Helium $3\,^3S$ decay rates in a high-pressure afterglow

J. E. Lawler, J. W. Parker, and L. W. Anderson
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

W. A. Fitzsimmons
National Research Group Inc., Madison, Wisconsin 53705
(Received 26 June 1978)

We report a total collisional quenching rate of $(6.4\pm0.3)\times10^{-12}$ cm^3 sec^{-1} at 292°K (or a thermally averaged cross section of 0.36×10^{-16} cm^2) for He $3\,^3S$ atoms colliding with ground-state He atoms. This rate is determined by using a pulsed dye laser to populate the $3\,^3S$ level in a He aftergow and then observing the decay of the $3\,^3S\rightarrow2\,^3P$ fluorescence. We see no evidence for three-body collisional quenching of $3\,^3S$ atoms at pressures up to 300 Torr.

I. INTRODUCTION

In this paper we report a study of the kinetics of the He $3\,^3S$ atoms in a high-pressure afterglow. The 3*s* levels are of particular interest because substantial experimental and theoretical effort has not conclusively determined whether $3\,^1S$ or $3\,^3S$ atoms are associatively ionized. All He levels above the 3*s* levels are rapidly associatively ionized in a high-pressure afterglow. Bennet, Kindlemann, and Mercer have measured total collisional quenching cross sections of $(1.4\pm0.5)\times10^{-16}$ and $(2.1\pm0.5)\times10^{-16}$ cm^2 at a temperature of 450 °K for $3\,^1S$ and $3\,^3S$ atoms, respectively.[1] Kubota, Davies, and King have measured total collisional quenching cross sections of $(1.4\pm0.1)\times10^{-16}$ cm^2 and $(0.13\pm0.1)\times10^{-16}$ cm^2 at 600° K for $3\,^1S$ and $3\,^3S$ atoms, respectively.[2] Gauthier, Devos, and Delpech have measured the temperature dependence of the total collisional quenching rate for $3\,^3S$ atoms.[3] Their measurements indicate that the rate is not strongly temperature dependent from 300 to 600 °K. They reported a rate of $(0.268\pm0.01)\times10^{-11}$ cm^3 sec^{-1} at 300 °K. This rate corresponds to a thermally averaged cross section of 0.156×10^{-16} cm^2.

Wellenstein and Robertson have reported that the cross sections for associative ionization of $3\,^1S$ and $3\,^3S$ atoms are apparently zero at 320 °K with experimental upper limits of 0.1×10^{-16} and 0.01×10^{-16} cm^2, respectively.[4] Cohen has calculated a thermally averaged associative-ionization cross section for $3\,^3S$ atoms of 0.06×10^{-16} cm^2 at 300 °K.[5] He has also calculated a thermally averaged cross section of 5.83×10^{-16} cm^2 at 300 °K for the reaction

$$\mathrm{He}(3\,^3S)+\mathrm{He}(1\,^1S)\rightarrow\mathrm{He}(2\,^3P)+\mathrm{He}(1\,^1S)\,. \qquad (1)$$

Steets and Lane have also calculated a substantial cross section for the reaction of Eq. (1).[6] Gauthier, Devos, and Delpech suggested that Cohen's calculated associative-ionization cross section may be accurate, and that his cross section for the reaction of Eq. (1) is too large.

In this paper we report a total collisional quenching rate for $3\,^3S$ atoms of $(6.4\pm0.3)\times10^{-12}$ cm^3 sec^{-1} at 292 °K. This corresponds to a thermally averaged quenching cross section of 0.36×10^{-16} cm^2. Previous experimental determinations of this rate involved measuring the pressure dependence of the decay rate over the range from a few Torr to 30 Torr. Over a pressure range of 30 Torr there is only a 10%–20% increase in the total decay rate above the He $3\,^3S$ radiative decay rate of 27.8×10^6 sec^{-1}.[7] By observing the $3\,^3S$ decay rate as a function of pressure to 300 Torr we have determined a more accurate value for the total collisional quenching rate. We have also determined that three-body collisions are not an important quenching mechanism for $3\,^3S$ atoms at pressure $\leq$ 300 Torr.

II. EXPERIMENTAL APPARATUS

Figure 1 is a schematic of the experimental apparatus used in this study. A National Research Group Inc. thyratron-switched N_2 laser is used to pump a tunable dye laser. The 3-nsec-duration[8] dye-laser pulse is attenuated and focused into a He discharge cell. Fluorescence from the focal volume is collected and imaged onto the entrance slit of a Jobin Yvon HR1000 monochromator. Dye filters are used to eliminate light scattered from the dye-laser beam. The fluorescence from a selected transition is detected with an EMI 9785 photomultiplier. The photomultiplier signal is large enough to display on a Tektronics 475 oscilloscope. The laser is attenuated when necessary to avoid saturation of the photomultiplier. The rise time of the detection-system electronics is 2.5 nsec. Individual oscilloscope traces are

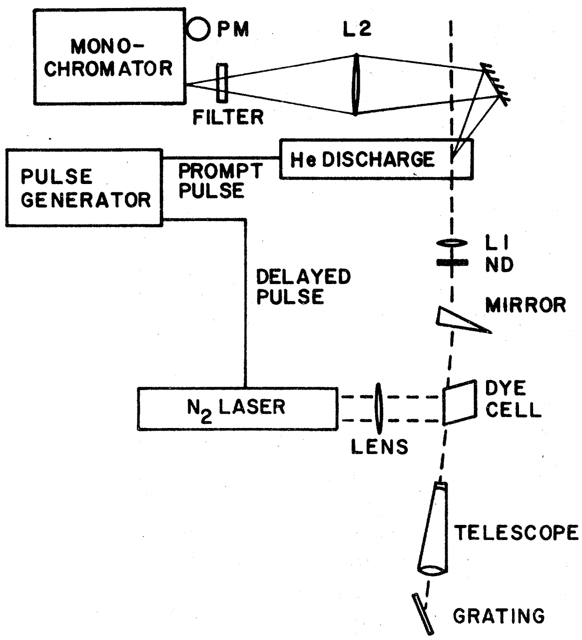

FIG. 1. Schematic diagram of the experimental apparatus. A N_2 laser pumps a dye laser. The dye-laser radiation, after attenuation by a neutral-density filter, ND, is focused by a lens $L1$ onto the center of the He discharge. The focal region is imaged onto the entrance slit of the monochromator by a second lens $L2$. A dye filter blocks scattered 388.9-nm dye-laser light while permitting the 706.5-nm fluorescence to enter the monochromator and photomultiplier tube PM.

photographed, digitized, and analyzed to determine the temporal characteristic of the fluorescence.

The He discharge system is similar in construction to the Blumlein pulsed discharge laser described by Fitzsimmons, Anderson, Riedhauser, and Vrtilek.[9] The Blumlein circuit is charged to 19 kV using a 60-Hz resonant charging circuit. A substantial fraction of the $\frac{1}{2}$ J of electrical energy that the discharge system stores is delivered to a discharge volume of about 5 cm^3 of He in about 20 nsec. The He discharge system and the N_2 laser are each switched by an EGG HY-1102 thyratron. The N_2 laser, used to pump the dye laser, is triggered from 0 to 500 μsec after the He discharge is triggered. This system allows us to probe the afterglow of an intense uniform discharge over a wide range of time delays and at pressures up to 300 Torr with a very small timing jitter.

In our discharge system the He is exchanged many times per second in order to control the amount of residual ionization persisting from one pulse to seed the next. This precludes the use of cataphoretically cleaned He, but ensures that the gas in the discharge tube is essentially at cylinder purity (99.995%). A careful assessment of possible effects due to impurities is necessary. Also an assessment of possible effects due to collisions of He 3 ^3S atoms with other excited He atoms or He_2 molecules is necessary because of the high density of metastable He atoms and He_2 molecules in the afterglow. These concerns are discussed in Sec. III.

III. He 3 ^3S RESULTS

To study the 3 ^3S kinetics we tune the dye-laser wavelength to $\lambda = 388.9$ nm, which corresponds to the 2 $^3S \rightarrow$ 3 ^3P transition. There is a metastable 2 ^3S density of approximately 10^{14} cm^{-3} in the afterglow.[10] The population of the 3 ^3P level produced by the dye-laser pulse is collisionally quenched in a time comparable to or shorter than the 3 nsec duration of the dye-laser pulse at the pressures used in this experiment.[3-5] At the termination of the dye-laser pulse a substantial population generated by collisional transfer remains in the 3 ^3S level. The radiation at $\lambda = 706.5$ nm from the 3 $^3S \rightarrow$ 2 ^3P transition is detected.

We use the approach of Gauthier, Devos, and Delpech[3] to eliminate effects due to superelastic electron collisions on 3 ^3S atoms. The delay of the dye-laser pulse after breakdown is increased until the observed 3 ^3S decay rates become delay independent. This occurs with delays of 10 to 25 μsec depending on the pressure. At these large delays there is sufficient time between breakdown in the He discharge and the arrival of the 388.9-nm dye-laser pulse for most of the free electrons to recombine. This is confirmed by measuring the intensity of electronic recombination radiation as a function of time. Also, the greatly decreased electron concentration in the late afterglow is confirmed by the disappearance of dye-laser-induced fluorescence from the 3 ^1S, 3 ^1P, and 3 ^1D levels. If the dye laser is pulsed during the first few microseconds of the afterglow, electron-atom spin-exchange collisions convert some of the $n = 3$ triplet atoms to $n = 3$ singlet aoms.

Possible sources of dye-laser-induced hot electrons are two-photon ionization of the 2 ^3S level by the dye laser and associative ionization of the dye laser produced $n = 3$ levels. If a significant concentration of hot electrons were produced by either of these mechanisms, then existing 3 ^3S as well as 3 ^3P and 3 ^3D atoms would be quenched by superelastic collisions and additional $n = 3$ atoms might be formed by recombination. The absence of observable dye-laser-induced fluorescence from any of the $n = 3$ singlet levels indicates that the dye laser was attenuated sufficiently that the electron density produced by the dye laser is not high enough to quench the $n = 3$ triplet levels. The energy difference between the $3\,^3S$ and the $3\,^1S$ levels is large enough that hot electrons are required to quench the $3\,^3S$ level by a spin-exchange collision, but the energy separation of the $3\,^3P$ and the $3\,^1P$ levels is only a few times kT and the separation between the $3\,^3D$ and the $3\,^1D$ levels is less than kT so that the $3\,^3P$ or $3\,^3D$ levels would be quenched by thermal electrons. Thus the absence of radiation from any of the singlet levels indicates that neither the $n=3$ singlet nor triplet levels are being rapidly populated by recombination in the late afterglow.

The $3\,^3S$ decay rate as a function of pressure is shown in Fig. 2. Each datum point for the $3\,^3S$ decay curve is obtained by averaging the decay rates obtained from five to seven oscilloscope trace photographs of the 706.5-nm fluorescence signal. The error bars represent one standard deviation in the mean. By using a least-squares fit of our data for the decay rate for the $3\,^3S$ level to the expression $a+bP$, we obtain $a=(2.63\pm0.20)\times10^7\ \mathrm{sec}^{-1}$ and $b=(2.12\pm0.11)\times10^5\ \mathrm{Torr}^{-1}\,\mathrm{sec}^{-1}$. The zero-pressure intercept compares favorably with the accepted $3\,^3S$ spontaneous decay rate of $2.78\times10^7\ \mathrm{sec}^{-1}$.[7] The slope represents a total collisional quenching rate for the $3\,^3S$ atom on ground-state He atoms of $(6.4\pm0.3)\times10^{-12}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$ at 292 °K.

To assess the magnitude of effects due to collisions of $3\,^3S$ atoms with impurities, with other excited He atoms, and with He molecules we observe the $2\,^3S$ population as a function of time. The He $2\,^3S$ metastables are not readily quenched by collisions with ground-state He atoms because of a potential barrier and because of the Wigner spin-

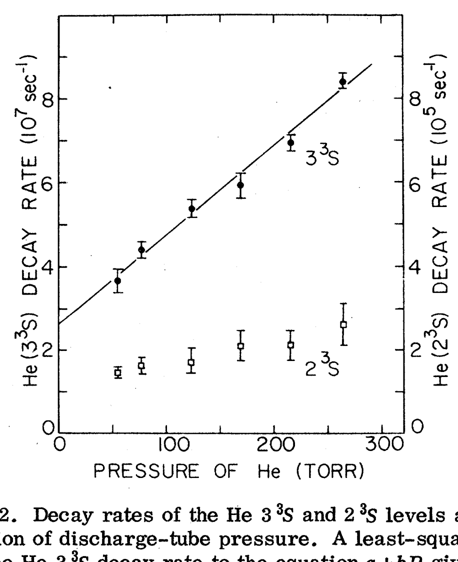

FIG. 2. Decay rates of the He $3\,^3S$ and $2\,^3S$ levels as a function of discharge-tube pressure. A least-squares fit of the He $3\,^3S$ decay rate to the equation $a+bP$ gives $a=(2.63\pm0.20)\times10^7\ \mathrm{sec}^{-1}$ and $b=(2.12\pm0.11)\times10^5\ \mathrm{Torr}^{-1}\,\mathrm{sec}^{-1}$. The error bars represent one standard deviation in the mean decay rate at each pressure.

conservation rule. However, the $2\,^3S$ metastables are readily quenched by collisions between pairs of $2\,^3S$ metastables, by collisions with $He_2\ a\,^3\Sigma$ metastables, and by collisions with any impurity in the system. The relative $2\,^3S$ population as a function of time in the afterglow is determined by measuring the total $3\,^3S$ fluorescence as a function of time delay between breakdown in the He discharge cell and the arrival of the dye-laser pulse. At each pressure the maximum $2\,^3S$ decay rate, which is graphed in Fig. 2, is observed after the bulk of molecular recombination has occurred. The $2\,^3S$ decay rates are smaller than the $3\,^3S$ decay rates by a factor of 200. The pressure dependence of the $2\,^3S$ decay rate is smaller than the pressure dependence of the $3\,^3S$ decay rate by a factor of 500. First we assess the contributions of collisions between $3\,^3S$ atoms and $2\,^3S$ metastable atoms and of collisions between $3\,^3S$ atoms and $a\,^3\Sigma$ metastable molecules to the $3\,^3S$ decay rate. Let us assume for the moment that the $2\,^3S$ decay rate is solely due either to collisions between $2\,^3S$ atoms and $a\,^3\Sigma$ molecules or to collisions between pairs of $2\,^3S$ atoms. The total collisional quenching rate of $2\,^3S$ atoms on the $a\,^3\Sigma$ molecules is $(2.5\pm1.5)\times10^{-9}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$,[11] which corresponds to a thermally averaged cross section of $1.6\times10^{-14}\ \mathrm{cm}^2$. The total collisional quenching rate of $2\,^3S$ atoms on $2\,^3S$ atoms is only slightly smaller being $(1.5\pm0.3)\times10^{-9}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$.[11] Because it is improbable that the total collisional quenching rate of $3\,^3S$ atoms on $2\,^3S$ metastable atoms or $a\,^3\Sigma$ metastable molecules is as much as ten times larger than the very large $2\,^3S$ on $2\,^3S$ quenching rate, we conclude that collisions of He $3\,^3S$ atoms with $2\,^3S$ atoms or $a\,^3\Sigma$ molecules do not contribute appreciably to the $3\,^3S$ decay rates.

Next we assess the contribution of collisions with impurities to the $3\,^3S$ decay rate. Let us assume that the $2\,^3S$ decay rates are due solely to collisions with impurities. Chemitron, the supplier of the He, states that N_2 and O_2 are the most abundant impurities with four times as much N_2 as O_2. The total collisional quenching rate for $2\,^3S$ metastables on N_2 is 6.96×10^{-11} (±30%) $\mathrm{cm}^3\,\mathrm{sec}^{-1}$,[12] corresponding to a thermally averaged cross section of $5.21\times10^{-16}\ \mathrm{cm}^2$. The $3\,^3S$ collisional quenching rate on N_2 is not known; however, it would have to be more than 250 times as large as the $2\,^3S$ rate on N_2 in order to account for 50% of the $3\,^3S$ collisional quenching rate. Collisional quenching rates for 3^3S atoms measured so far indicate that the $3\,^3S$ atom is only a few times more reactive than the $2\,^3S$ metastable when chemionization is an open reaction channel.[2,12] Therefore, we conclude that collisions of $3\,^3S$ atoms with impurities do not contribute appreciably to the observed

3 ^3S decay rates.

IV. SUMMARY

We have measured a rate of $(6.4\pm0.3)\times10^{-12}$ $cm^3\,sec^{-1}$ for the collisional quenching of 3 ^3S atoms colliding with ground-state He atoms at 292 °K. This corresponds to a thermally averaged cross section of 0.36×10^{-16} cm^2. We observe that three-body collisional quenching of 3 ^3S atoms is negligible at pressures up to 300 Torr.

ACKNOWLEDGMENT

Research was supported in part by the University of Wisconsin Graduate School with funds provided by the Wisconsin Alumni Research Foundation.

---

[1]W. R. Bennet, Jr., P. J. Kindelmann, and G. N. Mercer, Appl. Opt. Suppl. 2, 34 (1965).

[2]S. Kubota, C. Davies, and T. A. King, J. Phys. B 8, 1220 (1975).

[3]J. C. Gauthier, F. Devos, and J. F. Delpach, Phys. Rev. A 14, 2182 (1976).

[4]H. F. Wellenstein and W. W. Robertson, J. Chem. Phys. 56, 1072 (1972); 56, 1077 (1972).

[5]J. S. Cohen, Phys. Rev. A 13, 99 (1976).

[6]W. J. Steets and N. F. Lane, Phys. Rev. A 11, 1994 (1975).

[7]W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, U. S. Natl. Bur. Stand. Ref. Data Ser. No. 4 (U.S. GPO, Washington, D.C., 1966), Vol. I, pp. 11–14.

[8]J. E. Lawler, W. A. Fitzsimmons, and L. W. Anderson, Appl. Opt. 15, 1083 (1976).

[9]W. A. Fitzsimmons, L. W. Anderson, C. E. Riedhauser, and J. M. Vrtilek, IEEE J. Quantum Electron. 12, 624 (1976).

[10]J. E. Lawler, J. W. Parker, L. W. Anderson, and W. A. Fitzsimmons, Phys. Rev. Lett. 39, 543 (1977).

[11]R. Deloche, P. Monchicourt, M. Cheret, and F. Lambert, Phys. Rev. A 13, 1140 (1976).

[12]A. L. Schmeltekopf and F. C. Fehsenfeld, J. Chem. Phys. 53, 3173 (1970).