{011} mode) were used in order to study the possible effect of the spatial electron density distribution on the measurements. The measuring method and the gas purification technique were identical to those described in a previous paper.[16]

II. METHOD OF MEASUREMENT

The method of determining the electron density as a function of time during the afterglow period consisted of measuring the time dependence of the resonant frequency change of a microwave cavity containing the plasma.

Slater[17] has evaluated the influence of a rarefied electron gas on the properties of a cavity at microwave frequencies. His formula (III.82), reduces to the following first-order approximation, which includes the changes in both the quality and angular-resonant frequency[18].

$$\left(\frac{1}{Q(t)}-\frac{1}{Q_0}\right)-2j\frac{\Delta\omega(t)}{\omega_0}=\frac{1}{\epsilon_0\omega_0}\frac{\int\sigma_c(\mathbf{r},t)E^2(\mathbf{r})dV}{\int E^2(\mathbf{r})dV}. \tag{4}$$

Here $Q(t)$ and Q_0 are the qualities of the cavity with

[12] J. J. Lennon and M. C. Sexton, J. Electron. Control **7**, 123 (1959).
[13] R. B. Holt, J. M. Richardson, B. Howland, and B. T. McClure, Phys. Rev. **77**, 239 (1950).
[14] J. M. Richardson, Phys. Rev. **88**, 895 (1952).
[15] M. C. Sexton and J. D. Graggs, J. Electron. Control **4**, 493 (1958).
[16] H. J. Oskam and V. R. Mittelstadt, preceding paper, Phys. Rev. **32**, 1435 (1963).
[17] J. C. Slater, Rev. Mod. Phys. **18**, 480 (1946).
[18] S. J. Buchsbaum, L. Mower, and S. C. Brown, Phys. Fluids **3**, 1 (1960).

and without the electron gas, respectively; ϵ_0 is the permitivity of free space; ω_0 is the angular-resonant frequency of the empty cavity; dV is a volume element of the cavity; $E(\mathbf{r})$ is the amplitude of the electric field [time factor $\exp(j\omega t)$] applied to measure the frequency shift $\Delta\omega$ and the change in the quality, while the conductivity σ_c is the complex ratio of current density and field strength. Formula (4) holds in so far as the influence of the electron gas may be considered as a small perturbation of the case of an empty cavity.

The complex conductivity of an electron gas for a high-frequency electric field has been shown to be[19]

$$\sigma_c=-\frac{4\pi}{3}\frac{e^2}{m}\int_0^\infty \frac{1}{\nu_m+j\omega}\frac{\partial f_0^0}{\partial v}v^3dv, \tag{5}$$

where e and m are the electron charge and mass, respectively; ν_m is the collision frequency for momentum transfer of the electrons with the gas particles; f_0^0 is the steady-state isotropic part of the velocity distribution of the electrons, and ω is the angular frequency of the electric field.

When it is assumed that the collision frequency ν_m is independent of the electron velocity v, the complex conductivity is given by[20]

$$\sigma_c(\mathbf{r},t)=\frac{e^2n(\mathbf{r},t)}{m}\left[\frac{\nu_m}{\nu_m^2+\omega^2}-j\frac{\omega}{\nu_m^2+\omega^2}\right], \tag{6}$$

independent of the form of f_0^0. Substitution of (6) into (4) leads to

$$\frac{1}{Q(t)}-\frac{1}{Q_0}=\frac{e^2}{\epsilon_0 m\omega_0^2}\frac{ap_0}{1+(ap_0)^2}K(t) \tag{7}$$

and

$$\frac{\Delta\omega(t)}{\omega_0}=\frac{e^2}{2\epsilon_0 m\omega_0^2}\frac{1}{1+(ap_0)^2}K(t), \tag{8}$$

where

$$a\equiv\nu_{m,0}/\omega_0 \tag{9}$$

and

$$K(t)\equiv\frac{\int n(\mathbf{r},t)E^2(\mathbf{r})dV}{\int E^2(\mathbf{r})dV}. \tag{10}$$

Here, p_0 is the gas pressure (reduced to 273°K) and in the definition (9) the quantity $\nu_{m,0}$ is the collision frequency for momentum transfer of electrons in a gas at a pressure of 1 Torr. The integral $K(t)$ has been calculated by Oskam[7] for various types of microwave cavities both for diffusion and recombination spatial electron density distributions.

The presence of the factor $[1+(ap_0)^2]^{-1}$ in formula (8) has no influence on the measurement of the ambipolar diffusion coefficient D_a, since this quantity is calculated from the slope of the curve representing the logarithm of the electron density as a function of time during the afterglow period. Consequently, the absolute value of the electron density does not need to be known. When, however, the measurements are conducted for the determination of the coefficient α_r, relating to the electron-ion recombination process, it may easily be shown that

$$\alpha_m=[1+(ap_0)^2]\alpha_r, \tag{11}$$

where α_m refers to the recombination coefficient calculated from the $1/n_e(t)$ versus time curve when the influence of ν_m on the measured frequency shift is neglected.

For electrons having an average energy of 0.04 eV, the mean free paths in the rare gases have been measured with the aid of microwave techniques.[21,22] The following l_0 values in cm were found: 0.055 for helium, 0.30 for neon, 0.48 for argon, 0.019 for krypton, and 0.0056 for xenon. The frequency of the microwave measuring signal used during the present studies was about 9000 Mc/sec. When relating the collision frequency ν_m to the most probable electron speed, the pressure at which the measured value α_m is 10% larger than the actual value α_r can be calculated for the various rare gases. The pressures found are 100 Torr for helium, 550 Torr for neon, 870 Torr for argon, 36 Torr for krypton, and 10 Torr for xenon. These values should be considered as estimates only since the assumption of constant ν_m, which was used in the derivation of expression (11), is, in general, not correct.

Another influence of the collision frequency ν_m on the measurements was observed during the studies. According to formula (7), the change in the quality Q of a microwave cavity due to the presence of an electron gas depends, for a given gas and pressure, on the electron density. This change in quality causes a change in coupling of the probing signal to the cavity during the afterglow period. The change in the resonant frequency of the cavity during the afterglow period was measured by determining the instant at which the resonant frequency was equal to the frequency of the constant probing signal. This time, in general, is assumed to be the moment at which the signal reflected by the cavity has its minimum value. When the coupling of the cavity to the waveguide changes appreciably during the period that the cavity absorbs part of the probing signal, the reflected signal may be distorted so that the moment of maximum absorption (minimum reflection) does not coincide anymore with the time at which the

[19] W. P. Allis, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 383.

[20] When ν_m depends on the electron velocity v, the symbol ν_m in expression (6) refers to a weighted average. The studies were performed during the afterglow period, so that ν_m refers to a constant average electron energy of 0.04 eV. Thus, ν_m can be considered to be independent of time.

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[22] L. Gould and S. C. Brown, Phys. Rev. **95**, 897 (1954).

resonant frequency of the cavity is equal to the probing signal frequency. For example, if the coupling increases during the afterglow period, the minimum of the reflected signal may occur at a time appreciably later than the time at which the two frequencies are equal.

The phenomenon discussed above was observed during studies in helium, krypton, and xenon in the high-pressure region. This is consistent with the relatively large values of the collision frequency ν_m of electrons with gas particles in these gases. The influence of the change in probing signal coupling to the cavity on the measurements was eliminated by sweeping the frequency of the probing signal through the resonant frequency of the cavity, at a given time during the afterglow period, within a time interval during which the electron density could be assumed to be constant.

III. THE INFLUENCE OF PLASMA EXCITATION PULSE ON THE MEASUREMENTS

Various authors[12–15] have reported an influence of the length and magnitude of the plasma excitation pulse on the value of the recombination coefficient α_r. The electron density ranges from which the values of α_r were calculated, however, were small and the purity of the gas samples used was often questionable. When α_r relates to a recombination process involving an electron and one type of positive ion, the value of α_r must be independent of the type and intensity of plasma excitation.[23]

In order to investigate the influence of plasma excitation on the determination of α_r, the duration of the plasma-excitation pulse was varied for most gases and pressures studied. Typical examples of the results obtained are shown in Fig. 1 for the case of plasmas produced in argon. In this figure, the reciprocal of the resonant frequency shift is given as a function of time for various values of duration of the plasma-excitation pulse.

Curve (a) was measured when the duration of the plasma excitation pulse was 15 μsec; curve (b) relates to a pulse length of 150 μsec, while curve (c) was measured for a pulse length of 1000 μsec and larger. The spatial distribution of the intensity of the visible light emitted by the discharge during the pulse was observed to be very inhomogeneous for excitation pulses of about 15 μsec. The light was most intense in the regions of high-excitation field strength, or where the plasma tended to "pinch." It may be assumed that the production of charged particles during the pulse is largest in the regions of strongest light intensity. Although the diffusion process is considerably faster during plasma excitation than during the afterglow period, a minimum excitation time is required for the hot plasma to diffuse

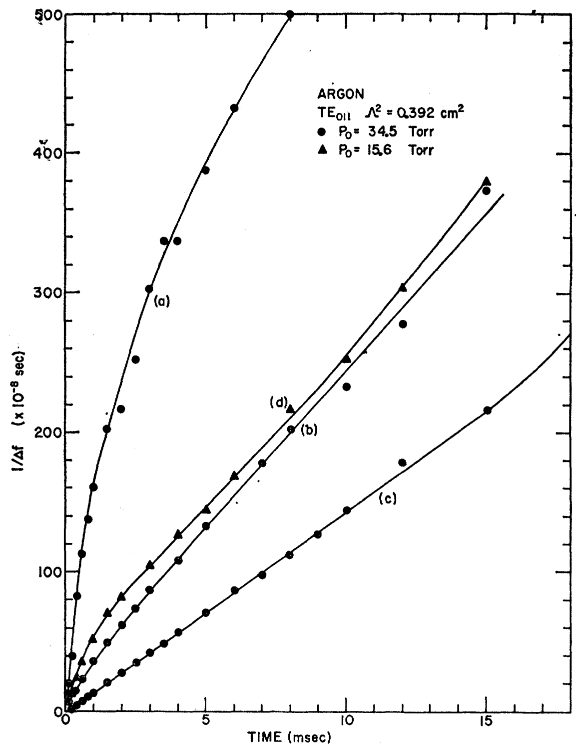

FIG. 1. Reciprocal of the frequency shift as a function of time during the decay period for various excitation pulse lengths: (a) and (d) 15 μsec, (b) 150 μsec, and (c) 1000 μsec.

throughout the plasma container. Furthermore, it was observed that an increase in pulse length, in general, resulted in a more homogeneous spatial light distribution. Inadequate pulse lengths do not permit the plasma to fill the container before the excitation ceases and the subsequent rapid cooling of the electrons during the very early afterglow period "freezes in" the spatial electron density distribution. Consequently, only part of the plasma container will then be filled with a more or less uniformly distributed plasma and the value of the recombination coefficient α_m calculated from the measured curve, under the false assumption of a completely filled plasma container, will lead to a possibly severe overestimation of α_r. When plotting, for example, curve (a) on a more extended time scale, the curvature of the initial part may be sufficiently masked, so as to indicate that the $1/\Delta f$ versus time curve is a straight line over an electron density ratio of about 10. The value α_m calculated from the slope of this line is more than 10 times larger than the value resulting from curve (c), for which the value of f is larger than 250. When inserting the value α_m and that of the ambipolar diffusion coefficient D_a in Eq. (3), the value of β is found to be larger than 10^4. According to Gray and Kerr's analysis, this value of β predicts a value of f larger than 100, which is in agreement with curve (c). A wrong analysis of curve (b) might lead in a similar way to a false result for α_r.

[23] The process of three-body recombination involving an ion and two electrons is expected to be of no importance during the present studies since the electron densities are smaller than 10^{11} electrons/cm³. This neutralization process has been discussed first by N. d'Angelo [Phys. Rev. **121**, 505 (1961)].

The time needed by the "hot" plasma to diffuse through the container can be expected to decrease with decreasing pressure. This is demonstrated by curve (d) of Fig. 1. Here, the gas pressure was 15.6 Torr, while the duration of plasma excitation was the same as that for curve (a), which was measured at a gas pressure of 34.5 Torr. When the pulse length was increased until its influence on the measurements disappeared, the studies at 15.6 Torr gave a value of α_r equal to that calculated from curve (c).

As was expected, the effect of the duration of plasma excitation on the measurements was found, for given gas pressure, to be more pronounced in krypton and xenon than in argon, as a consequence of the slower ambipolar diffusion process.

IV. THE RECOMBINATION COEFFICIENT OF He_2^+ IONS

A considerable number of studies concerning the recombination coefficient of He_2^+ ions has been reported. The values given in the literature, however, indicate that as yet no reliable value of $\alpha_r(He_2^+)$ is available. A brief summary of the studies will be given; for more detailed information the references should be consulted.

Biondi and Brown[1] reported $\alpha_r(He_2^+) = 1.7\times10^{-8}$ cm^3 sec^{-1}. The studies were conducted at gas pressures of 21.2 and 28.7 Torr, while the electron-density ratio from which α_r was determined was about 3.

Johnson, McClure, and Holt[24] found $\alpha_r(He_2^+) = 9.5\times10^{-9}$ cm^3 sec^{-1} at a helium pressure of 15 Torr; the electron-density ratio was only 1.2. These authors measured also the total energy radiated in the wavelength range of 2000 to 8000 Å and arrived at $\alpha_r(He_2^+) = 9.8\times10^{-9}$ cm^3 sec^{-1} from these studies.

Oskam[7] was unable to determine a reliable value for the recombination coefficient for pressures up to 30 Torr. He observed a large influence of the excitation pulse on the properties of the early afterglow period and concluded that $\alpha_r(He_2^+)$ was smaller than 10^{-8} cm^3 sec^{-1}.

Sexton and Craggs[15] also found a dependence on the excitation pulse and reported values varying from 3.9 to 6.8×10^{-8} cm^3 sec^{-1} at a pressure of 32 Torr. The electron-density ratio from which α_r was calculated was only 1.2.

Chen, Leiby, and Goldstein[25] studied the recombination coefficient in the pressure range of 15 to 30 Torr. They found $\alpha_r(He_2^+) = (8.9\pm0.5)\times10^{-9}$ cm^3 sec^{-1}, independent of helium pressure, while the electron-density ratio reported was 3.6. From the measurement of the time dependence of the total visible light radiated during the afterglow period, these authors determined a value of α_r which was within 6% of the value found by means of the electron density studies.

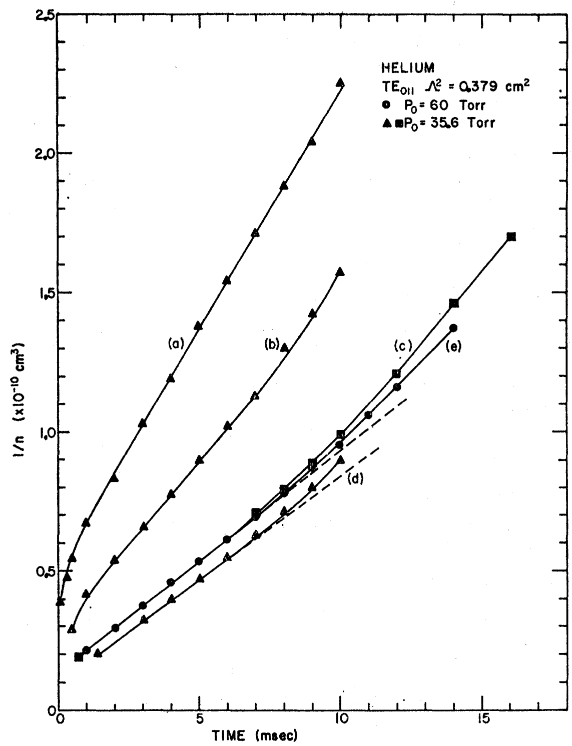

FIG. 2. Reciprocal of the electron density in helium as a function of time during the decay period. The excitation pulse lengths were (a) 100 μsec, (b) and (c) 250 μsec, (d) 1000 μsec, and (e) 5000 μsec.

Gray and Kerr[26] derived, from studies in the pressure range of 15 to 20 Torr, the value $\alpha_r(He_2^+) = 1.3\times10^{-9}$ cm^3 sec^{-1}. These authors arrived at this value by considering the rate in which the electron disappearance approached the exponential time dependence, which characterizes electron disappearance by ambipolar diffusion.

Kerr and Leffel[27] measured the absolute magnitude of the total light emitted in and near the visible region for both atomic and molecular radiation and estimated that $3\times10^{-10} < \alpha_r(He_2^+) < 2\times10^{-9}$ cm^3 sec^{-1}.

The present studies were conducted up to a helium pressure of 60 Torr. Typical $1/n_e(t)$ versus time curves obtained are shown in Fig. 2. The curves (a) and (b) were obtained with plasma excitation pulses of length 100 and 250 μsec, respectively. The coupling of the excitation source to the cavity was such that the light distribution during the pulse was very inhomogeneous. The curves (c) and (d) were measured at the same pressure of 35.6 Torr, but the coupling to the cavity was changed to produce a better electron-density dis-

[24] R. A. Johnson, B. T. McClure, and R. B. Holt, Phys. Rev. **80**, 376 (1950).
[25] C. L. Chen, C. C. Leiby, and L. Goldstein, Phys. Rev. **121**, 1391 (1961).
[26] E. P. Gray and D. E. Kerr, Bull. Am. Phys. Soc. **5**, 372 (1960).
[27] D. E. Kerr and C. S. Leffel, Bull. Am. Phys. Soc. **7**, 131 (1962).

tribution.[28] The pulse lengths were 250 and 1000 μsec, respectively. At a pressure of 60 Torr and a pulse length of 5000 μsec, curve (e) was measured. Even at this pressure and pulse length, the value f of the electron density ratio over which the $1/n_e(t)$ versus time curve appears to be a straight line is only 4. The value α_m, which could be calculated from this curve is 7×10^{-9} cm^3 sec^{-1}. The quantity f is too small, however, to assign too much significance to the value α_m determined in this way. The value of β, as defined by (3), is about 14 for this curve. Gray and Kerr's analysis predicts a corresponding f value of about 4, which is in agreement with the measurement. When assuming that their calculations are applicable for the cavity and configuration used in the present experiment, the small value of β (and f) results in the conclusion that $\alpha_r(He_2^+)\leqslant 4\times10^{-9}$ cm^3 sec^{-1}. This estimate seems to be in fair agreement with the limits for α_r given by Kerr and Leffel.[26] The values of $\alpha_r(He_2^+)$ published by other authors are all larger.[1,15,24,25] It should be mentioned that most of these authors were not able to take the recently published machine computations of Gray and Kerr into account, and that the values of $\alpha_r(He_2^+)$ reported were calculated from $1/n_e(t)$ versus time curves which had the appearance of a straight line only over a very small electron density range.

V. THE RECOMBINATION COEFFICIENT OF Ne_2^+ IONS

The value of the recombination coefficient of Ne_2^+ ions is considerably better established than that of He_2^+ ions. The first studies were conducted by Biondi and Brown.[4] The electron-density ratio f was 9 and the pressure-independent value determined for gas pressures of 15 to 30 Torr was $\alpha_r(Ne_2^+)=(2.07\pm0.05)\times10^{-7}$ cm^3 sec^{-1}. This value was independent of gas temperatures between 195 and 410°K. At a temperature of 77°K, the value of α_r increased with increasing gas pressure.

Holt *et al.*[13] reported $\alpha_r(Ne_2^+)=1.1\times10^{-7}$ cm^3 sec^{-1} at a neon pressure of 20 Torr, while the electron-density ratio from which this value was determined was 3.5. They observed that the value α_m increased with decreasing plasma excitation power; the variation in α_m was about 100%. The same authors also measured the total visible light emitted during the decay period.

Oskam[7] measured $\alpha_r(Ne_2^+)=2.6$ and 2.3×10^{-7} cm^3 sec^{-1} at pressures of 18.1 and 19.8 Torr, respectively; the electron-density ratio was 7.

Very recently, Biondi[29] reported values of 3.6 and 3.4×10^{-7} cm^3 sec^{-1} at pressures of 9.5 and 23.5 Torr, respectively. The electron-density ratio was 5; this author corrected the measured values according to the theoretical analysis of Gray and Kerr[10] and obtained $\alpha_r(Ne_2^+)=2.3\pm0.1)\times10^{-7}$ cm^3 sec^{-1}.

The present studies were conducted in the pressure range of 17 to 35 Torr. Part of the $1/n_e(t)$ versus time curve obtained at the highest pressure is shown in Fig. 3; the density ratio f over which this curve is a straight line within 2% is about 30. During the later part of the afterglow period, the influence of the ambipolar diffusion process clearly becomes noticeable. This effect was more pronounced at lower gas pressures, as it should be. The measurements indicated that the recombination coefficient was pressure-independent and the value found was $\alpha_r(Ne_2^+)=2.2\pm0.2)\times10^{-7}$ cm^3 sec^{-1}. The value of β, defined by (3), was for a neon pressure of 35 Torr about 500. According to Gray and Kerr's analysis, this predicts a value of f between about 20 and 60, which is in agreement with the experimental value of 30. The value of β (and f) ensures that the values of $\alpha_r(Ne_2^+)$ can be considered to be accurate within 10 to 15%.

The value of $\alpha_r(Ne_2^+)$ determined during the present studies is in excellent agreement with previous studies[4,7,29] with the exception of the data reported by Holt *et al.*[13]

VI. THE RECOMBINATION COEFFICIENT OF Ar_2^+ IONS

Various studies related to the recombination coefficient of Ar_2^+ ions have been conducted. Although $\alpha_r(Ar_2^+)$ is believed to be larger than $\alpha_r(Ne_2^+)$, the differences between the reported values are more severe.

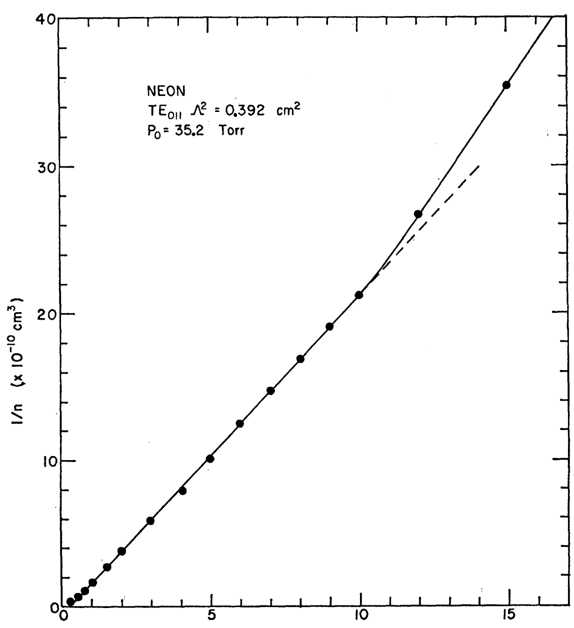

FIG. 3. Reciprocal of the electron density in neon as a function of time during the decay period.

[28] The source used for producing the pulsed plasma was a 104 Mc/sec power generator. The coupling of this source to the gas inside the microwave cavity has been discussed in a previous paper. (See Ref. 16.)

[29] M. A. Biondi, Phys. Rev. **129**, 1181 (1963).

The first studies were performed by Biondi and Brown.[4] They reported $\alpha_r(Ar_2^+)=3.0\times10^{-7}$ cm^3 sec^{-1}, but suspected the purity of the argon used. These authors did not indicate the pressure and the electron density ratio over which the measurements were conducted.

Redfield and Holt[30] calculated the value $\alpha_r(Ar_2^+)=1.1\times10^{-6}$ cm^3 sec^{-1} from an indicated electron-density ratio of 6.[31] The value of α_r was independent of pressure between 20 and 30 Torr. At 30 Torr and high-plasma-excitation power, two straight portions of the $1/n_e(t)$ versus time curve were observed. The authors assigned to the initial straight line a recombination coefficient equal to 0.65×10^{-6} cm^3 sec^{-1}. The value calculated from measurements at pressures between 0.5 and 1.5 Torr was 4×10^{-8} cm^3 sec^{-1}.[32] The same authors also measured the light emitted during the afterglow period but did not arrive at a value of $\alpha_r(Ar_2^+)$ from these measurements.

Biondi[6] remeasured $\alpha_r(Ar_2^+)$ and found a value of 8.8×10^{-7} cm^3 sec^{-1} at 14 Torr. This was the first study in which the electron-density ratio, over which the reported $1/n_e(t)$ versus time curve showed a linear relationship, was appreciable ($f=30$). The author mentioned in a later publication[29] that the value for $\alpha_r(Ar_2^+)$ should, as a consequence of Gray and Kerr's analysis,[10] be reduced by about 30%. He, therefore, estimates $\alpha_r(Ar_2^+)=6\times10^{-7}$ cm^3 sec^{-1}.

Sexton and Craggs[15] observed a dependence of $\alpha_m(Ar_2^+)$ on both the pressure and plasma excitation power. For pressures between 30 and 50 Torr, the value depended only on the excitation power and varied between 4×10^{-7} and 8×10^{-7} cm^3 sec^{-1}. For lower pressures the value increased with decreasing gas pressure. The maximum reported value of the electron density ratio used for the determination of $\alpha_r(Ar_2^+)$ was only 4.

Sexton *et al.*[33] reported $\alpha_r(Ar_2^+)=2\times10^{-7}$ cm^3 sec^{-1}. The difference between this value and that measured previously by the same authors was believed to be a consequence of improved gas purity and smaller magnitude of the microwave probing signal. It should be mentioned that a larger probing signal, which may increase the average electron energy, should lead to smaller value of α_r, since α_r is believed to decrease with increasing electron energy.[25] The authors assumed that, during the earlier measurements, the relatively large probing signal increased the average electron energy, which meant that the electron loss by the ambipolar diffusion process had a larger influence on their measurements. The electron-density ratio from which α_r was determined, was the same as that obtained during the previous studies.

The present studies were conducted in the pressure range of 9 to 35 Torr and the resulting $\alpha_r(Ar_2^+)=(6.7\pm0.5)\times10^{-7}$ cm^3 sec^{-1} was found to be independent of gas pressure. Pertinent parts of $1/n_e(t)$ versus time curves are shown in Fig. 4. The influence of electron loss by ambipolar diffusion again becomes noticeable at low pressures and/or small electron densities. For the TE_{011} cavity and $p_0=35$ Torr the value of β was about 10^4, which predicts a theoretical value of f larger than 100.[10] The value of f measured at this pressure was about 250. The obtained $\alpha_r(Ar_2^+)$, therefore, is believed to be accurate within 10%.

When comparing the value of $\alpha_r(Ar_2^+)$ obtained during the present studies with those reported previously, it follows that good agreement exists with the value estimated by Biondi[29] and Sexton and Graggs.[15] The values given by Redfield and Holt[30] and Sexton *et al.*,[33] however, differ considerably.

VII. THE RECOMBINATION COEFFICIENT OF Kr_2^+ IONS

Two studies concerning the recombination coefficient of Kr_2^+ ions have been reported.[12,14] The values of the electron density ratios were small and the concentration of impurity atoms was rather large. This made the interpretation of the measurements difficult.

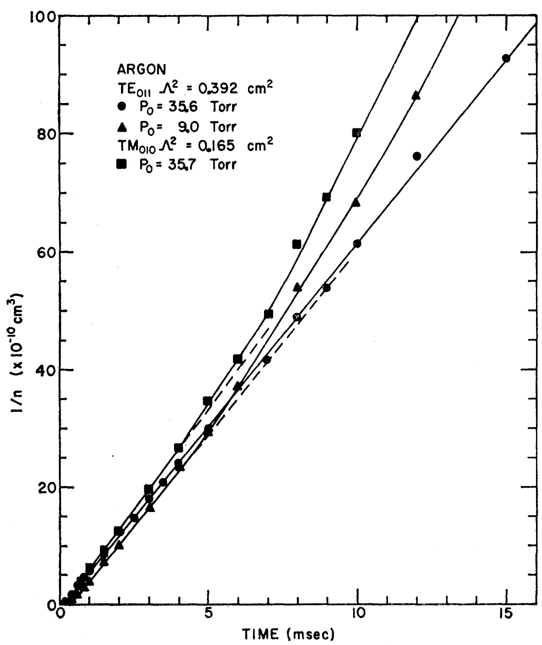

FIG. 4. Reciprocal of the electron density in argon as a function of time during the decay period.

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[30] A. Redfield and R. B. Holt, Phys. Rev. **82**, 874 (1951).

[31] The electron-density ratio 6 was estimated from the published data. The authors mention that this ratio was appreciably larger.

[32] The procedure used by the authors consisted of correcting the curve, representing the logarithm of the electron density as a function of time, for the small effect of the electron-ion recombination process on the disappearance of electrons by ambipolar diffusion. This procedure is inaccurate and speculative. [H. J. Oskam, Philips Res. Rept. **13**, 335 (1958)].

[33] M. C. Sexton, M. J. Mulcahy, and J. J. Lennon, in *Fourth International Conference on Ionization Phenomena in Gases, Uppsala, Sweden* (North Holland Publishing Company, Amsterdam, 1960).

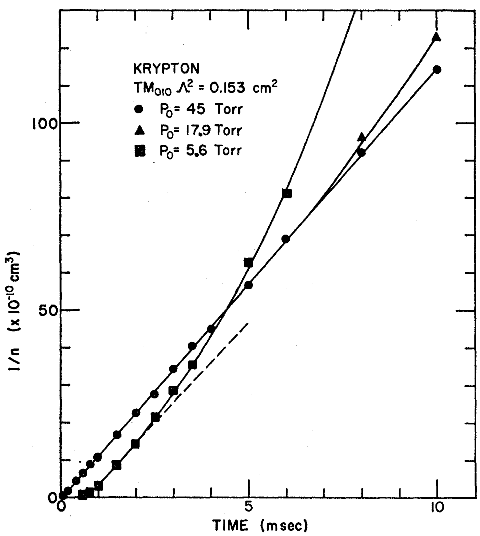

FIG. 5. Reciprocal of the electron density in krypton as a function of time during the decay period.

Richardson[14] measured values $\alpha_m(Kr_2^+)$ varying from 0.6 to 1.2×10^{-6} cm^3 sec^{-1} for pressure ranging from 6 to 25 Torr. The value of the electron-density ratio, used for calculating α_m, was about 4. The author believed that the Kr_2^+ ions were replaced by another type of molecular ion during the later part of the afterglow period. The spectrum emitted during this period was found to be the atomic xenon spectrum, while the atomic krypton spectrum was observed during the early afterglow period.

Lennon and Sexton[12] studied the recombination coefficient in krypton which contained most probably a large number of xenon atoms. They reported that less than 0.5% xenon was present in the krypton gas used. Only one of the curves published showed a true linear relationship between $1/n_e(t)$ and time over an appreciable electron density range. The value of f was about 14 and the recombination coefficient calculated from this curve was 2.3×10^{-6} cm^3 sec^{-1}. The authors assumed that the value referred to Xe_2^+ ions, since it was close to that of $\alpha_r(Xe_2^+)$ measured when studying recombination phenomena in xenon. The conclusion drawn from curves which do not constitute true straight lines was that $\alpha_r(Kr_2^+)$ is not greater than 1.1×10^{-6} cm^3 sec^{-1}. The measurements were carried out over a pressure range of 5 to 40 Torr.

The present studies were conducted in the pressure range of 6 to 45 Torr. The krypton used contained less than 2.5×10^{-3}% xenon and was further purified by means of the cataphoretic segregation process.[34] It was believed that the purity of the krypton was sufficient, since a krypton-xenon mixture does not constitute a Penning mixture.[35] Typical examples of $1/n_e(t)$ versus time curves are shown in Fig. 5. The curves for pressures of 45 and 17.9 Torr coincided during the major part of the afterglow period. The curve relating to 17.9 Torr deviated from the straight line for small electron densities, where the influence of ambipolar diffusion becomes important. The effect is very pronounced at a pressure of 5.6 Torr, where the value of f is only about 5 compared to about 650 at 45 Torr. The curvature at 5.6 Torr at very early times during the afterglow period is assumed to be caused by a nonuniform initial electron density distribution and/or a production of electrons by metastable atom-metastable atom collisions.

The value of β was, for the high-pressure region, larger than 10^4. Combined with the predicted and measured large values of f, the obtained $\alpha_r(Kr_2^+)=(1.2\pm0.1)\times10^{-6}$ cm^3 sec^{-1} is believed to be accurate within 10%.

VIII. THE RECOMBINATION COEFFICIENT OF Xe_2^+ IONS

The uncertainty concerning the value of $\alpha_r(Xe_2^+)$ has been about the same as that of $\alpha_r(Kr_2^+)$. Richardson[14] obtained values varying from 1.2 to 2.1×10^{-6} cm^3 sec^{-1}. These values were measured in krypton containing xenon impurity atoms of a sufficient number

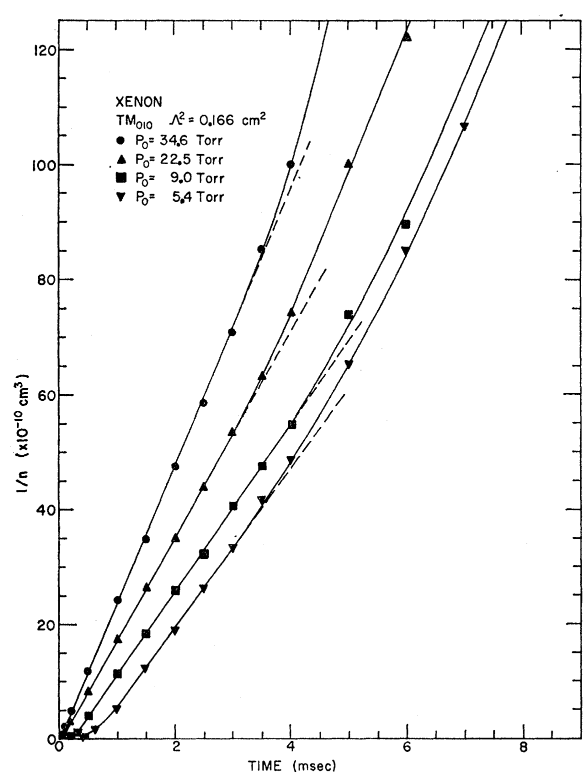

FIG. 6. Reciprocal of the electron density in xenon as a function of time during the decay period.

[34] R. Riez and G. H. Dieke, J. Appl. Phys. 25, 196 (1954). This type of gas purification technique was used for all gases studied. The pressure-independent value of $\alpha_m(Kr_2^+)$ obtained during the present experiment indicated a sufficient purity of the krypton used.

[35] F. M. Penning, Physica 1, 1028 (1934).

TABLE I. The recombination coefficient of molecular rare-gas ions measured with microwave techniques.

Author	$\alpha_r(\text{cm}^3\,\text{sec}^{-1})\times10^{-7}$	Maximum f	Pressure (Torr)
	Helium		
M. A. Biondi and S. C. Brown[a]	0.17	3	21.2; 28.7
R. A. Johnson *et al.*[b]	0.095	1.2	15
H. J. Oskam[c]	<0.1	[d]	up to 30
M. C. Sexton and J. D. Graggs[e]	0.5	[d] 1.2	32
E. P. Gray and D. E. Kerr[f]	0.013	[g]	15 to 20
C. L. Chen *et al.*[h]	0.089±0.005	[i] 3.6	15 to 30
Present studies	⩽0.04	[j] 4	up to 60
	Neon		
M. A. Biondi and S. C. Brown[k]	2.07±0.5	[i] 9	15 to 30
R. B. Holt *et al.*[l]	1.1	[d] 3.5	20
H. J. Oskam[c]	2.4±0.2	7	18.1; 19.8
M. A. Biondi[m]	2.2±0.1	[j] 5	9.5; 23.5
Present studies	2.2±0.2	[i] 30	17 to 35
	Argon		
M. A. Biondi and S. C. Brown[k]	3	[n]	
A. Redfield and R. B. Holt[o]	11	[p] 6	20 to 30
M. A. Biondi[m,q]	6	[j] 30	14
M. C. Sexton and J. D. Graggs[e]	6±2	[d] 4	30 to 50
M. C. Sexton *et al.*[r]	2	4	18.3
Present studies	6.7±0.5	[i] 250	9 to 35
	Krypton		
J. M. Richardson[s]	6	[t] 4	6 to 25
J. J. Lennon and M. C. Sexton[u]	11	[t] 2	6 to 30
Present studies	12±1	[i] 650	6 to 45
	Xenon		
J. M. Richardson[s]	20	[v] 10	6 to 25
J. J. Lennon and M. C. Sexton[u]	23	[w] 18	5 to 40
Present studies	14±1	[i] 250	5.4 to 35.6

[a] See Ref. 1.
[b] See Ref. 24.
[c] See Ref. 7.
[d] This symbol means dependence on plasma excitation.
[e] See Ref. 15.
[f] See Ref. 26.
[g] This symbol means estimated from deviation from exponential time dependence.
[h] See Ref. 25.
[i] This symbol means independent of gas pressure.
[j] This symbol means measured value corrected by using the analysis of E. P. Gray and D. E. Kerr.
[k] See Ref. 4.
[l] See Ref. 13.
[m] See Ref. 29.
[n] This symbol means gas purity suspected.
[o] See Ref. 30.
[p] This symbol means at 30 Torr dependence on plasma excitation; second value 6.5×10^{-7} cm³ sec⁻¹ determined at 30 Torr.
[q] See Ref. 6.
[r] See Ref. 33.
[s] See Ref. 14.
[t] This symbol means krypton contained appreciable xenon impurity.
[u] See Ref. 12.
[v] This symbol means measured in krypton containing xenon.
[w] This symbol means dependence on pressure; value relates to minimum value, which was measured at 10 Torr.

density, so that during the late afterglow period only the atomic xenon spectrum was emitted. The krypton pressure range studied was from 6 to 25 Torr, while the maximum reported value of f was 10.

Lennon and Sexton[12] conducted the only study in xenon. The pressure range investigated was from 5 to 40 Torr. They observed that the measured recombination coefficient was pressure dependent and assumed that the lowest value measured was the correct value, i.e., $\alpha_r(Xe_2^+)=2.3\times10^{-6}$ cm³ sec⁻¹ at 10 Torr. The value of f indicated was about 18. The increase in the measured value for increasing pressure above 10 Torr was attributed to the increasing influence of the collision frequency for momentum transfer ν_m of the electrons with the gas particles on the constant relating the frequency shift of the microwave cavity to the electron density. They, however, failed to observe a pressure dependence as predicted by Eq. (11). The increase in the measured value for decreasing pressure below 10 Torr was believed to be a consequence of the increasing importance of the ambipolar diffusion process.

The present studies refer to pressures varying from 5.4 to 34.6 Torr. The concentration of krypton impurity atoms was less than 10^{-3}%. Typical examples of measured $1/n_e(t)$ versus time curves are shown in Fig. 6. Even at the lowest pressure, the value of f was larger than 8; while at 34.6 Torr, the density ratio used for the determination of the recombination co-

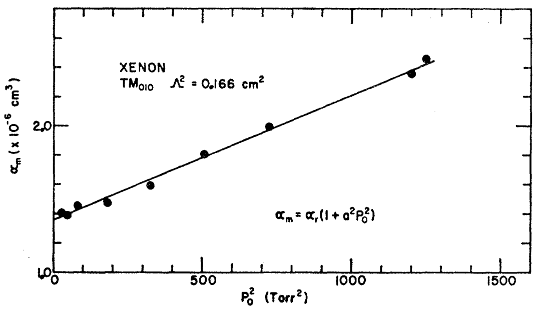

FIG. 7. The measured recombination coefficient α_m in xenon as a function of the square of the gas pressure.

efficient was about 250. The origin of deviations from the straight line in the very early afterglow period at low pressures is believed to be the same as in krypton. The curves of Fig. 6 were obtained by using the frequency sweep method, since the effect of the changing coupling of the probing signal to the cavity during the afterglow period was very pronounced in xenon due to the large value of ν_m.

The value of the measured recombination coefficient $\alpha_m(Xe_2^+)$ was found to depend on the gas pressure. Figure 7 shows α_m as a function of p_0^2 and from this figure it follows that α_m exhibits the pressure dependence as predicted by formula (11). The intersect at $p_0^2=0$ gives $\alpha_r(Xe_2^+)=1.36\times10^{-6}$ cm³ sec⁻¹, while, when assuming that ν_m is independent of the electron energy, the value of l_0 at an electron energy of 0.04 electron is found to be 0.007 cm.[36] Taking into account the assumptions made, this is in fair agreement with the value $l_0=0.0056$ cm determined by Phelps *et al.*[21] The value of β at 34.6 Torr is larger than 10^4, so that, combined with the large values obtained for f, the recombination coefficient $\alpha_r(Xe_2^+)=(1.4\pm0.1)\times10^{-6}$ cm³ sec⁻¹ is believed to be accurate within 10%.

IX. SUMMARY

In order to compare the values of the recombination coefficients of molecular rare-gas ions measured by various authors by means of the microwave technique, these values are summarized in Table I. The value of α_r, which, according to the authors is most accurate at the moment of publication of the results, is given. The electron density ratio f used for the determination of α_r as was available from the references is indicated, since the magnitude of this value is believed to be a good indication of the reliability of the reported values of α_r. The pressure ranges over which the studies were conducted are also given, while the observed dependences on gas pressure and/or plasma excitation power is indicated. The data refer to a gas and electron temperature of about 300°K.

The present studies show that, within the accuracy of measurement, the values of α_r are independent of gas pressure. The dependence on plasma excitation power disappears, provided the pulse length is sufficiently large to allow the plasma to fill the entire plasma container and provided the gas is of sufficient purity. The value of $\alpha_r(He_2^+)$ was estimated to be smaller or equal to 4×10^{-9} cm³ sec⁻¹. The values of α_r for the other molecular rare-gas ions, were determined from $1/n_e(t)$ versus time curves which satisfied the theoretical analysis performed by Gray and Kerr.[10] The following values, believed to be accurate within 10%, were determined: $\alpha_r(Ne_2^+)=(2.2\pm0.2)\times10^{-7}$, $\alpha_r(Ar_2^+)=(6.7\pm0.5)\times10^{-7}$, $\alpha_r(Kr_2^+)=(1.2\pm0.1)\times10^{-6}$ and $\alpha_r(Xe_2^+)=(1.4\pm0.1)\times10^{-7}$ cm³ sec⁻¹. The apparent dependence of the recombination coefficient of Xe_2^+ ions on the gas pressure was found to be caused by the influence of the collision frequency ν_m on the relationship between the measured frequency shift Δf and the electron density $n_e(t)$. When the influence of ν_m on the measured value of the recombination coefficient α_m is large, the dependence of α_m on the pressure p_0 may be used to obtain a value of ν_m, provided the recombination coefficient α_r is independent of p_0. The present results showed that the value of ν_m estimated from measurements in xenon is in fair agreement with previous studies.

ACKNOWLEDGMENTS

The many discussions with L. M. Chanin and other members of the study group on Plasma Physics contributed largely to the interpretation of the experimental results. The skill of our glassblower, J. Smulders, made the excellent performance of the vacuum system and the quartz bottles possible.

[36] The measurements conducted in krypton indicated, within the accuracy of measurement, little or no dependence of $\alpha_m(Kr_2^+)$ on pressure up to pressures of 45 Torr. This resulted in an estimate of $l_0 \geqslant 0.025$ cm, while Phelps *et al.* (See Ref. 21) measured $l_0=0.019$ cm.