Experimental Measurements of Dissociative Recombination in Vibrationally Excited Gases

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Measurements of the temperature dependence of the dissociative recombination coefficients α in Ne_2^+ and Ar_2^+ are reported under conditions in which $T=T_i=T_e$. For both gases, the low-temperature variation of α was found to have an exponent of $-0.5^{+0.2}_{-0.1}$, while at high temperatures the exponent was -1.5 ± 0.1. The break between the high- and low-temperature dependencies, which occurred at 900°K for neon and at 670°K for argon, is seen to be a measure of the spacing between the ground and first vibrational levels in these molecular ions.

Recent measurements reported by Biondi and co-workers on the variation of the molecular ion-electron dissociative recombination coefficient α with electron temperature T_e, show that the dependence described by $\alpha=\alpha_0(T_e/300)^{-\gamma}$ is followed, and that $\gamma=0.43$ for[1] Ne_2^+ and 0.67 in the case[2] of Ar_2^+. These results were obtained using the elevated electron temperature technique in which the decaying afterglow contained in a microwave cavity has the electron temperature raised to predeterminable values by means of a constant microwave heating field; the ions are presumed to be at room temperature.

However other measurements in argon[3] have shown that when the gas, ion, and electron temperatures are equal, $T=T_i=T_e$, the recombination coefficient behaves as $\alpha=\alpha_0(T/300)^{-1.5}$ in the temperature range 1000°–3000°K. It is of interest that recent measurements[4] in NO^+ show a similar $T^{-1.5}$ dependence in the range $2000°K < T_e < 7000°K$. In this case the translational temperature of the ions varied between 2000° and 7000°K in a nozzle expansion and the electron temperature was, depending on the distance downstream from the nozzle, equal to or greater than the gas temperature.

The technique employed by Fox and Hobson has now been developed for use in a 4-cm-i. d. shock tube which gives longer experimental time in the flow between the shock front and contact surface. The apparatus is shown schematically in Fig. 1 and will be described in detail elsewhere. Shock waves in the Mach number range from $M=1.5$ to $M=6$ are driven into neon and argon raising the temperature of the test gas to a precisely determinable value in the range $450°K < T < 3500°K$. A geometrically well-defined plasma ellipsoid is created in the electrode region by means of a single pulse of rf power of about 800 μsec duration. The rf pulse is triggered using an upstream platinum film detector and is terminated before the advancing shock wave reaches the electrode region. Suitable electrode orientation is used to ensure a radially isotropic afterglow, as shown, and this is determined by scanning a collimated photomultiplier across the tube diameter. The plasma ellipsoid is swept into the advancing shock front and moves between shock front and contact surface as the shock heated gas travels down the shock tube. Gas and ion temperatures are equalized within a few collisions in the shock heated gas, and the electron temperature is brought to equilibrium with the gas in about 10^5 collisions; this represents a time of about 20 μsec under typical conditions. Measurements of ion number density in the plasma at later times are made by the double probe detectors indicated. The latter are positioned so that the plasma has spent about 500 μsec in the shock heated gas before encountering the first probe at which a typical number density recorded was about 10^{11} ions cm^{-3}. The particle flow behavior with time between shock front and contact surface is now well known[5,6] and can be determined readily from the flow parameters. Initial pressure in the shock tube is set so that the pressure in the shock heated gas is greater than 20 Torr, thus limiting diffusion effects.

The difference current i_d measured between the elements of a double probe with saturation voltage applied between them and in a supersonic flow has been related to ion number density by means of

$$i_d=\tfrac{1}{4}N^+Ae(8kT_+/\pi m_+)^{1/2} ,$$

and this will be discussed further elsewhere; a partial discussion is contained in Ref. 7. The measurements in Ar_2^+ in a 1-cm-i. d. shock tube, reduced on the same basis (referred to as raw probe data in Ref. 3), are included in Fig. 3 and are seen to agree well with the present results. Plots of $1/n$ versus t over about 1 msec gave straight-line relationships from which α was obtained at the corresponding gas temperature.

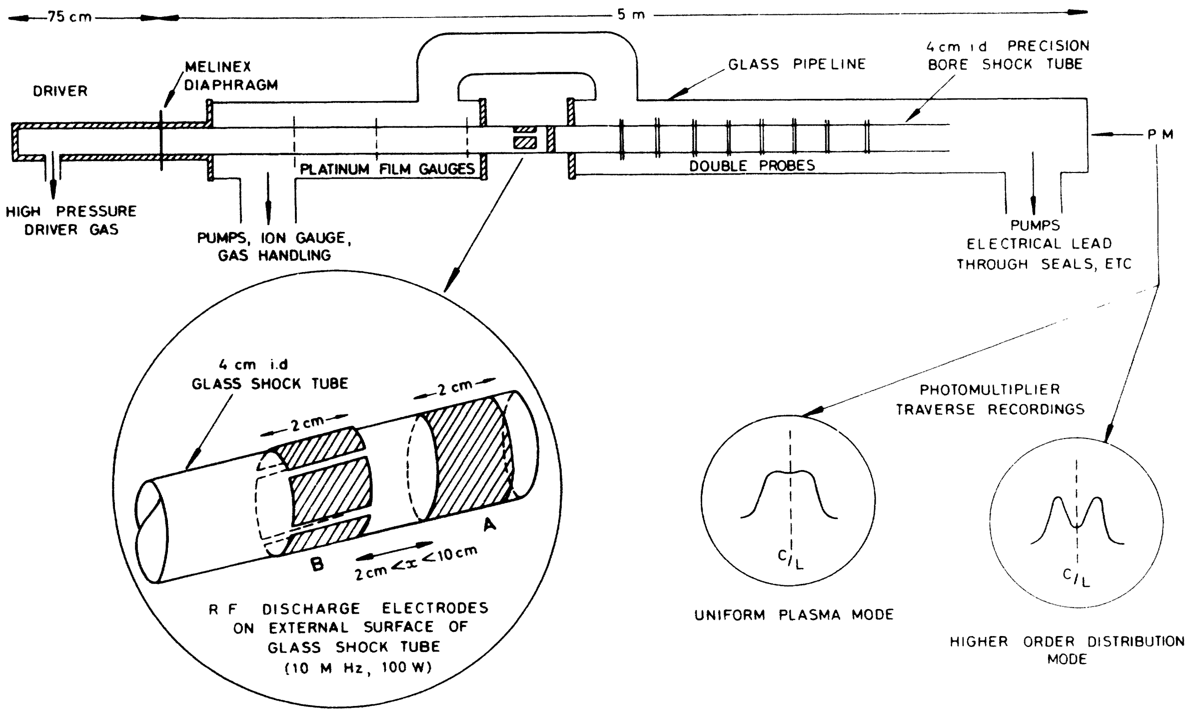

FIG. 1. Experimental apparatus.

The results for Ne_2^+ recombination are shown in Fig. 2 which includes the value $\alpha_0 = 1.7 \pm 0.2 \times 10^{-7}\,\mathrm{cm^3\,sec^{-1}}$ at 300°K deduced by Frommhold, Biondi and Mehr[1] by comparing a number of experimental values (see Sec. V of Ref. 1). The

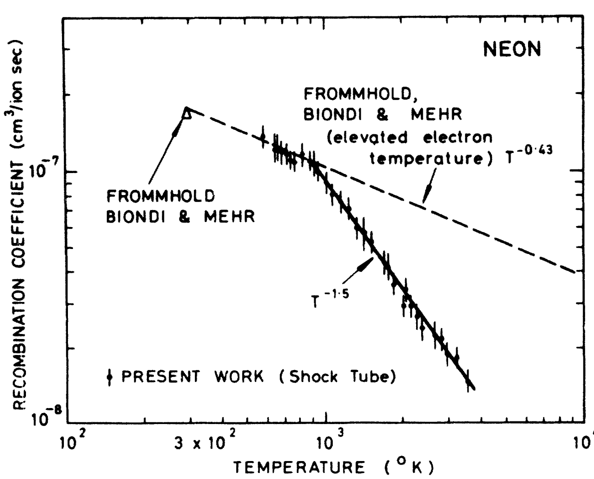

FIG. 2. Variation of the dissociative recombination coefficient α for neon with temperature under conditions where $T = T_i = T_e$. The results of Frommhold *et al.* measured under the condition $T_e > T_i \approx 300$°K are shown for comparison.

results obtained by these authors using their elevated electron temperature technique are also shown. Above 900°K their temperature dependence $T_e^{-0.43}$ differs substantially from the $T^{-1.5}$ measured in the shock tube under the conditions $T = T_i = T_e$. However, below 900°K there is good agreement between the two sets of results both in temperature dependence and in absolute values.

The results for Ar_2^+ recombination are shown in Fig. 3, including the 300°K values reported by Oskam and Mittlestadt[8] and Biondi.[9] The experimental values reported recently by Mehr and Biondi[2] are also shown. These are seen to include a value of $\alpha = 8.5 \pm 0.8 \times 10^{-7}\,\mathrm{cm^3\,sec^{-1}}$ at 300°K. Above 670°K the elevated electron-temperature measurements give a dependence of $T_e^{-0.67}$ in contrast to the shock-tube results which are close to $T^{-1.5}$. Below 670°K both experimental results are in substantial agreement as to temperature dependence and differ only in absolute value. The shock-tube results below 670°K, extrapolated using a $T^{-0.67}$ dependence give an absolute value of $\alpha_0 = 6.5 \times 10^{-7}\,\mathrm{cm^3}$, $\mathrm{sec^{-1}}$ at 300°K more in agreement with the lower values reported previously. However, this relatively small difference will not be labored here as the current interest lies in the temperature dependence.

The temperature dependence of dissociative recombination involving only ground-state molecular ions has been discussed by Bardsley,[10] and it is predicted that this should be $T_e^{-0.5}$. In

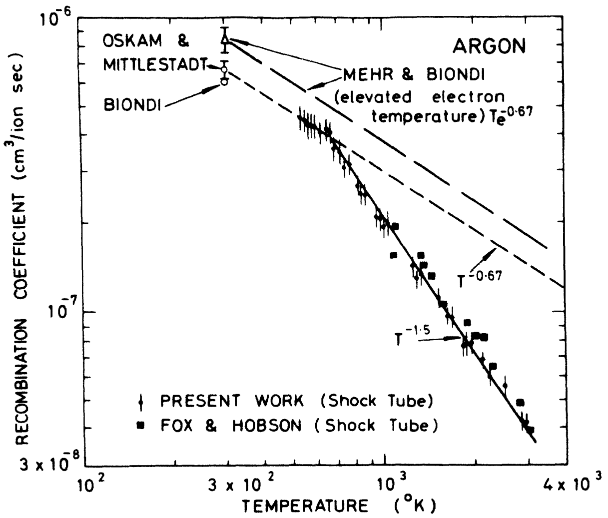

FIG. 3. Variation of the dissociative recombination coefficient α for argon with temperature under conditions where $T = T_i = T_e$. The results of Mehr and Biondi, measured under the condition $T_e > T_i \approx 300°$ K are shown for comparison.

the case of NO^+ recombination, Bardsley[11] has calculated that variation of the crossing point of the neutral molecule repulsive potential curve and the ground-state molecular ion curve within the Franck-Condon region can lead to variations in the range $T_e^{-0.4}$ to $T_e^{-0.7}$. Biondi's results for Ne_2^+ and Ar_2^+ are not therefore in disagreement with the ground-state recombination mechanism. The stronger temperature dependence of $T^{-1.5}$ reported here for Ne_2^+ and Ar_2^+ is associated with recombination involving vibrationally excited states of the molecular ion.[12] An analysis by O'Malley[13] satisfactorily embraces both Biondi's and our results. The latter analysis relies on the cross section for dissociative recombination of ground-state ions σ_0 being very much greater than the corresponding σ_v for vibrationally excited ions. The shock-tube results, and the NO^+ results,[4] are consistent with such variations in cross section. Furthermore the points at 900°K in Ne_2^+ and 670°K in Ar_2^+ at which ground-state recombination is depleted, due to the onset of vibrational excitation, provide an indication of the spacing between the ground and first vibrational states in Ne_2^+ and Ar_2^+, respectively.

It should be noted that the limited temperature range over which ground-state recombination persists in our results does not at present enable the temperature variations of the ground-state recombination rate to be established with the precision stated in Biondi's elevated electron temperature experiments which are able to cover a much larger range in electron temperature. The present results may be more formally ascribed to the following temperature dependencies:

$T^{-0.5\,^{+0.2}_{-0.1}}$ lower-temperature region,

$T^{-1.5\pm 0.1}$ higher-temperature region.

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