Ionizing Collisions of Two Metastable Helium Atoms $(2\,^3S)$†

A. Wayne Johnson and J. B. Gerardo
Sandia Laboratories, Albuquerque, New Mexico 87115
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The rate coefficient β_1 for the ionizing collision of two metastable helium atoms $(2\,^3S)$ is evaluated from measurements in a steadily decaying helium afterglow plasma with three different techniques. The value of β_1 is also determined with a perturbation technique. All the values of β_1 determined by these techniques lie within the range $(4.5\pm1.0)\times10^{-9}$ cm^3 sec^{-1}. This value is larger than that observed directly from the decay of the density of the triplet helium metastable atom because the dissociative recombination of He_2^+ is a significantly large source of atomic metastables.

I. INTRODUCTION

The rate coefficient β_1 for the ionizing collision of two metastable atoms in the $2\,^3S$ level was first examined by Phelps.[1] He monitored the time dependence of the triplet metastable atoms in a helium afterglow plasma by measuring the absorption of 3889-Å line radiation from a separate source. More recently, Miller *et al.*[2] measured the phase shift of the neon-laser line (1.0798 μ, $2s_3$-$2p_7$ transition) to determine the time history of the triplet metastables in a similar helium afterglow plasma. In both cases (Refs. 1 and 2) the value of β_1 was obtained from the slope of the straight line in a plot of $1/M_1$ versus time, where M_1 represents the density of the atoms in the $2\,^3S$ levels. Since Johnson and Gerardo[3] have shown that He_2^+ recombines dissociatively with electrons, it is now clear that the slope of $1/M_1$ versus time gives only the effective rate coefficient β_{1e} for the ionizing collision between two triplet metastable atoms rather than the actual coefficient β_1.

In this paper we evaluate the value of the rate coefficient β_1 for the reaction between two helium atoms $(2\,^3S)$, which results in an ion (atomic or molecular), by various related but independent techniques. In the text these techniques are labeled (i) rate equation, (ii) equilibrium and particle densities, and (iii) equilibrium and rate parameters. These results will clearly indicate that β_1 is larger than the effective value β_{1e}. Each technique used to evaluate β_1 requires different assumptions or approximations. Partial justification and credibility for our reported value of β_1 are derived from the reasonable agreement of the values of β_1, even though each technique requires different assumptions.

The equipment and techniques employed in this experiment have been described elsewhere.[3–5] Briefly, a helium afterglow plasma was produced in a discharge tube of 12.8-cm diameter by a 5-A current pulse of 6-μsec duration. The electron density was measured with a variable-frequency free-space microwave interferometer. Most of this work was done at a frequency of about 25 GHz. The atomic-metastable density $(2\,^3S)$ of helium was monitored by measuring the absorption of 3889-Å radiation from a separate source. The relative density of the triplet molecular metastables was monitored similarly with the 4650-Å band radiation. In the perturbation technique,[3] the rate of recombination of electrons with He_2^+ was reduced by heating the electrons with a second, 1-A or less current pulse of 200-μsec duration. The same results were obtained with different current levels.

II. RATE EQUATION

The rate equation governing the decay of the triplet metastable atoms in the helium plasma under study is

$$\frac{dM_1}{dt}=-\beta_1 M_1^2-\beta_{12}M_1M_2+\alpha_1 N_e^2\equiv-\beta_{1e}M_1^2\,, \qquad (1)$$

where β_{12} is the rate coefficient for ionizing collisions between atomic metastables and molecular metastables, M_2 is the molecular-metastable density, α_1 is the rate coefficient for the electronic recombination of He_2^+ that results in an atomic metastable, and N_e is the electron density. The density of He_2^+ ions is set equal to N_e, because at the gas pressures considered here (15 – 25 Torr) atomic ions are rapidly converted to molecular ions. The conversion of atomic metastables to molecular metastables has been neglected, because this rate is slow compared to the other terms in Eq. (1) at the low gas pressures considered here. Equation (1) is set equal to $-\beta_{1e}M_1^2$ (β_{1e} = const), because by experimental observation both here and elsewhere[1,2] the metastable decay can be described in this manner for the plasma conditions considered here.

Theoretical estimates and experimental observations indicate that both inelastic and superelastic collisions of electrons with atomic metastables are negligible in the investigated plasmas. Experimentally we observed that during the heating pulse the sum of the densities of the $2\,^1S$, $2\,^1P$, and $2\,^3P$ lev-

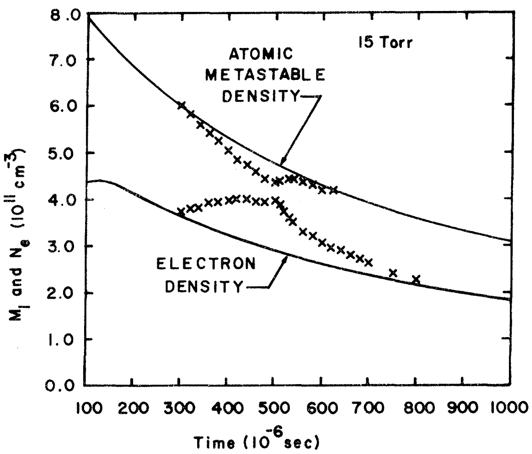

FIG. 1. Time history of the density of the triplet atomic-helium metastables M_1 and of the electron density N_e at 15 Torr. The solid lines represent the measured values from the unperturbed helium afterglow and the X's the measured values from the perturbed helium afterglow. The perturbation was a current pulse which heated the electrons from 300 to 500 μsec after the initial discharge to a temperature of ~ 1200K.

els of helium was less than 10^{10} cm^{-3}, while the density of the $2\,^3S$ level was typically 5×10^{11} cm^{-3}. We take this as sufficient evidence that inelastic collisions can be neglected during the heating pulse. The superelastic-collision rate (A) was estimated by using detailed balance and the experimental cross section[6,7] for excitation of ground-state helium to the $2\,^3S$ energy state. For all electron temperatures (T_e) of importance to this discussion, we estimate that $A = 2.5 \times 10^{-11} \sqrt{T_e}$ cm^3 sec^{-1}. By equating the rate of joule heating to the rate of elastic energy loss of electrons against 300 °K helium atoms, we estimate that the electron temperature is 1200 °K when the heating pulse is on. The electron temperature with no joule heating is estimated to be approximately 450 °K. The measured values of M_1, M_2, and n_e, the rate of decay of M_1 during the heating pulse (see Fig. 1), and the estimated values of A at the electron temperatures given above indicate that superelastic collisions of electrons with M_1 may account for 15% of the rate of loss of M_1 during heating and less than 5% in the absence of heating. In addition, we have observed that following the termination of the heating pulse, all measurements of the plasma properties indicate that the plasma returns to its nonheated state. Since superelastic collisions produce a permanent loss of metastables and since the return to the unheated state of the plasma indicate that the heating pulse did not introduce a large permanent loss of metastables, we conclude that superelastic collisions are not important in the plasma under study.

The incorrectness of equating β_1 with β_{1e} (i.e., $dM_1/dt = -\beta_1 M_1^2$) is clearly demonstrated when the rate of recombination of the electrons and ions is reduced by heating the electrons in a helium afterglow plasma as described previously.[3] The value of β_{1e} in the undisturbed helium afterglow at 15 Torr is 2.2×10^{-9} cm^3 sec^{-1} (Fig. 1). When the rate of electronic recombination is perturbed (see Fig. 2), the value of β_{1e} is increased to 3.5×10^{-9} cm^3 sec^{-1}. Since β_1 is not dependent upon the electron temperature, the change in β_{1e} with the change in the electron temperature indicates that it is incorrect to equate β_1 with β_{1e}.

Equation (1) can be used to evaluate β_1. By rearrangement, β_1 can be expressed as

$$\beta_1 = \beta_{1e} - \beta_{12}\,(M_2/M_1) + \alpha_1\,(N_e/M_1)^2. \qquad (2)$$

The values of β_{1e}, N_e, and M_1 were measured as described. The value of α_1 is given[3] approximately by 0.65α, where α is the total electronic recombination coefficient of He_2^+.[4] The second term in Eq. (2) contains the parameters about which assumptions must be made. The first assumption is that the value of the average absorption coefficient of the 4650-Å band of He_2 is one-tenth as large as the integrated absorption coefficient of the 3889-Å line of He as suggested by Phelps.[1] The second assumption is that β_1 equals β_{12}. Although Johnson and Gerardo[5] have suggested that the values of β_1 and β_{12} are nearly the same, this last assumption could introduce the largest error in the following

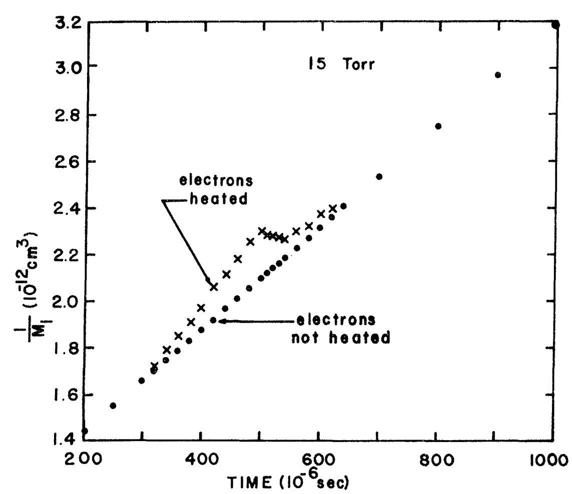

FIG. 2. Time history of $1/M_1$ where M_1 is the triplet atomic-helium-metastable density at 15 Torr. The value of the effective ionizing collision rate β_{1e} for two atomic metastables for the unperturbed helium afterglow is obtained from the slope of the dots. The value of β_{1e} during the perturbation is obtained from the crosses over the time range 300–500 μsec. The perturbation was a current pulse which heated the electrons from 300 to 500 μsec. Note that the ordinate and abscissa do not start at zero.

TABLE I. Estimated values of β_1. The techniques used to calculate β_1 listed above are described in the text with "A" and "B" described in Sec. II, "C" in Sec. III, and "D" in Sec. IV.

Pressure (Torr)	Technique A	B	C	D	Range	Units
15	4.7	3.8	5.3	5.1	4.6±1.0	10^{-9} cm^3 sec^{-1}
25	4.4	3.8	5.5	4.9		

calculation of β_1. At a pressure of 15 Torr, the ratio of M_2/M_1 was determined to be approximately 0.3 for times into the afterglow from 0.2 to 2 msec. Although dissociative recombination of He_2^+ is the largest recombination mechanism in a 15-Torr room-temperature helium afterglow,[3] other recombination mechanisms are present that produce some molecular metastables. The ratio of N_e/M_1 was essentially constant from 0.1 to 2.0 msec into the afterglow and was found to be equal to 0.6. With the above assumptions and measurements, the value of β_1 at 15 Torr is given by

$$\beta_1 = (\beta_{1e} + 0.36\,\alpha_1)/1.3\,. \qquad (3)$$

The value of β_1 can be evaluated both from the measured parameters in the undisturbed helium afterglow and from the measured parameters in the perturbed afterglow. In the undisturbed afterglow, the value of α (1.74×10^{-8}cm^3 sec^{-1} at 15 Torr) is taken from Ref. 5. The value of β_{1e} is taken from the curve in Fig. 1. This gives a value $\beta_1 = 4.7\times10^{-9}$ cm^3 sec^{-1}, which is tabulated in Table I under "A". The value of α during the heating pulse (perturbed afterglow) is taken to be equal to one-third of its value before the heating was applied. This is the value determined from comparison of numerical solutions to the experimental electron density measured during the heating pulse.[5] Within the experimental error, this is consistent with the relation,[5] $\alpha \propto (1/T_e)$, and the estimated value of T_e with heating is 1200 °K and without heating, 450 °K. The value of β_{1e} is taken from Fig. 2. The value of β_1 evaluated from the perturbed afterglow is equal to 3.8×10^{-9} cm^3 sec^{-1} and is tabulated in Table I under "B." Similar evaluations at 25 Torr give 4.4×10^{-9} cm^3 sec^{-1} and 3.8×10^{-9} cm^3 sec^{-1} for the value of β_1.

III. EQUILIBRIUM AND PARTICLE DENSITIES

With the assumption that all helium metastables (molecular and atomic) have equal rates ($\beta_1 = \beta_{12} = \beta_2 \equiv \beta$) for ionizing collisions,[5] the rate equation for the electron density is given by

$$\frac{dN_e}{dt} = -\alpha N_e^2 + \tfrac{1}{2}\beta M^2 \equiv -\alpha_e N_e^2. \qquad (4)$$

(β_2 is the ionizing rate coefficient for two molecular metastables.) The sum of the atomic-metastable density and the molecular-metastable density is represented by M, and the effective electronic recombination coefficient[4,5] is given by α_e. The effective recombination coefficient is independent of time over a wide range of conditions.[4,5] Solution of Eq. (4) for β gives the following:

$$\beta = 2(\alpha - \alpha_e)\,(N_e/M)^2\,.$$

The values of α and α_e at 15 Torr are taken from Ref. 5. The value of M is taken to be equal to $1.3M_1$ for the reasons described in Sec. II. The value of β is thereby evaluated to be 5.3×10^{-9} cm^3 sec^{-1} at 15 Torr and is listed in Table I under "C". Since the above evaluation was made at low pressures where atomic metastables dominate, the value of β should be closer to the value of β_1 than it is to the value of β_2.

IV. EQUILIBRIUM AND RATE PARAMETERS

With the assumption of equal ionization rates for all metastables, the rate equation for the total metastable density is given by

$$\frac{dM}{dt} = -\beta M^2 + k\alpha N_e^2 \equiv -\beta_e M^2\,, \qquad (5)$$

where k is the total fraction of recombination events which result in metastable species and β_e is a constant defined by the equation. Experimental results show that the electron density can be expressed by $N_e = [(1/N_e^0) + \alpha_e t)]^{-1}$, where N_e^0 is the initial electron density at time $t=0$. Equation (4) implies that M and N_e have the same functional dependence on time. By substituting the relation between M and N_e from Eq. (4) into $N_e = [(1/N_e^0) + \alpha_e t)]^{-1}$, by using $dM/dt = -\beta_e M^2$, and by equating the coefficients of t^2, one obtains some necessary relations between β, α, and α_e which are given in Ref. 5. We also assume that all recombination events end up in a metastable state and, thus, set $k=1$. This is reasonable since only a very small fraction of the resonance radiation of the singlet atomic levels will escape the plasma at these pressures. Thus, most of the helium atoms in an excited helium state that results from dissociative recombination will terminate in a metastable level. Additionally, the nondissociative electronic-recombination preferentially results in a molecular triplet level and these levels terminate in a metastable state. Some of the singlet diatomic energy levels produced by nondissociative electronic recombination will also be permanently transferred into triplet levels by collisions. (In Ref. 5 the value of k was stated to be equal to 0.7. This value was calculated with β set equal to β_{1e}. Since β_1 is surely larger than β_{1e}, the value 0.7 is the lower limit of k.) With the assumptions made above, the dependence of β on α and α_e can be expressed as follows:

$$\beta = \frac{2\alpha_e^2\,(\alpha - \alpha_e)}{(\alpha - 2\alpha_e)^2}\,. \qquad (6)$$

With the values of α and α_e given in Ref. 5 at 15 Torr, β is evaluated to be equal to 5.1×10^{-9} cm^3 sec^{-1} and is presented in Table I under "D." Again, because β is evaluated at low pressures, it should be nearly equal to β_1.

Using the entire range of α and α_e (Ref. 5) which was measured at gas pressures between 15 and 55 Torr, we evaluated β with Eq. (6) and found it yielded values from 4.5×10^{-9} to 5.1×10^{-9} cm^3 sec^{-1}. In this pressure range, the conditions changed from the case at low pressure, where the total metastable density was nearly equal to the atomic-metastable density, to the case at high pressure, where the molecular metastables completely dominated after a time into the afterglow. The fact that β changed by only a small amount over this pressure range is a self-consistent justification that all metastable ionizing rates are nearly equal.

V. DISCUSSION

In the above calculations, various severe, although reasonable, assumptions were made in each case. A major justification for the derived value of β_1 is that the values of β_1 determined by different techniques vary about the mean value by only 20%. All of the derived values of β_1 evaluated from the different techniques are between the maximum and minimum values given under "Range" in Table I. A more accurate evaluation of β_1 requires a more accurate value for the oscillator strength of the 4650-Å band of He_2. When this oscillator strength is more accurately known, the technique described here can also be used to evaluate β_{12} and β_2.

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Photoionization of Atomic Nitrogen and Atomic Oxygen*

P. S. Ganas†
University of Florida, Gainesville, Florida 32601
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We utilize an atomic independent-particle model to calculate photoionization cross sections for atomic nitrogen and atomic oxygen as a function of the wavelength of the incident radiation, from threshold down to 10 Å. Comparison is made with available experimental data and the results of Hartree–Fock calculations.

I. INTRODUCTION

Atomic photoionization cross sections are useful in probing the details of atomic structure. A knowledge of such cross sections is helpful in the understanding of gaseous discharges, ionospheric layers, and stellar atmospheres. Photoionization is known to play an essential role in the propagation of sparks, lightning, and other types of discharges. It is important for the atomic theorist to be able to make accurate *a priori* calculations of atomic photoionization cross sections. When accurate experimental cross sections exist, the calculations serve as a test of atomic theories and methods of calculation.

The photoionization cross sections of atomic nitrogen and atomic oxygen for incident radiation from threshold (≈900 Å) down to 10 Å are calculated. These particular cross sections are important in the interpretation of solar-terrestrial effects. They have been calculated by Dalgarno and Parkinson,[1] Bates and Seaton,[2] McGuire,[3] Thomas and Helliwell,[4] Kahler,[5] and Henry,[6] using the Hartree–Fock approach. In contrast to this approach, the present calculations are based upon the independent-particle model (IPM) of the atom. In comparison to Hartree–Fock–Slater calculations and to experiment, a simple two-parameter IPM potential has been found to provide a good representation of atoms and electron-atom interactions.[7–10] The potential for an electron in a neutral atom may be written (in atomic units)[7]

$$V(r) = -\frac{2}{r}\left(\frac{Z-1}{H(e^{r/d}-1)+1}+1\right), \qquad (1)$$

where d and H are adjustable parameters. This