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Electron-temperature dependence of dissociative recombination of electrons with $N_2{}^+ \cdot N_2$ dimer ions

Marlin Whitaker, Manfred A. Biondi, and Rainer Johnsen
Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
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A microwave-afterglow mass-spectrometer apparatus has been used to determine the dependence on electron temperature T_e of the recombination coefficient of electrons with the dimer ion $N_2{}^+ \cdot N_2$. We find $\alpha = (1.4 \pm 0.2) \times 10^{-6} [T_e(\mathrm{K})/300]^{-0.41}$ cm^3/s over the range $300 \leq T_e \leq 5600$ K, and $T_+ = T_n = 300$ K. These results are quite similar to those found for the $CO^+ \cdot CO$ dimer ion but quite different from the T^{-1} dependence inferred from previous measurements in nitrogen in which the ions were not mass identified.

I. INTRODUCTION

The present study of the variation with electron temperature T_e of the dissociative recombination of electrons with $N_2{}^+ \cdot N_2$ dimer ions was undertaken to extend our recent investigations[1] of the mechanism of dimer-ion recombination and to provide needed data for modeling lower-ionospheric regions and high-pressure laser plasmas where such ions might be expected. While the variation with T_e of the dissociative recombination coefficient α for simple diatomic ions has been found[2] to approximate the $T_e^{-1/2}$ dependence predicted theoretically for relatively simple diatomic ions, recombination coefficients for cluster ions containing strongly polar molecules, e.g., $H_3O^+ \cdot H_2O$ and $NH_4{}^+ \cdot NH_3$, exhibit[3,4] a very weak variation, approaching T_e^0.

A fast dissociative process is expected to be largely controlled by the initial Coulomb-collision capture step whose cross section σ_{capt} varies as $1/\epsilon$ (ϵ is the electron energy) leading to a $\sim T_e^{-1/2}$ variation of $\alpha \equiv \langle \sigma v_e \rangle$, where v_e is the electron velocity and the angular brackets indicate averaging over the velocity distribution. Thus, the finding[1] of a $T_e^{-0.34}$ variation of α for the case of the dimer cluster ion ($CO^+ \cdot CO$) seemed quite reasonable, in contrast to the hydronium and ammonium cluster ion results.[3,4] However, for the case of the dimer ion ($N_2{}^+ \cdot N_2$), an earlier inference[5] of a T^{-1} dependence (for $T = T_n = T_+ = T_e$) from studies without mass identification of the ions was difficult to understand, motivating us to reinvestigate this dimer ion with an apparatus providing positive identification of the ions under study.

II. METHOD OF MEASUREMENT AND DATA ANALYSIS

The microwave-afterglow mass-spectrometer apparatus and method of measurement have been described in detail previously.[6] A microwave discharge lasting typically 1 ms and repeated at a 10-Hz rate is generated in mixtures of ~10–100 mTorr of nitrogen and ~8–20 Torr of neon. The decay curves of the various afterglow ions are determined by sampling the ions which diffuse to the cavity wall and effuse through a small orifice into a differentially pumped quadrupole mass filter. The "microwave-averaged" electron density $\bar{n}_{\mu w}$ during the afterglow is obtained from measurements of the resonant-frequency shift of the high-Q TM_{010} cavity mode, while steady electron heating is achieved by application of microwave power via a low-Q TE_{111} cavity mode. Since, as discussed in an earlier paper,[7] the heating microwave electric field produces an essentially Maxwellian electron velocity distribution,[8] it is appropriate to use the electron temperature T_e to characterize the elevated electron mean energy.

The principal steps in the formation of the nitrogen dimer ion are thought to be the following: (a) electron-impact excitation of neon to a metastable state Ne^m, (b) Penning ionization via $Ne^m + N_2 \rightarrow Ne + N_2{}^+ + e^-$, and (c) the clustering and breakup reaction

$$N_2{}^+ + N_2 + Ne \rightleftharpoons N_2{}^+ \cdot N_2 + Ne\,. \qquad (1)$$

The relative abundance of ions in the afterglow is controlled by varying the partial pressure of N_2, thereby affecting the equilibrium of reaction (1).

For the case in which only one ion is present in an afterglow dominated by electron-ion recombination and ambipolar diffusion loss, the continuity equation for the electrons is given by[6]

$$\frac{\partial n_e}{\partial t} \simeq -\alpha n_e^2 + D_a \nabla^2 n_e\,, \qquad (2)$$

where D_a is the ambipolar diffusion coefficient. A point-by-point computer solution[9] of Eq. (2)

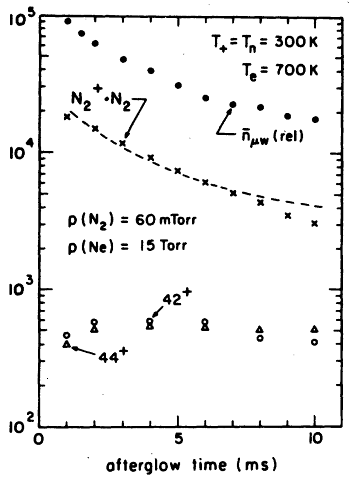

FIG. 1. Comparative decays of volume electron density $\bar{n}_{\mu w}$ and ion wall current during the afterglow. The dashed line represents renormalized values of $\bar{n}_{\mu w}$.

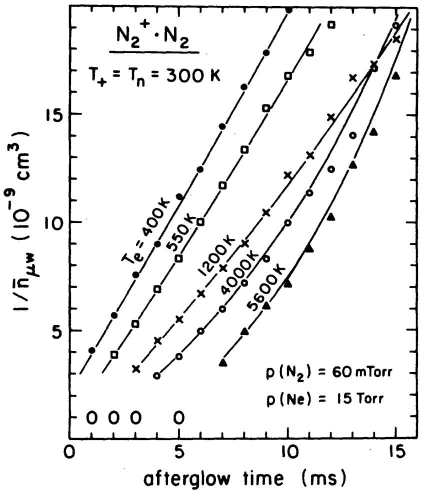

FIG. 2. "Recombination decay" plots of $1/\bar{n}_{\mu w}$ vs time for various electron temperatures. The solid lines represent best-fit computer solutions of Eq. (2) to the data. The zero times for the different T_e runs are displaced for clarity.

yields the predicted spatial and temporal variation of the electron density, $n_e(\vec{r}, t)$, from which values of $\bar{n}_{\mu w}(t)$ may be computed.

The measurements of the microwave cavity's resonant-frequency shift during the afterglow yield directly the values of the microwave-averaged electron density $\bar{n}_{\mu w}(t)$.[6] The value of the recombination coefficient α is determined by obtaining a best fit to the $\bar{n}_{\mu w}$ data of the computer-generated solutions of Eq. (2), using values of D_a for N_4^+ ions in Ne calculated from the Langevin polarization interaction formula[10] (empirically increased by ~25% to match data for other ions in neon) and treating α as a parameter.

III. RESULTS

The recombination coefficient of the $N_2^+ \cdot N_2$ ion was determined from those runs in which the dimer was the only ion of significance in the afterglow, thereby allowing us to employ the simple analysis described above. An example of the measured decays of electron density and ion wall currents is given in Fig. 1. The ion $N_2^+ \cdot N_2$ is dominant, with small amounts (~5%) of 42^+ ($N^+ \cdot N_2$) and 44^+ (probably N_2O^+) the only other detectable ions. In addition, the $N_2^+ \cdot N_2$ ion wall current "tracks" the electron density reasonably well throughout the afterglow (the dashed line represents the $\bar{n}_{\mu w}$ curve normalized to the $N_2^+ \cdot N_2$ data at 5 ms). The slight deviation at 8–10 ms probably reflects the increasing importance of the $N^+ \cdot N_2$ and N_2O^+ ions in the late afterglow, since, if one compares $\bar{n}_{\mu w}$ to the *total* ion count, the tracking is improved.

The variation of the electron density decays with electron temperature T_e is illustrated in Fig. 2. The zero time for the different T_e runs has been displaced for clarity. The solid lines through the data points are the computer solutions of Eq. (2) which provided a best fit to the data. The α values inferred from these fits to the data yield the variation of the recombination coefficient with electron temperature. The results of these and our other measurements are summarized in the plot of $\alpha(N_2^+ \cdot N_2)$ vs T_e given in Fig. 3. The extent of the bar symbols indicates our estimates of possible systematic and random errors in the determinations.

A least-squares fit of the experimental data to a simple power-law dependence of the form $\alpha \sim T_e^{-x}$ yields the result indicated by the dashed line in Fig. 3 and given by the expression

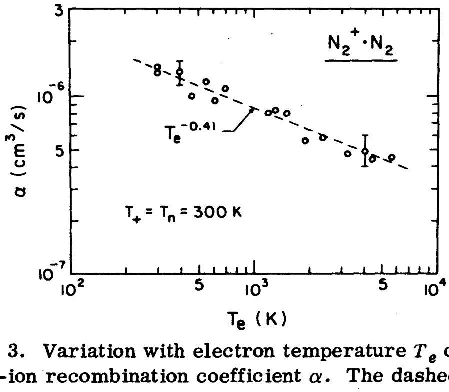

FIG. 3. Variation with electron temperature T_e of the dimer-ion recombination coefficient α. The dashed line represents a least-squares fit to the data of a simple power-law dependence, $\alpha \sim T_e^{-x}$, yielding $x = 0.41$.

$$\alpha(\mathrm{N_2}^+\cdot\mathrm{N_2})(\mathrm{cm^3/s})=(1.4\pm0.2)\times10^{-6}[T_e(\mathrm{K})/300]^{-0.41}\,, \tag{3}$$

valid over the measured range $300 \leq T_e \leq 5600$ K. The data show no significant systematic deviations from the simple law.

IV. DISCUSSION AND CONCLUSIONS

The measured T_e variation, $\alpha(\mathrm{N_2}^+\cdot\mathrm{N_2})\sim T_e^{-0.41}$, for the nitrogen dimer ion is similar to that observed in our recent study[1] of the carbon monoxide dimer ion, $\alpha(\mathrm{CO}^+\cdot\mathrm{CO})\sim T_e^{-0.34}$, and is consistent with the expected energy dependence $\sim T_e^{-1/2}$ for a fast dissociative process, as discussed in the Introduction. The recombination may well involve a process of the form

$$\mathrm{N_2}^+\cdot\mathrm{N_2}+e^-\rightleftarrows\mathrm{N_2}^*\cdot\mathrm{N_2}\rightarrow\mathrm{N}^*+\mathrm{N}+\mathrm{N_2}\,, \tag{4}$$

that is, dissociation of the neutralized "core" ion together with detachment of the previously clustered neutral molecule.

Thus, the dimer ions of both nitrogen and carbon monoxide, involving a nonpolar or a weakly polar molecule clustered to the ion core do not exhibit the very feeble dependence of α on electron temperature noted for the $\mathrm{H_3O}^+\cdot\mathrm{H_2O}$ and $\mathrm{NH_4}^+\cdot\mathrm{NH_3}$ dimerlike cluster ions formed with strongly polar molecules. At present we have no satisfactory explanation, in terms of the recombination mechanism, of the "pathological" behavior of the hydronium and ammonium-series cluster ions.

The measured $T_e^{-0.41}$ dependence for $\alpha(\mathrm{N_2}^+\cdot\mathrm{N_2})$ is much weaker than the $\sim T_e^{-1}$ dependence inferred earlier[5] by combining data from two experiments, one involving an afterglow measurement at 300 K of mass-identified $\mathrm{N_2}^+\cdot\mathrm{N_2}$ ions,[11] the other an afterglow measurement of the temperature dependence of α over the range 300–600 K (with $T_e=T_+=T_n$) for an unknown mixture of ions in nitrogen at relatively high pressures (> 10 Torr).[12] In our view, the results of the present experiment, in which the identity of the ions undergoing recombination with the electrons is determined, should take precedence over the earlier results.

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