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Electron Temperature Dependence of Recombination of Ne₂⁺ Ions with Electrons*

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The electron temperature dependence of the recombination of mass-identified Ne₂⁺ ions with electrons is studied by means of a microwave-afterglow/mass-spectrometer apparatus employing microwave heating of the electrons. Under conditions where the ion wall current "tracks" the volume electron-density decay, the electron-decay data indicate that $\alpha(\text{Ne}_2^+)$ decreases as $T_e^{-0.49}$ over the range $300^\circ\text{K} \leq T_e \leq 4600^\circ\text{K}$, starting at a value $(1.75 \pm 0.2) \times 10^{-7} \text{ cm}^3/\text{sec}$ at $T_e = 300^\circ\text{K}$. This value and this variation with T_e are in good agreement with the results of other studies, all but one of which did not employ mass identification of the ions under study.

I. INTRODUCTION

Experimental determinations of the variation of the dissociative recombination coefficient with electron temperature provide insight concerning the details of the process of electron capture by molecular ions and guidance for improved theoretical calculations of the process. The capture of electrons by what are presumably Ne₂⁺ ions is probably the recombination reaction most extensively studied to date¹⁻⁹; however, until now, only one study⁸ has identified, by mass analysis, Ne₂⁺ as the ion undergoing recombination. Therefore when studies of the electron temperature dependence of recombination between mass-identified ions and electrons were undertaken¹⁰ (see preceding paper), it seemed appropriate to extend the studies to Ne₂⁺ in order to compare the results with recent electron-temperature studies which did not employ mass analysis.⁹

In the next sections, we very briefly describe the measurement technique, present examples of the measured electron and ion decays during the afterglow, give the inferred values of the recombination coefficient $\alpha(\text{Ne}_2^+)$ as a function of

electron temperature T_e , and compare our results with previous measurements.

II. APPARATUS AND MEASUREMENTS

The microwave-afterglow/mass-spectrometer apparatus is shown in a highly simplified block diagram in Fig. 1. (For a more detailed description see preceding paper and Ref. 8.) Pure neon¹¹ at 6 Torr is ionized by a ~2.5-msec pulse of energy from a magnetron (repeated 10 times a second), and the electron density decay is determined from measurements of the resonant frequency shifts of a high Q (~2000) TM₀₁₀ cavity mode during the afterglow.¹² The electrons are heated to constant, controlled temperatures during the afterglow by excitation of a low Q (~9) TE₁₁₁ mode with a $c-w$ magnetron.^{9,10,13} The electron temperature is calculated from the measured cavity Q and incident microwave power. The thermal conductivity of the electron "gas" is sufficiently high that an essentially isothermal behavior results in spite of the spatially dependent heating fields. The afterglow ions which diffuse to the wall and effuse through a small hole

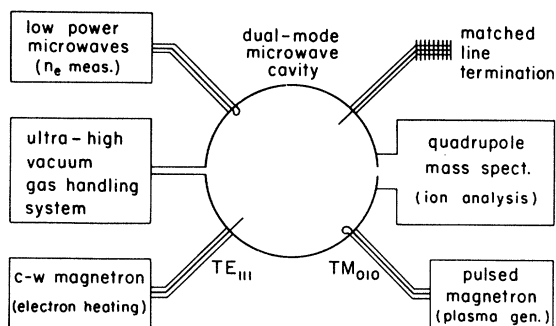


FIG. 1. Highly simplified block diagram of microwave-afterglow/mass-spectrometer apparatus used to determine the recombination of Ne_2^+ ions with electrons at various electron temperatures.

are mass analyzed by a differentially pumped quadrupole mass spectrometer.

At pressures greater than a few Torr, a single positive ion, Ne_2^+ , is found to predominate throughout the afterglow; in addition, experimental conditions (e.g., discharge pulse length) are arranged so that ionization processes are negligible,⁹ and dissociative recombination and ambipolar diffusion are the significant electron-ion loss processes. Thus the electron continuity equation becomes

$$\frac{\partial n_e(\vec{r}, t)}{\partial t} \simeq -\alpha n_e^2(\vec{r}, t) + D_a \nabla^2 n_e(\vec{r}, t), \quad (1)$$

where n_e , the electron density, has been set equal to the ion density (quasineutrality) and D_a is the ambipolar diffusion coefficient.

Since the solution of Eq. (1) under recombination controlled conditions indicates that $[n_e(\vec{r}, t)]^{-1}$ increases linearly with time, we display our "microwave-averaged" electron-density^{9,10} data as plots of $1/\bar{n}_{\mu w}$ versus time to indicate such recombination control (see Fig. 2, which presents examples of the measurements at several electron temperatures). It will be seen that at low electron temperatures (e.g., 300°K) there is a substantial range of electron densities over which $1/\bar{n}_{\mu w}$ increases linearly with time (dashed line) before curving upward as a result of the increasing importance of ambipolar diffusion. At high electron temperatures (e.g., 4600°K) the need for the computer solution⁹ of Eq. (1) in obtaining quantitative values of $\alpha(\text{Ne}_2^+)$ becomes evident. (In this computer program, the known value^{5,14} of $D_a p = 140 \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{Torr}$ is used to obtain D_a values at each electron temperature, an initial "fundamental diffusion mode" or "fundamental mode squared" spatial distribution is assumed, and α is treated as a parameter.) The solid curves indicate "best fits" of the computer solutions to the experimental curves.

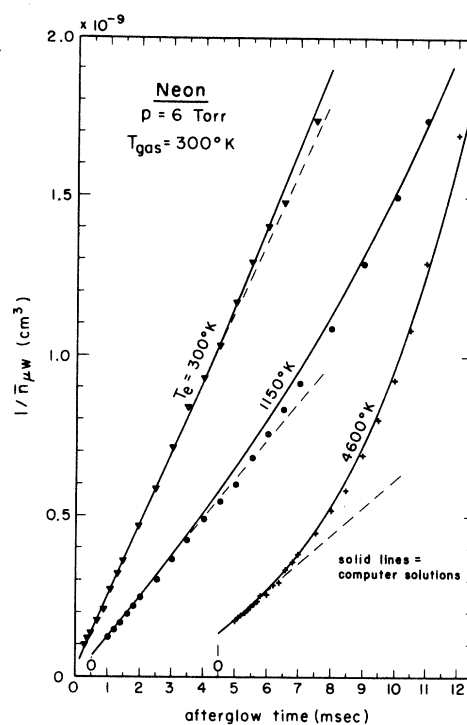


FIG. 2. Electron-density decay data presented as plots of $(\bar{n}_{\mu w})^{-1}$ versus afterglow time for various electron temperatures at a gas temperature of 300°K. (The time zero on each curve has been displaced for clarity.)

We assign the inferred α values to recombination between Ne_2^+ ions and electrons on the basis of the ion history data, examples of which are given in Figs. 3 and 4. It will be seen that, throughout the recombination controlled portion of the afterglow ($t < 10$ msec), Ne_2^+ is the dominant ion. In addition to the slight Ne^+ signal, we find small amounts of CO^+ , C^+ , and O^+ , which are typical of background ions in a system containing large amounts of stainless steel. Also shown in the figures are relative values of $\bar{n}_{\mu w}$ (solid lines) which have been renormalized (dashed lines) to the Ne_2^+ wall current data. At $T_e = 300^\circ\text{K}$ (Fig. 3) the ion decay "tracks" the electron decay after ~ 2 msec (as explained previously,^{8,15} "tracking" between ion wall current and volume electron-density decay can occur only if the spatial distribution of the ions and electrons assumes an essentially time-invariant form, which condition takes some time to achieve). At $T_e = 1150^\circ\text{K}$ (Fig. 4) the tracking is less perfect in the late afterglow and becomes even poorer as we go to higher electron temperatures; however, in all cases Ne_2^+ wall currents exceed all other ions by a factor $\gtrsim 30$ at afterglow times < 10 msec.

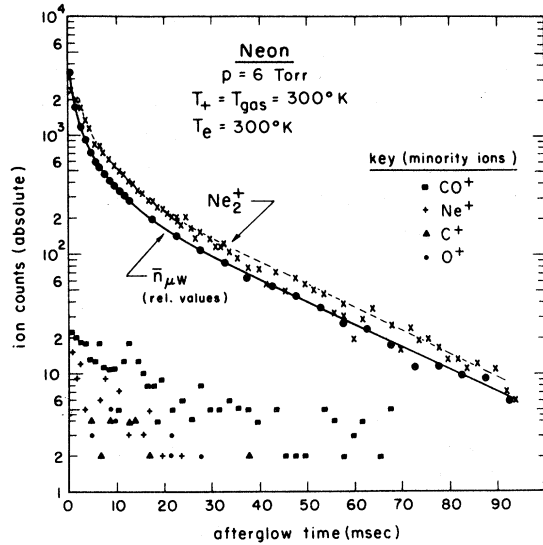


FIG. 3. Comparison of ion wall current decay with the decay of electron density from the afterglow plasma at $T_e = 300^\circ\text{K}$. The dashed curve is the electron decay renormalized to the Ne_2^+ curve at $t = 10$ msec.

The observed variation of $\alpha(\text{Ne}_2^+)$ with electron temperature is shown in the log-log presentation of Fig. 5. The values of $\alpha(\text{Ne}_2^+)$ have been obtained in two ways; the solid circles indicate the values deduced from the somewhat laborious "best fit" of computer solutions⁹ of Eq. (1) to the $1/\bar{n}_{\mu w}(t)$ data, while the crosses indicate corrections of the slopes of the linear portions of the $1/\bar{n}_{\mu w}$ versus t curves (which are proportional to α) for the effects of diffusion by use of tabulated β -correction factors¹⁶ ($\beta \equiv \alpha n_0 \Lambda^2 / D_a$ is the ratio of the recombination to the ambipolar diffusion rate, where n_0 is the initial electron density at the center of the cavity, whose fundamental diffusion length $\Lambda = 1.3$ cm). The β corrections do not, however, provide as rigorous a test of the analysis as the attempts to fit the computer solutions to the data. The scatter in the data gives some measure of the reproducibility of the results under variations of experimental conditions such as initial electron density. Except for the value at $T_e = 4600^\circ\text{K}$, the data fit a simple variation of $\alpha(\text{Ne}_2^+)$ as $T_e^{-0.49}$ (solid line).

III. DISCUSSION

The present measurements indicate that the recombination coefficient of mass identified Ne_2^+ ions and electrons at a gas temperature of 300°K decreases from a value $\alpha(\text{Ne}_2^+) = (1.75 \pm 0.2) \times 10^{-7}$ cm^3/sec at $T_e = 300^\circ\text{K}$ to a value $(4.0 \pm 0.6) \times 10^{-8}$ at $T_e = 4600^\circ\text{K}$. This behavior may be compared with the results of Frommhold, Biondi, and Mehr⁹

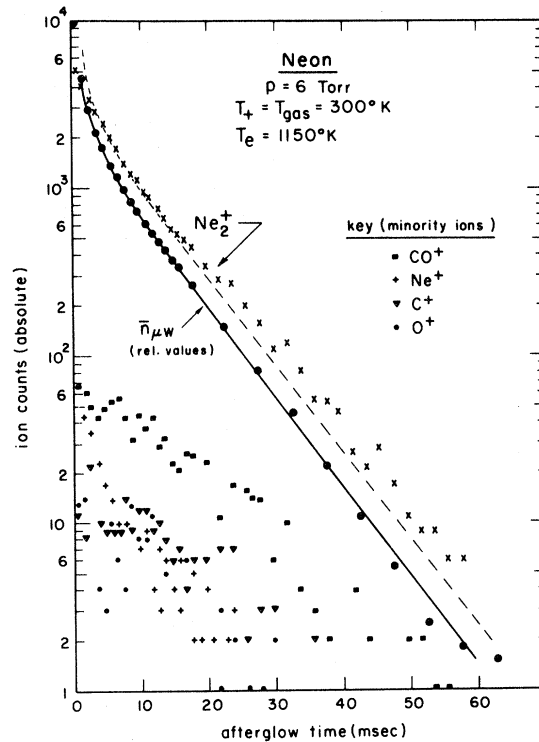


FIG. 4. Comparison of ion and electron decays at $T_e = 1150^\circ\text{K}$. While Ne_2^+ remains the principal afterglow ion, the "tracking" between Ne_2^+ ions and electrons becomes poorer very late in the afterglow.

(FBM) who used a nonresonant waveguide heating mode (which permitted more accurate determinations of the electron temperature) but did not employ mass analysis. Their results, which extend over the range $300^\circ\text{K} \leq T_e \leq 11\,000^\circ\text{K}$ and are accurate to $\pm 5\%$, are indicated by the dashed curve in Fig. 5. The results of the two experi-

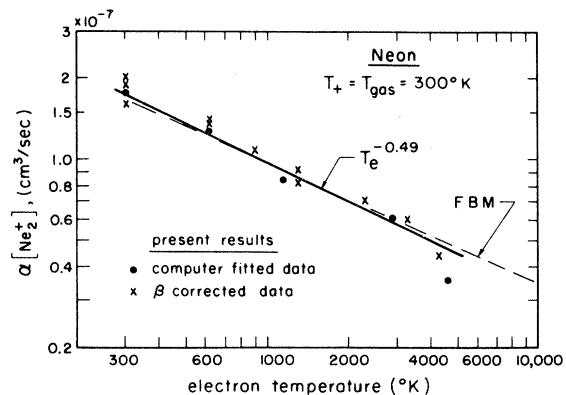


FIG. 5. Measured variation of $\alpha(\text{Ne}_2^+)$ with electron temperature. The present results are indicated by the solid line, while the dashed line represents the results of Frommhold, Biondi, and Mehr, who did not employ mass analysis of the ions under study.

ments are in excellent agreement (with the exception of our data at $\sim 4600^\circ\text{K}$, which appear inexplicably low). In addition, our value at $T_e = 300^\circ\text{K}$ is in excellent agreement with the results of eight other neon experiments¹⁻⁸ carried out at room temperature (see corrected α values for these measurements given in Ref. 9). Finally, within the experimental errors, the variation of $\alpha(\text{Ne}_2^+)$ with temperature is the same when T_+

$= T_{\text{gas}} = 300^\circ\text{K}$ and T_e is varied (present case) and when T_e , T_+ , and T_{gas} are covaried (in this case, Kasner⁸ found that $\alpha(\text{Ne}_2^+) \sim T^{-0.42}$ over the range $295\text{--}503^\circ\text{K}$). Thus it appears that dissociative recombination between Ne_2^+ ions and electrons approximates the $T_e^{-1/2}$ energy dependence predicted¹⁷ if the initial radiationless-capture step is rate limiting.

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