Electron Temperature Dependence of Recombination of O_2^+ and N_2^+ Ions with Electrons*

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A microwave-afterglow/mass-spectrometer apparatus which employs microwave heating of the electrons is used to determine the recombination coefficients, $\alpha(O_2^+)$ and $\alpha(N_2^+)$, of mass-identified ions with electrons as a function of electron temperature. From electron-density decay data taken under good "ion-tracking" conditions it is found that $\alpha(O_2^+)$ varies as $T_e^{-0.70}$ over the range $300°K \leq T_e \leq 1200°K$ [starting from a value $(1.95 \pm 0.2) \times 10^{-7}$ cm^3/sec at $T_e = 300°K$] and then varies as $T_e^{-0.56}$ between 1200 and 5000°K. In the nitrogen studies the "ion tracking" of the electron decay is less perfect, but N_2^+ remains the principal afterglow ion and $\alpha(N_2^+)$ is found to vary as $T_e^{-0.39}$ over the entire range $300°K \leq T_e \leq 5000°K$, starting from a value $(1.8 \pm {}^{0.4}_{0.2}) \times 10^{-7}$ cm^3/sec at $T_e = 300°K$. These results are compared with other laboratory determinations, results of theoretical calculations, and values inferred from analyses of ionospheric measurements.

I. INTRODUCTION

The recombination of molecular positive ions with electrons constitutes one of the principal charge limiting processes in various regions of the ionosphere. Photo-ionization of the abundant oxygen and nitrogen in the atmosphere leads to substantial production of O_2^+ and N_2^+ ions in the E and F regions. Thus models of ionospheric behavior require accurate determinations of the rates of recombination of these ions with electrons under conditions encountered in the upper atmosphere. In the E region the electron temperature T_e is probably equal to the ion and neutral temperature ($T_+ = T_n \simeq 250°K$), while as one goes into the F region T_e exceeds T_+ and T_n, approaching 2500°K at 300-km altitude. While a number of careful laboratory measurements[1-4] of the two-body recombination coefficients, $\alpha(O_2^+)$ and $\alpha(N_2^+)$, have recently been carried out over the temperature range ~200 to ~600°K under conditions such that $T_e \simeq T_+ = T_n$, none have permitted independent control of the electron temperature to permit an accurate determination of the dependence of α on T_e and to duplicate, as nearly as possible, the expected ionospheric conditions.

In the next section we describe a microwave-afterglow/mass-spectrometer apparatus which permits us to identify the ions undergoing recombination and to measure their recombination rate as a function of electron temperature. In Sec. III we present examples of the experimental measurements from which the desired information is obtained. In Sec. IV we give the results of our measurements, discuss their relationship to theoretical ideas concerning the dissociative recombination process for the ions O_2^+ and N_2^+, and compare our results with other experimental data.

II. APPARATUS AND METHOD OF MEASUREMENT

The microwave-afterglow/mass-spectrometer apparatus used in the present studies is that used by Weller and Biondi,[5] modified to include an additional cavity excitation mode (TE_{111}) to permit controlled electron heating during the afterglow, following the method employed by Frommhold *et al.*[6] The highly simplified diagram of Fig. 1 indicates the cylindrical microwave resonant cavity into which gas samples are introduced from an ultrahigh-vacuum gas-handling system. For plasma generation and resonant frequency shift (average electron density) determinations[7] during the afterglow, a high Q (~2000) TM_{010} mode is excited by small magnetic coupling

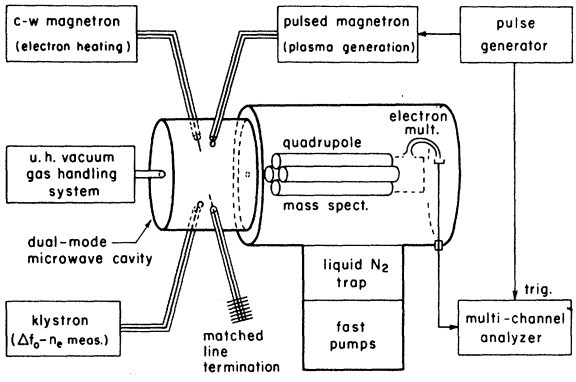

FIG. 1. Simplified block diagram of microwave-afterglow/mass-spectrometer apparatus used in the recombination studies.

loops located at the cavity's median plane. The plasma is generated by a ~2-msec pulse of energy from a magnetron which can be operated in either a "single pulse" (one pulse every 5 sec) or a repetitive pulse (10–100 per sec) mode. The resonant frequency shifts, Δf_0, are determined by noting the times of maximum reflection of a low-energy probing signal for various signal frequencies. These frequency shifts are used to calculate the "microwave-averaged" electron density,[6] $\bar{n}_{\mu w}(t)$, defined by

$$\bar{n}_{\mu w}(t) \equiv \frac{\int_{\text{vol}} n_e(\vec{r},t) E_p^2(\vec{r})\, dV}{\int_{\text{vol}} E_p^2(\vec{r})\, dV} = \Delta f_0(t)/C, \quad (1)$$

where $n_e(\vec{r},t)$ is the electron density, $E_p(\vec{r})$ is the microwave probing field amplitude, and C is a constant involving a group of physical constants and the cavity's resonant frequency.

Controlled electron heating is achieved by exciting the TE_{111} mode with two large electric field probes located along a diameter in the cavity's median plane. The coaxial line leading from one probe is terminated in a matched load, the resulting loading yielding the desired low $Q(=9.0)$ for the TE_{111} mode. Thus even though we use a fixed microwave heating frequency, the small resonant frequency shift of the TE_{111} mode during the afterglow electron decay leads to a negligible change in the response of the cavity to the microwave heating field. The steady power level from the c-w magnetron then produces an essentially constant electron temperature throughout the afterglow. In an earlier publication[6] [see Ref. 6, Eq. (13)] it was shown that the electron temperature, T_e, is related to the microwave heating field amplitude, E_h, by

$$T_e \simeq T_n + (e^2 M/6k\omega^2 m^2)\langle E_h^2 \rangle , \quad (2)$$

where e and m are the electron charge and mass, respectively, M is the neutral atom mass, ω is the microwave radian frequency, and k is Boltzmann's constant. Inasmuch as the microwave field varies with position in the cavity, but the electron-electron collisions distribute the energy absorbed to create a uniform electron temperature throughout the plasma,[8] it is appropriate to use an electron-density weighted average of the square of the field in Eq. (2) [see Ref. 6, Eq. (14)]; namely

$$\langle E_h^2 \rangle \equiv \frac{\int_{\text{vol}} n_e(\vec{r}) E_h^2(\vec{r})\, dV}{\int_{\text{vol}} n_e(\vec{r})\, dV} . \quad (3)$$

An electron spatial distribution (e.g., "fundamental diffusion mode") appropriate to the expected experimental conditions is used in Eq. (3). We calculate the heating field strength in the cavity by standard microwave procedures[9] involving determinations of the power absorbed and the loaded Q of the heating mode. The power measuring apparatus has been described earlier.[6]

In order to obtain the values of the recombination coefficient as a function of electron temperature from the determinations of the variation of $\bar{n}_{\mu w}(t)$, we seek experimental conditions such that, during the afterglow, (a) a single-positive-ion species is dominant and negative-ion concentrations are negligible; then $n_+ \simeq n_e$, (b) electron-ion production is negligible, and (c) recombination greatly outweighs ambipolar diffusion (coefficient, D_a). Under these circumstances, the electron continuity equation simplifies to

$$\frac{\partial n_e(\vec{r},t)}{\partial t} \simeq -\alpha n_e^2(\vec{r},t) + D_a \nabla^2 n_e(\vec{r},t) , \quad (4)$$

which, in cases where the diffusion term is negligible, yields the "recombination solution",

$$1/n_e(\vec{r},t) = 1/n_e(\vec{r},0) + \alpha t . \quad (5)$$

Although, we suggested by the form of Eq. (5), we display our data as plots of $1/\bar{n}_{\mu w}(t)$ *versus* t, we obtain accurate values of α from our data by computer solution[10] of Eq. (4) to find $n_e(\vec{r},t)$ and hence $\bar{n}_{\mu w}(t)$ for various values of α (known D_a values are inserted). Comparison of the computer-generated curves with the measurements permits selection of the α value from the curve which gives the best fit to the data.

Finally, the time history of the afterglow ions is obtained by mass analyzing the ions diffusing to the cavity end wall and effusing through a small hole. To reduce statistical fluctuations in the data resulting from the small ion counting rate, data from many afterglows are added together by use of a multichannel analyzer operating in a multiscaling mode (0.5-msec/channel dwell time).

III. EXPERIMENTAL MEASUREMENTS

A. O_2^+ Recombination

In the oxygen studies, complex-ion formation is avoided by using high purity neon[11] as the majority buffer gas (~10 Torr), and small amounts of oxygen (3–8 mTorr) are added to permit Penning ionization by neon metastable atoms to form O_2^+ ions. [Such ionization may create O_2^+ not only in its ground electronic ($X^2\Pi_g$) but also the excited ($a^4\Pi_u$) state.] Negative-ion formation is inhibited by the small oxygen partial pressures, and accumulation from pulse to pulse is avoided by operating in a "single-pulse" mode.[1,5] In practice, no dependence of the electron-decay curves

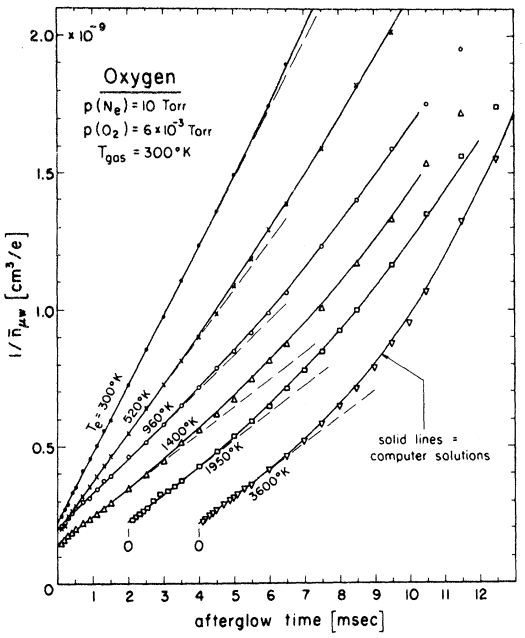

FIG. 2. Electron-density decay data in O_2-Ne mixtures at $T_{gas}=300°K$ presented as plots of $(\bar{n}_{\mu w})^{-1}$ *versus* afterglow time, with electron temperature as a parameter. The time zero on the $T_e=1950$ and 3600°K curves has been shifted for clarity.

on repetition frequency below 1 Hz is noted; also no dependence on the discharge pulse length over the range 1.5–4 msec nor on the O_2 pressure between the limits 3–8 mTorr is observed.

Examples of the measured frequency-shift data, converted to $\bar{n}_{\mu w}$ values, are shown by the points in Fig. 2, which presents graphs of $1/\bar{n}_{\mu w}$ *versus* afterglow time for various electron temperatures. The dashed lines are extensions of the linear portions of the data [the "recombination solution" form of Eq. (5)], while the solid lines are the "best-fit" computer solutions to the data. These solutions involve known D_a values obtained from the relation, $D_a=D_+(1+T_e/T_+)$, with $T_+=T_n=300°K$ and the value[12] $D_+p=180$ (cm²/sec)·Torr. An initial "fundamental diffusion mode" electron distribution provides the best fit to the early afterglow (<0.5-msec) data; however the α values inferred from the over-all curve fitting process are not particularly sensitive to this choice of initial distribution form (see discussion in Ref. 6). It will be seen that very good fits are obtained even when large diffusion losses (curved portions) are encountered at the elevated electron temperatures.

In order to attribute the recombination coefficients inferred from the electron-decay data of Fig. 2 to recombination with O_2^+ ions it is necessary to show that O_2^+ is the principal afterglow ion and that the ion diffusion current to the wall reasonably "tracks" the volume electron-density decay.[1,3–5] Figure 3 presents two of the electron-density decay curves of Fig. 2, together with the corresponding ion wall current curves, on a semilogarithmic scale. The left-hand portion, at $T_e=300°K$, shows O_2^+ as the principal afterglow ion (a small NO^+ impurity[13] quickly decays below detectability), and the renormalized electron-density data (dashed line) follows the ion decay very well after ~2 msec. However, at elevated electron temperatures (right-hand portion of Fig. 3, at $T_e=1950°K$) the "tracking" is less perfect, the O_2^+ decaying somewhat more slowly than n_e and the NO^+ impurity ion persisting at a low level throughout the afterglow. The "tracking" becomes progressively less accurate as the electron temperature is increased, but even at the highest temperature, $T_e\sim5000°K$, O_2^+ is clearly the dominant ion throughout the recombination controlled portion of the afterglow.

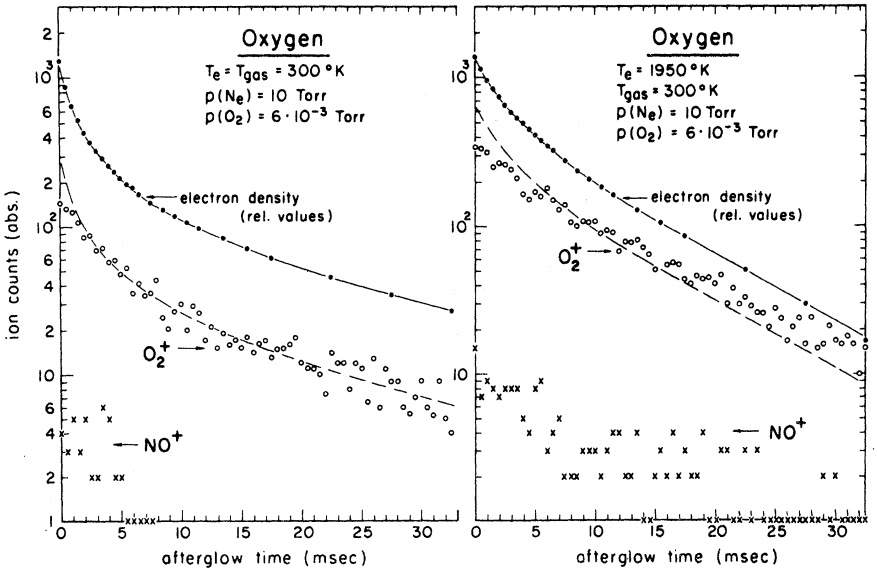

FIG. 3. Comparative decays of afterglow ion wall currents and volume electron density at $T_e=300°K$ and at $T_e=1950°K$. The dashed lines represent electron-density decay data renormalized to the O_2^+ curves at $t=3$ and 6 msec, respectively.

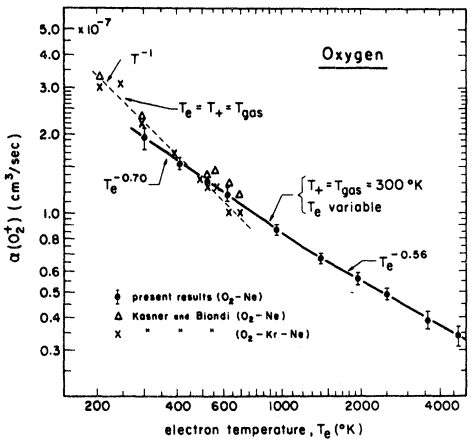

FIG. 4. Variation of $\alpha(O_2^+)$ with electron temperature.

The variation of the inferred $\alpha(O_2^+)$ values with electron temperature is shown on a log-log plot in Fig. 4. The present results are indicated by the solid line drawn through the data points (solid circles with estimated error bars attached). Over the range $300\,°K \leq T_e \leq 1200\,°K$ the data follow a simple $T_e^{-0.70}$ variation, while between 1200 and 5000°K they follow a $T_e^{-0.56}$ law. A comparison of the present results with other investigations is presented in Sec. IV.

B. N_2^+ Recombination

Qauntitative determinations of the dependence of $\alpha(N_2^+)$ on electron temperature proved to be unexpectedly difficult, in spite of the absence of the complicating effect of negative-ion formation (a potential problem in the oxygen studies). The investigations were first carried out[14,15] on the three-mode microwave apparatus of Frommhold *et al.*[6] which used a nonresonant waveguide heating mode but did not employ mass analysis. While this apparatus proved quite satisfactory for $\alpha(Ne_2^+)$ and $\alpha(Ar_2^+)$ studies[6,16] (in the noble gases, diatomic molecular ions are readily made the dominant afterglow ion), in the atmospheric-ion studies the derived recombination coefficients varied substantially with experimental conditions such as discharge pulse length and partial pressure of the added atmospheric gas (i.e., nitrogen or oxygen), even when these parameters were kept within the limits employed in successful $\alpha(O_2^+)$ and $\alpha(N_2^+)$ studies by Kasner and Biondi[1,3] and by Kasner.[4]

Since it was suspected that these difficulties arose from the presence of more than one ion species, the present microwave afterglow apparatus, which provides simultaneous mass analysis of the ions undergoing recombination, was employed. Although the $\alpha(O_2^+)$ studies proved relatively straightforward with this apparatus, the $\alpha(N_2^+)$ studies were complicated by our inability to find any experimental conditions in which ions more complicated than N_2^+ (i.e., N_3^+ and N_4^+) were negligible. The best conditions were achieved at a very low partial pressure of nitrogen (0.2 mTorr), where the N_3^+ and N_4^+ concentrations were relatively small.[17] Lower nitrogen pressures, which might have further reduced the N_3^+ and N_4^+ concentrations, could not be used because neon ions from the buffer gas then became appreciable in comparison with the N_2^+ concentration.

Examples of the electron-density decay data obtained under conditions where the ratio of the concentration of N_2^+ to other ions is a maximum are shown in a graph of $1/\bar{n}_{\mu w}$ *versus* afterglow time in Fig. 5 As in the case of Fig. 2, the dashed lines are extensions of the linear portions of the data, while the solid lines are the "best-fit" computer solutions of Eq. (4), treating α as a parameter and using the value[12] $D_+ p = 240$ (cm^2/sec) · Torr at $T_+ = T_n = 300\,°K$ and an initial "fundamental diffusion mode squared" distribution.

While the agreement between the computer solutions for recombination plus diffusion loss and the observed electron decays is seen to be very good in these examples, it is not clear that we have obtained a highly accurate (within 10%) determination of $\alpha(N_2^+)$, since the ion "tracking" of the electron decay is imperfect and small concentrations of N_3^+ and N_4^+ ions are present throughout the afterglow. Figure 6 shows the ion data corresponding to the $T_e = 300\,°K$ electron decay of

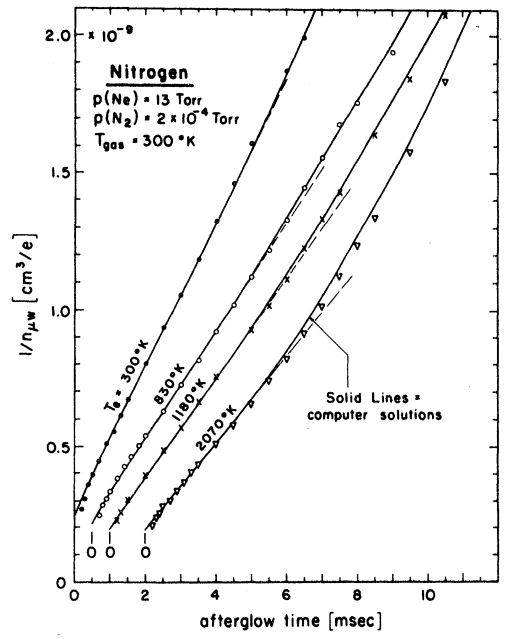

FIG. 5. Electron-density decays in N_2-Ne mixtures at $T_{gas} = 300\,°K$ presented as plots of $(\bar{n}_{\mu w})^{-1}$ *versus* afterglow time, with electron temperature as a parameter. For clarity, the time zero on the various curves has been shifted.

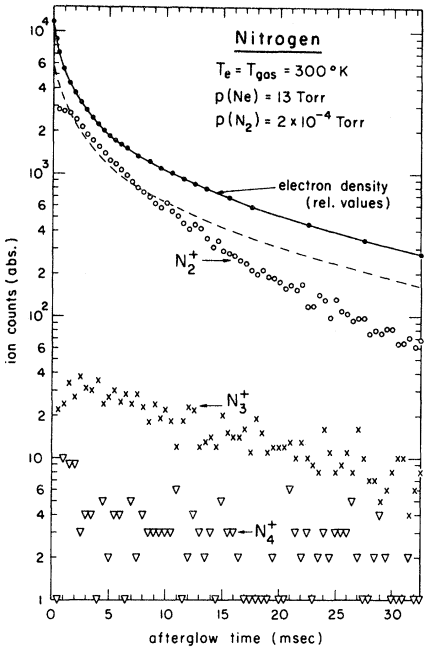

FIG. 6. Comparison of the ion wall current decays with the electron-density decay indicating the predominance of N_2^+ as the principal afterglow ion but rather poor "ion tracking" of the electron decay.

Fig. 5. It will be seen that after ~4 msec the N_2^+ wall current decays more rapidly than the electrons (and than the minority N_3^+ and N_4^+ ion currents).

Thus while it appears we are studying principally the recombination of N_2^+ ions with electrons, we are unable to assess the uncertainties in the inferred $\alpha(N_2^+)$ values suggested by the imperfect "tracking". These values are plotted as a function of electron temperature on a log-log scale in Fig. 7. (The error bars on the data points refer to the "usual" systematic and random errors which we can evaluate – see Sec. IV.) Over the entire measured range, $300°K \leq T_e \leq 5000°K$, $\alpha(N_2^+)$ is seen to follow a simple $T_e^{-0.39}$ variation. These results are compared with other investigations in the next section.

IV. RESULTS AND DISCUSSION

The present results may be compared with other work in terms of the absolute values of the coefficients $\alpha(O_2^+)$ and $\alpha(N_2^+)$ and in terms of the variations of the coefficients with temperature. If Eq. (4) adequately describes the afterglow decay processes, our measured values should be accurate within ~± 10%; the major portion of this uncertainty arises from the range of α values which provide a satisfactory fit to the $1/\bar{n}_{\mu w}$ *versus* t data and from uncertainties in the determinations of the electron temperature scale. (Errors in measurements of quantities such as afterglow time and frequency shift are much smaller than this.)

The principal experimental measurements with which we can make a direct comparison are at $T_e = T_n = 300°K$. Using mass analysis of the afterglow ions, Kasner and Biondi[1,3] and Kasner[4] obtained thermal-energy values, $\alpha(O_2^+) = (2.2 \pm 0.2) \times 10^{-7}$ and $\alpha(N_2^+) = (2.7 \pm 0.3) \times 10^{-7}$ cm^3/sec, under good ion "tracking" conditions. The O_2^+ value is in good agreement with our 300°K value, $(1.95 \pm 0.2) \times 10^{-7}$ cm^3/sec; on the other hand, the N_2^+ value is substantially higher than our value, $(1.8 \pm {}^{0.4}_{0.2}) \times 10^{-7}$ cm^3/sec. We are unable to account quantitatively for this difference; however, if the recombination coefficient for N_3^+ ions is substantially smaller than that for N_2^+ ions, our inferred $\alpha(N_2^+)$ values would be too small. Even assuming a mass discrimination effect in our quadrupole mass spectrometer such that the N_3^+ density is several times larger than the ion wall current would indicate, a simple analysis indicates that the possible increase in our $\alpha(N_2^+)$ value is only about 10%, and so the disagreement is not removed. A more remote possibility is that substantial Penning ionization by neon metastables persists into the afterglow, leading to a slower electron-density decay and hence to inference of too small a value of $\alpha(N_2^+)$. However, crude optical-absorption measurements indicate small afterglow metastable concentrations; also, computer solutions of the electron continuity equation including an exponentially decaying ionization term predict rather different forms of the electron decays than are observed; therefore we tend to rule out persistent afterglow ionization as an explanation of our "low" $\alpha(N_2^+)$ values. In spite of these problems concerning the absolute values of $\alpha(N_2^+)$ our measurements do appear to provide a satisfactory determination of the rela-

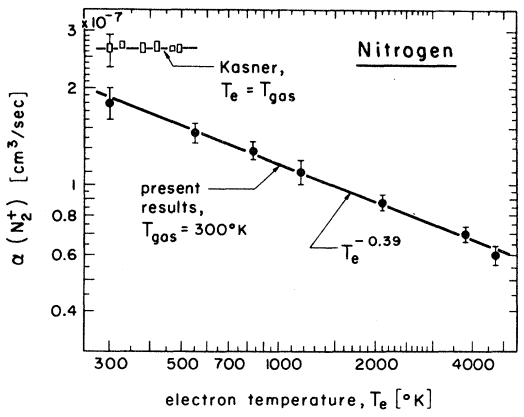

FIG. 7. Comparative variations of $\alpha(N_2^+)$ with electron temperature when T_{gas} is held at 300° K (present results) and when T_e, T_+, T_{gas} are covaried (Kasner).

tive variation of $\alpha(N_2^+)$ with T_e.

In view of the aforementioned difficulties in determining atmospheric-ion recombination coefficients with a mass-analysis afterglow apparatus under conditions where the desired ion dominates, we regard other experiments without mass analysis as intrinsically less reliable. Thus we defer a discussion of such experiments to later in this section.

The results[1,4] of studies of the temperature dependence of $\alpha(O_2^+)$ and of $\alpha(N_2^+)$ under conditions where $T_e = T_+ = T_n$ over the range ~200–700°K are shown in Figs. (4) and (7). Kasner and Biondi[1] found that $\alpha(O_2^+)$ varies approximately as T^{-1} for the case where the O_2^+ ions were probably in the ground electronic ($X^2\Pi_g$) state (the sequence – neon metastables ionizing krypton which charge transferred with O_2 – was used to achieve this condition). These data are shown by the X symbols in Fig. 4. Our results, obtained with O_2-Ne mixtures, where some of the O_2^+ ions may be produced in the metastable $a^4\Pi_u$ excited state, should more properly be compared with the corresponding data of Kasner and Biondi (triangular symbols). Over the corresponding temperature ranges the two experiments agree within the combined experimental uncertainties, suggesting that, up to at least 700°K, the effect of a changing vibration state population with T_+ has a negligible effect on $\alpha(O_2^+)$.

That this does not seem to be the case in the $\alpha(N_2^+)$ studies is indicated by the results of the two experiments shown in Fig. 7. In our studies, a variation of $\alpha(N_2^+)$ as $T_e^{-0.39}$ is noted, while Kasner[4] ($T_e = T_+ = T_n$) finds $\alpha(N_2^+)$ essentially independent of gas temperature. The N_2^+ ions in both experiments should be in the same state (ground electronic and a low vibrational state), since in both cases they were formed by Penning ionization of N_2 by neon metastables. Thus the increasing population of excited vibrational states of N_2^+ as T_{gas} is increased evidently leads to increased recombination which offsets the decrease of $\alpha(N_2^+)$ with increasing T_e for ions in a given vibrational state. The basis for such disparate variations when T_e alone and when T_e and T_+ are covaried has been discussed elsewhere.[16] In support of a decrease in $\alpha(N_2^+)$ with increasing T_e is a Langmuir probe determination by Sayers,[18] who found that for mass-identified ions, $\alpha(N_2^+) = 1.1\times10^{-7}$ cm^3/sec at $T_e = 3200$°K (no estimates of errors were given). With the same apparatus using helium-oxygen mixtures, Sayers obtained a value $\alpha(O_2^+) = 4\times10^{-8}$ cm^3/sec at $T_e = 2500$°K, in good agreement with the present results.

Turning now to measurements in oxygen and in nitrogen which did *not* employ mass analysis, Mentzoni[19] carried out studies in pure oxygen at 0.7–3 Torr and found that α decreased approximately as $T^{-0.4}$ ($T_e = T_+ = T_n = T$) over the range 300–900°K, starting from a value 2.1×10^{-7} cm^3/sec at 300°K. At the pressures of Mentzoni's studies, we would expect the presence of more complicated ions such as O_3^+ to interfere with the recombination coefficient determinations. Recently, Smith and Goodall[2] have used an improved version of Sayers'[18] Langmuir probe/mass-spectrometer apparatus to study recombination in helium-oxygen mixtures. While they worked with gas mixtures that had led to O_2^+ ion predominance in their ion-molecule reaction studies, they did not use the mass-analysis feature of their apparatus to identify the ions undergoing recombination.[20] They found that at 300°K, $\alpha = (2.1\pm0.3)\times10^{-7}$ cm^3/sec and decreased to $(1.5\pm0.2)\times10^{-7}$ cm^3/sec at 630°K, in disagreement with the present results and the behavior expected from the earlier measurements of Sayers.[18] Again, the appearance of other ions such as O_3^+ or O_4^+ may have interfered with their attempts to determine $\alpha(O_2^+)$.

There have been a number of attempts to determine $\alpha(N_2^+)$ without use of mass analysis. Bialecke and Dougal[21] found that in pure nitrogen between 0.2 and 2 Torr the inferred recombination coefficient varied strongly with gas pressure (at 300°K, from 1.3 to 8.5×10^{-7} cm^3/sec), suggesting the intrusion of substantial amounts of complex ions such as N_4^+. Faire and Champion[22] studied recombination in pure nitrogen ($p = 2$ Torr) and in nitrogen-helium mixtures. From data in which ambipolar diffusion loss and, in some cases, ionization by helium metastables were important afterglow processes they obtained a value, $\alpha = (4\pm0.3)\times10^{-7}$ cm^3/sec at 300°K, independent of the nitrogen pressure. Mentzoni[23] used pure nitrogen at pressures between 0.5 and 6 Torr and found a strong dependence of α on pressure (variation from 2 to 7×10^{-7} between 2 and 6 Torr at 300°K) and a pressure dependent rate of decrease with increasing gas temperature over the range 300–735°K. Finally, Hackam[24] found that, in pure nitrogen at high pressures (>10 Torr), α varied as $T^{-1.1}$ over the range 295–610°K, starting from a value of 2×10^{-6} cm^3/sec at 295°K. Since the value at 300°K corresponds in magnitude to $\alpha(N_4^+)$ as determined by Kasner and Biondi,[3] Hackam's measurements may refer to the N_4^+ ion.

We include the above-quoted results merely for completeness, inasmuch as without identification of the ions present during the various afterglow measurements we cannot assess the reliability of the determinations. The measurements, most of which exhibited substantial dependence of the inferred α values on nitrogen pressure, strongly suggest changing ion composition, e.g., $N_2^+ : N_4^+$, under these circumstances.

We may compare our values for $\alpha(O_2^+)$ and $\alpha(N_2^+)$ with the results of recent theoretical calculations of the direct dissociative process by

Warke[25] and by Chan.[26] These calculations make use of extrapolations into the curve crossing region of experimentally determined molecular potential curves for the appropriate O_2^+, O_2 and N_2^+, N_2 states, treat the atomic motion classically and treat the electronic transition from the molecular ion plus electron to the unstable molecule state quantum mechanically. At $T_e = 300°K$, Warke obtains the value of $\alpha(O_2^+) = 1.1\times10^{-7}$ cm^3/sec, while Chan, using somewhat different potential curves (he assumes that the unstable molecule curves cross the ion curve at its minimum) obtains a value $(2.8\pm0.2)\times10^{-7}$ cm^3/sec. For $\alpha(N_2^+)$, Warke obtains the value 2.0×10^{-7} cm^3/sec. While these values are in reasonable or even remarkable agreement with our experimental results, the gross simplification in using a "one active electron" approximation in the calculations may suggest that the agreement is fortuitous.

V. SUMMARY

The present paper presents the determinations of the recombination coefficients of mass-identified O_2^+ and N_2^+ ions under recombination controlled afterglow conditions over the range 300°K $\leq T_e \leq$ 5000°K. In the O_2^+ studies, as a result of the mode of ion generation (Penning ionization of O_2 by Ne^M) some of the ions may be in the metastable ($a^4\Pi_u$) as well as in the ground ($X^2\Pi_g$) state. The observed variation of $\alpha(O_2^+)$ with T_e (as $T_e^{-0.7}$ below $T_e = 1200°K$) is approximately the same as has been found[1] for covariation of T_e and T_+ over the common temperature range, 300–700°K. In the N_2^+ studies, inability to eliminate completely N_3^+ ions from the afterglow reduces the accuracy which we assign to the absolute values of $\alpha(N_2^+)$. In this case, however, the N_2^+ ions are expected to be solely in their ground electronic state. The observed variation of $\alpha(N_2^+)$ with T_e (as $T_e^{-0.39}$) is very different from the temperature independent behavior noted[4] in the case where T_e and T_+ are covaried. The variations of α as $T_e^{-0.7}$ to $T_e^{-0.56}$ and as $T_e^{-0.39}$ for O_2^+ and N_2^+, respectively, approximate the theoretical prediction of a $T_e^{-1/2}$ variation if the initial radiationless-capture step is rate limiting in the dissociative recombination process.[27] In addition, the difference in dependence on T_e is in the direction inferred by Donahue[28] from an analysis of ionospheric measurements; he suggests variations of $\alpha(O_2^+)$ and $\alpha(N_2^+)$ as $T_e^{-(0.7\pm0.2)}$ and as $T_e^{-(0.2\pm0.1)}$, respectively.

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Electron Temperature Dependence of Recombination of Ne_2^+ Ions with Electrons*

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The electron temperature dependence of the recombination of mass-identified Ne_2^+ 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 $\alpha(Ne_2^+)$ decreases as $T_e^{-0.49}$ over the range $300°K \leq T_e \leq 4600°K$, starting at a value $(1.75 \pm 0.2) \times 10^{-7}$ cm^3/sec at $T_e = 300°K$. 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 Ne_2^+ ions is probably the recombination reaction most extensively studied to date[1-9]; however, until now, only one study[8] has identified, by mass analysis, Ne_2^+ as the ion undergoing recombination. Therefore when studies of the electron temperature dependence of recombination between mass-identified ions and electrons were undertaken[10] (see preceding paper), it seemed appropriate to extend the studies to Ne_2^+ 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 $\alpha(Ne_2^+)$ 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 neon[11] 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) TM_{010} cavity mode during the afterglow.[12] The electrons are heated to constant, controlled temperatures during the afterglow by excitation of a low Q (~9) TE_{111} 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