Dissociative Recombination of Electrons with He_2^+†

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Experimental results are reported which conclusively show that diatomic molecular helium ions recombine dissociatively with electrons. It is shown that dissociative recombination accounts for at least half of the total electronic recombination of He_2^+ at a temperature of 300°K and in the pressure range from 15 to 55 Torr. The experimental technique which was used in this work includes measurement of the perturbation of the 2^3S metastable density which results from a time-dependent perturbation of the electronic recombination coefficient.

The dissociative recombination of molecular helium ions and electrons has been extensively discussed in the literature,[1] and, as described in a recent review article,[2] the results are somewhat conflicting. Since the value of the total electronic recombination coefficient of molecular helium ions has now been shown to be larger than previously suspected,[3,4] we undertook a re-examination of dissociative recombination of molecular helium ions. The results of these studies are reported in this paper, and they clearly indicate that dissociative recombination accounts for a large fraction of the total electronic recombination of He_2^+ ions at a temperature of 300°K.

The equipment used in this experiment has been described elsewhere.[4] The density of the 2^3S atomic metastables was determined from the amount of absorption of the 3889-Å line radiation from an external, helium-filled light source. The fine structure of the 3^3P level was taken into account in calculating the density from the measured absorption.[5] The effect of pressure broadening was found to have very little effect on the value of the measured changes of the atomic metastable density presented in this paper. In addition, the densities of the 2^1S, 2^1P, and 2^3P levels were monitored by the absorption of the 5016-, 7281-, and 7065-Å lines, respectively, emitted from the external light source.

The amount of dissociative recombination was determined by monitoring the change in the density of the 2^3S level of helium which resulted when the electronic recombination was quenched during a selected time interval in the afterglow. This technique of quenching the recombination is the same as that used previously to measure the true electronic recombination coefficient of He_2^+.[4] In Fig. 1, the density of the electrons and the density of the atomic metastables in the level 2^3S are plotted versus time into the afterglow period. When the electron heating pulse was applied (t =300 μsec), the electron density increased because the reduced loss from recombination became smaller than the source of free electrons which resulted from metastable-metastable ionizing collisions. The general rate equations which govern these processes in a molecular-ion-dominated helium afterglow have been described elsewhere.[4] The electron heating pulse reduced the rate of recombination and simultaneously reduced

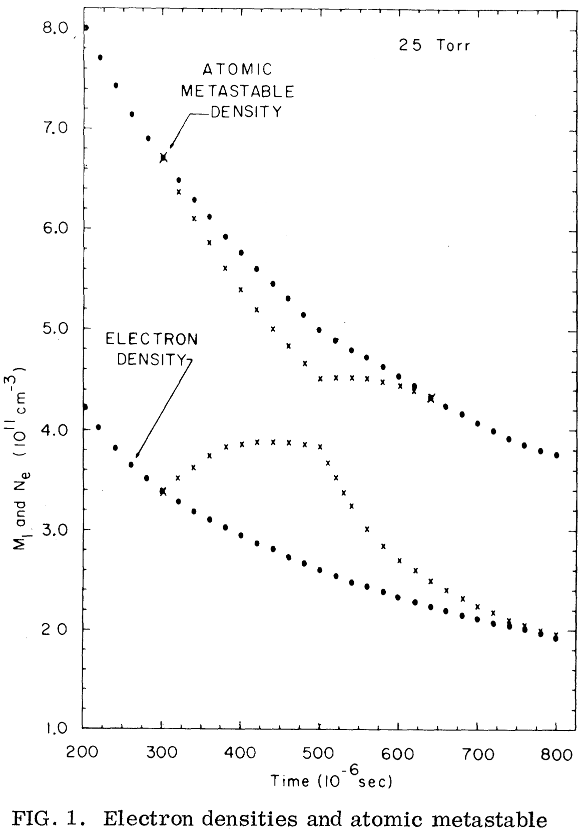

FIG. 1. Electron densities and atomic metastable densities during a selected part of the afterglow period. The electrons are heated from 300 to 500 μsec. The electron density and the atomic metastable density during and following the heating pulse are plotted with crosses. The unheated values are represented by dots.

the rate of production of the atomic helium metastable. This observation alone indicates that dissociative recombination is a significant recombination mechanism. The rate of production of the molecular metastables was presumably also reduced; however, we were unable to detect this change in the density with our apparatus, although we were able to set an upper limit on the percentage of change in the molecular metastable density at 10%. Following the start of the heat pulse, the reduced rate of production of the atomic metastables from recombination resulted in a more rapid decrease in the density of the metastables. The change in the rate of the decay of atomic metastables at 300 μsec also indicates that the rate coefficient for atomic-metastable–atomic-metastable ionizing collisions (β_1) is in fact larger than that predicted from the rate of decay of atomic metastables in the unheated helium afterglow. Following the removal of the heat pulse, the more rapid rate of recombination of electrons with $He_2{}^+$ caused the atomic metastable density to return approximately to its unheated value.

Since the electron densities and the atomic metastable densities returned approximately to their unheated values, it is evident that there was no significant permanent change in the loss processes of the metastable levels during the heat pulse. The possibility of electron excitation from the 2^3S level to atomic levels energetically nearby was investigated by measuring the absorption of line radiation which terminated on these levels. The sum of the 2^1S, 2^1P, and 2^3P densities was observed to be less than 10^{10} particles/cm^3 during the heat pulse and was therefore not significant.

In Figs. 2 and 3, the difference ΔN_e between the measured electron density with and without the electron heating pulse and the difference ΔM_1 in the measured atomic metastable density under the same conditions are plotted for two different gas pressures. In addition, the calculated change ΔM in the total metastable density, atomic and molecular, is given in Figs. 2 and 3. (Note that the negative values of ΔM_1 and ΔM have been plotted.) This calculated value of ΔM was obtained numerically by using Eqs. (8) in Ref. 4, by assuming all metastable-metastable ionizing rates β to be equal to 4×10^{-9} cm^3/sec, by using the recycling parameter as defined by Eqs. (10a) in Ref. 4, and with the measured electron density.

The value of β used in this calculation was chosen because it is the maximum value of β consistent with the assumption that the atomic-metastable–atomic-metastable ionizing rate β_1 is equal to β, where β_1 is obtained from the initial slope of the atomic metastable following the start of the heat pulse. In addition, the equilibrium conditions derivable from Eqs. (9) in Ref. 4 are consistent with the value of $\beta\simeq4\times10^{-9}$ cm^3/sec. If β is assumed to be equal to the value of β_1, which is given in the literature as approximately equal to 2×10^{-9} cm^3/sec,[6] then the calculated values of ΔM are almost exactly the same as the measured values of ΔM_1. This agreement indicates that if

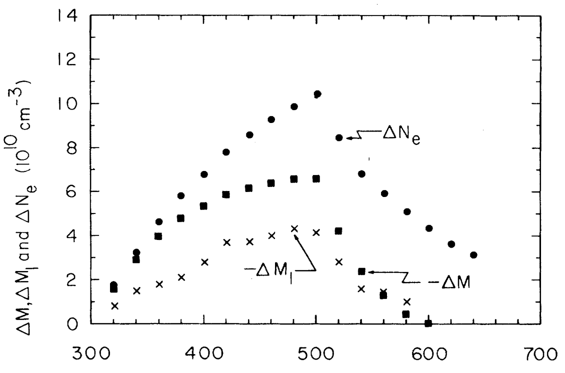

FIG. 2. The measured change (ΔN_e) in the electron density between the heated and unheated case and the measured change (ΔM_1) in the atomic metastable density at 15 Torr. The calculated values of the change (ΔM) in the sum of the atomic and molecular metastable densities with $\beta=4\times10^{-9}$ cm^3/sec are also shown. (Note that ΔM_1 and ΔM are negative in value.)

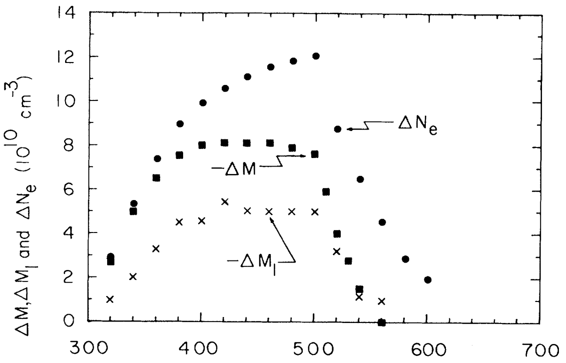

FIG. 3. The measured change (ΔN_e) in the electron density between the heated and unheated case and the measured change (ΔM_1) in the atomic metastable density between the heated and unheated case at 55 Torr. The calculated values of the change (ΔM) in the total atomic and molecular metastable density with $\beta=4\times10^{-9}$ cm^3/sec are shown. (Note that ΔM_1 and ΔM are negative in value.)

$\beta = 2\times10^{-9}$ cm^3/sec then dissociative recombination accounts for essentially all the recombination. However, because dissociative recombination populates the atomic metastable level, the value of β_1 obtained directly from the net decay of M_1 is the effective value $\beta_{1\text{eff}}$ and the correct value of β_1 must be greater than $\beta_{1\text{eff}}$. (We have measured the value of $\beta_{1\text{eff}}$ at 15 Torr to be 2.4×10^{-9} cm^3/sec to within an estimated experimental error of ±20%, in agreement with previous work.)

The results exhibited in Figs. 1, 2, and 3 unmistakably illustrate that dissociative recombination of $\text{He}_2{}^+$ accounts for a large percentage of the total recombination. In order to determine the dissociative recombination coefficient α_D from the data it is necessary to solve the complete set of tightly coupled rate equations. [See Eqs. (8) in Ref. 4.] This procedure was not followed in this study because all the rate coefficients were not known and the molecular metastable density M_2 was not known accurately. However, if it is assumed that (1) the three-body conversion of atomic metastable to molecular metastables was negligible during the time the heat pulse was applied, (2) the density perturbations caused by the heat pulse are small, and (3) the assumptions used to calculate ΔM are correct, then α_D/α is approximately equal to $\Delta M_1/\Delta M$. At 15 Torr, the molecular metastable density is considerably less than the atomic metastable density so the comparison between α_D/α and $\Delta M_1/\Delta M$ is justified. At 55 Torr, we estimate that the value of $\Delta M_1/\Delta M$ is 15% less than α_D/α because of the three-body conversion of atomic metastables to molecular metastables. Over the pressure range studied (15 to 55 Torr), the ratio $\Delta M_1/\Delta M$ remained nearly constant. For a value of $\beta = 4\times10^{-9}$ cm^3/sec, $\Delta M_1/\Delta M$ was 0.65 ± 0.1, where the error limits represent only the statistical error of the measurements.

In summary, the results reported here indicate that the experimentally measured perturbations of N_e and M_1 are consistent with the experimental measurement of $\beta_{1\text{eff}} \simeq 2\times10^{-9}$ cm^3/sec if $\beta = \beta_1 \simeq 4\times10^{-9}$ cm^3/sec and $\alpha_D/\alpha \simeq 0.55$ to 0.75. In Ref. 4, we measured α by assuming that the source term was not changed by application of the heating pulse and then estimated the maximum error introduced by this assumption. Because β_1 is larger than was thought at that time, we now estimate that α is about 10% less than the reported value. [The sign of this necessary correction was misstated in Ref. 4.]

These results evince that dissociative recombination is an important process for electronic recombination in a helium afterglow over the pressure range from 15 to 55 Torr. However, this experiment does not distinguish completely between a two-body dissociative and a three-body collisional dissociative recombination process. For example, the three-body recombination process of collisional stabilization of autoinizing levels proposed previously[4] can produce atomic metastables. Because the value of α_D/α remained approximately constant for different pressures and because α is pressure dependent, there is some pressure dependence of α_D. The pressure dependence could be due to either a combination of two-body dissociative recombination and three-body collisional dissociative recombinations or only three-body collisional dissociative recombination with some autoionizing levels nearly completely stabilized at the lowest pressures investigated. In either case, dissociation into the atomic system must be almost exclusively directly into the 2^1S, 2^1P, 2^3S, or 2^3P levels as evidenced by the small amount of atomic radiation.

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