Nonmetastable Penning ionization in He($3\,^1P$)-Ne, Ar, Kr, Xe collisions

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Time-dependent spectroscopy techniques have been used to determine the cross sections for the deexcitation of nonmetastable He($3\,^1P$) states by collision with Ne, Ar, Kr, or Xe atoms. The measured cross sections in 10^{-16} cm^2 at 600^{+200}_{-100} °K are, for Ne, $27.6^{+4.5}_{-2.8}$; Ar, $55.6^{+10.6}_{-7.8}$; Kr, $49.5^{+8.0}_{-4.8}$; and Xe, $73.0^{+12.9}_{-8.8}$. These cross sections are compared with theoretical Penning ionization cross sections having values of 20 for Ne, 40 for Ar, 39 for Kr, and 35 for Xe, in units of 10^{-16} cm^2 (at 600 °K).

INTRODUCTION

Interactions between electronically excited atoms (or molecules) and ground-state species are of interest both for a basic understanding of energy-transfer mechanisms and for their importance in processes in the upper atmosphere,[1] in gaseous lasers,[2] in plasmas,[3] and in other excited-gas media.[4] There have been several experimental investigations[5] on the deexcitation of metastable-state atoms, but few for nonmetastable excited atoms, mainly because of the experimental difficulties.

We report here on measurements of absolute cross sections for the deexcitation of He($3\,^1P$) states in collision with gas atoms X (X =Ne, Ar, Kr, and Xe) at approximately 600°K, observing the relaxation of He($3\,^1P$) states in helium containing known concentrations of X. The ionization potential of the added gas X is lower than the excitation energy of He($3\,^1P$) and the process studied involves the ionization of X atoms in a collision with an excited state by nonmetastable Penning ionization. Until recently, the existence of the nonmetastable Penning ionization process had been confirmed only from the additional ionization yield after excitation by charged particles in helium-neon,[6] argon-krypton,[6,7] and argon-xenon mixtures.[6]

EXPERIMENTAL TECHNIQUES

The experimental apparatus is similar to that described by Bridgett, King, and Smith-Saville[8] and has been further developed by Davies and King[9]; it is shown in diagrammatic form in Fig. 1 and will be discussed more fully elsewhere.[9] The He($3\,^1P$) level is excited by electron impact, using a pulsed beam of electrons of short duration and rapid time cutoff. The energy of the electrons is controlled to be as close to the energy of the $3\,^1P$ level as possible (threshold excitation). The decay function following the pulsed electron beam was determined from single-photon counting using the He 5016-Å spectral line ($3\,^1P$-$2\,^1S$ emission). A time-to-amplitude converter is started by a trigger pulse from the pulse generator at the pulse cutoff time and is stopped by the pulse from an amplifier-trigger unit which occurs when a single photon is detected by the photomultiplier. The output from the time-to-amplitude converter is proportional to the photon-emission time interval and is fed into a multichannel analyzer where the decay curve is accumulated. Background counts are removed by modulating the electron gun below threshold and subtracting at the pulse-height analyzer and at threshold, and adding counts.

A 5-cm×2-cm dispenser cathode is used in the electron gun. Figure 2 shows the excitation chamber filling system. The portion of the system in the oven is baked at 250°C for 12 h while being evacuated with an argon stable sputter-ion 50-liter/sec pump. The ultimate vacuum obtained is ~5 $\times 10^{-9}$ torr. The outgassing rate is less than 2×10^{-5} torr h^{-1}, even when the cathode is operating at 1050°C. Spectroscopically pure helium (obtained from British Oxygen Company and containing impurities of less than 10 ppm) is admitted to the excitation chamber via leak valves 1 and 2. In the spectral region from 2500 to 7300 Å only a few emission lines from impurity atoms were observed; for a helium pressure of 38 mtorr and electron excitation energy of 24.3 eV the light intensities from the impurity lines were 3 to 4 orders of magnitude lower than the intensities from the helium lines. The excitation chamber was filled with pure helium and the added gas was leaked through valves 3 or 4, while measuring the total pressure using a capacitance manometer (MKS Baratron, model 77).

He($3\,^1P$) DEEXCITATION CROSS SECTIONS

The lifetime of He($3\,^1P$) states in pure helium is a function of the helium pressure due to the destruction of He($3\,^1P$) by collision with neutral

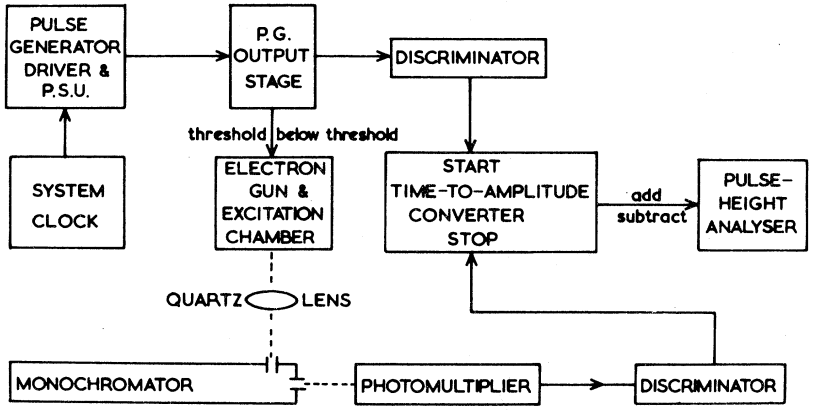

FIG. 1. Pulsed threshold electron excitation and single-photon counting decay-time apparatus.

helium atoms[10,11] and is also dependent on the effective size of the excitation chamber owing to the slight imprisonment of the He $3\,^1P$-$1\,^1S$ radiation. For a constant size of excitation chamber, the decay rate $1/\tau$ in pure helium is a function of the helium pressure, p_{He},

$$1/\tau = F(p_{\mathrm{He}}). \tag{1}$$

When added atoms X are introduced we can write (1) as

$$1/\tau = F(p_{\mathrm{He}}) + n\langle\sigma v\rangle p_X, \tag{2}$$

where σ is the added deexcitation cross section in question, v the relative velocity, n the number of X atoms per torr cm^3, and p_X the pressure of X in torr. Provided v does not vary with p_X, the quantity $\langle\sigma v\rangle$ can thus be obtained by keeping the helium-gas pressure constant and varying p_X.

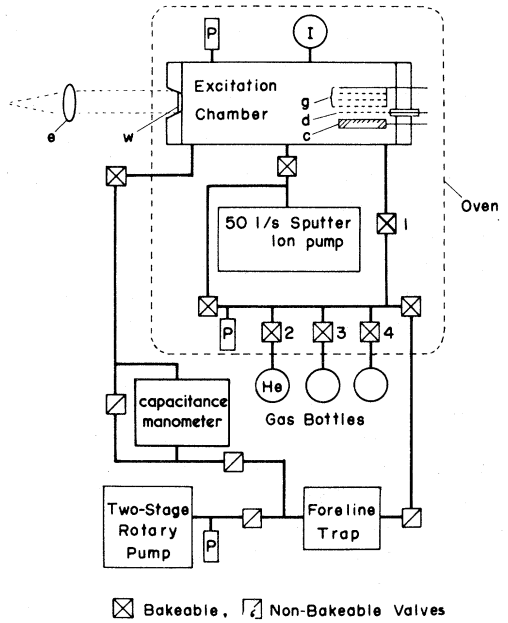

FIG. 2. Vacuum and gas handling system and excitation chamber. P—Pirani gauges, I—ionization gauge, c—cathode, d and g—control grids, w—exit window, e—condensing system.

Measurements were made at 1-torr helium pressure and 22.5-eV excitation energy[12] and for excitation pulse widths of less than 50 nsec which gave a negligible contribution of cascading photons to the $3\,^1P$ level from higher excited states, for example, from the $4\,^1S$ state.[11] The He($3\,^1P$) state at 23.09 eV is then only weakly excited and one loses up to two orders of magnitude of signal intensity compared with excitation at 23.0 eV by this technique. Figure 3 shows a typical He 5016-Å emission curve with and without added Ne. As seen from the figure, data points for times greater than 110 nsec are not described in terms of a single-exponential decay. It was found that all decays studied fit, within statistical error, a functional form of the type

$$N(t) = Ae^{-t/\alpha} + B, \tag{3}$$

where A and B are constants and in all cases B is much smaller than A. As an example to indicate this type of behavior, A, B, and α for 0.59-torr Ne in Fig. 3 were 20 300 ±140, 100 ±20, and 35.6 ±0.2 nsec, respectively. The lifetime β obtained from the fit from the straight line up to 110 nsec was 35.8 ±0.2 nsec. The difference in the lifetimes between α and β is less than 1.0% over all the range of added gas concentrations. The mean value of α and β is used as a measure of τ in this paper. The origin of the constant term B is not completely understood. This may arise from reciprocal transfer effects from $3\,^1D$ states.[13] As an over-all system check, the lifetimes of the $3\,^1S$ and $4\,^1S$ states in the zero pressure limit measured with the above technique are 55.7 ±0.5 and 87.0 ±3.0 nsec, respectively.[11] These compare favorably with the theoretical lifetimes of

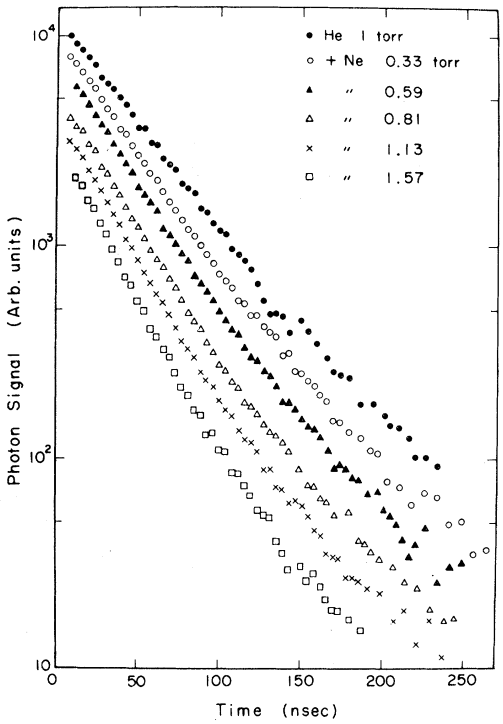

FIG. 3. Decay functions for He($3\,^1P$) atoms observed by the $3\,^1P \rightarrow 2\,^1P$, 5016-Å emission line for varied set pressures of Ne.

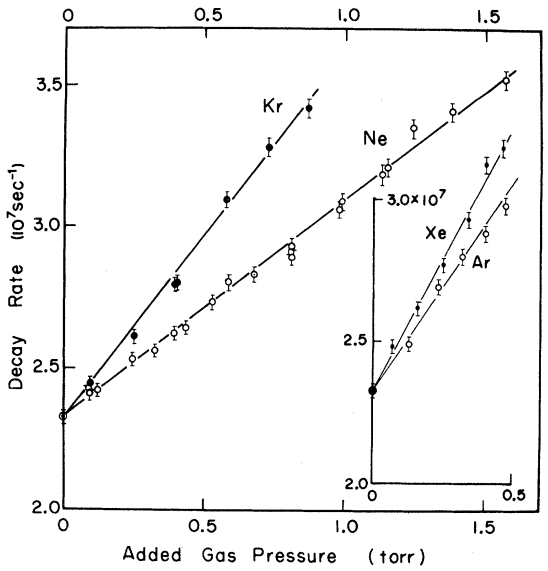

FIG. 4. Variation of He($3\,^1P$) decay rate with pressure of added Ne, Ar, Kr, and Xe; initial He pressure is 1 torr. Standard-deviation errors are shown for the data points.

55.2 and 89.7 nsec[14] and with 55.2 ±2.8 and 84.0 ±10.6 nsec measured by Bennett *et al.*[15] The pressure dependences of the lifetimes of the He ($n=3$, $n=4$) states in pure He have been extensively studied by us[11] and other workers. Figure 4 shows the plot of the decay rates as a function of added gas pressure, the error bars include the standard deviations of the data points. The plotted points lie reasonably well on straight lines over the measured p_X region. Any systematic errors, which are expected to be due primarily to possible errors in calibrating the time-to-amplitude converter, are estimated to be less than 2%.

The measured values of $n\langle\sigma v\rangle$ for He($3\,^1P$) atoms reacting with X are shown in Table I. The velocity-averaged total deexcitation cross section σ_{expt} at an absolute temperature T is obtained by dividing $n\langle\sigma v\rangle$ by $n_0 T^{-1}(2kT/M^*)^{1/2}$, and these are also listed in Table I. Here, k is the Boltzmann's constant, M^* the reduced mass of the colliding partners, and n_0 is the number of atoms per cm^3 torr at 273°K. The error values quoted in Table I include statistical errors and systematic errors of +15%/−8% due to the uncertainty in the determination of the atom temperature. The temperature of the atoms in the excitation chamber was estimated to be $600 \pm {}^{200}_{100}$°K by measuring the temperatures of the parts of the apparatus in and around the region of the excitation chamber. The uncertainty in determining the temperature of the colliding atoms in the excitation chamber is the main source of error and is included in the final result for the deexcitation cross section.

DISCUSSION

The cross sections reported here include all processes that deexcite the He($3\,^1P$) atom in a collision with the added noble-gas atom. In all of these collision pairs the excitation energy of the He($3\,^1P$) atom exceeds the ionization potential of the target. Thus, the initial state of the collision complex is imbedded in a continuum and is subject to rapid autoionization. This process (chemi-ionization) is expected to be the predominant mode of deexcitation under these conditions. We thus associate our measured cross sections primarily with the chemi-ionization process and, to our knowledge, they are the first to be measured for an optically allowed excited state.

The ionization process due to the optically-allowed transition $A^* + X \rightarrow A + X^+ + e^-$ has been theoretically studied by Katsuura,[16] Watanabe and Katsuura,[17] Mori and Fujita[18] and Mori.[19] Using a semiclassical calculation with rectilinear relative motion with constant velocity, Watanabe and Katsuura[17] have found that the ionization cross section, averaged over the polarization of the initial excitation of A^*, is given by

$$\sigma = 13.9(\mu^2\mu_E^2/\hbar v)^{2/5}, \qquad (4)$$

TABLE I. Experimental values of $n\langle\sigma v\rangle$ and comparison of the He($3\,^1P$) deexcitation cross section at 600^{+200}_{-100} °K from experiment and theory.

Added gas	$n\langle\sigma v\rangle$ (10^7 sec^{-1} torr^{-1})	σ_{expt} (10^{-16} cm^2)	σ_{calc} (10^{-16} cm^2)	σ_{ph} (10^{-18} cm^2)	μ_E^2 (a.u.)
Ne	0.77 ± 0.04	$27.6^{+4.5}_{-2.8}$	19.8–20.7	6.4–7.1 [a]	0.93–1.03
Ar	1.49 ± 0.16	$55.6^{+10.6}_{-7.8}$	39.8–40.5	35–37 [b]	5.1–5.4
Kr	1.29 ± 0.06	$49.5^{+8.0}_{-4.8}$	38.2–40.5	29.5–35.5 [c]	4.4–5.2
Xe	1.88 ± 0.16	$73.0^{+12.9}_{-8.8}$	32.8–37.4	21–26 [d]	3.0–4.1

[a] References 20 and 21.
[b] References 20, 22, and 23.
[c] References 20 and 24.
[d] References 20, 24, and 25.

where μ is the transition dipole moment for $A^* \rightarrow A$, μ_E is the corresponding moment for $X \rightarrow X^+ + e$, and v is the velocity of A relative to X. μ_E^2 is related to the photoionization cross section, σ_{ph}, by

$$\sigma_{ph} = 4\pi^2 E \mu_E^2/\hbar c, \tag{5}$$

where c is the velocity of light and E is here taken to be the excitation energy of A^*. The reaction rate constant $\langle\sigma v\rangle$, i.e., the mean value of σv averaged over the Maxwellian velocity distribution, can be derived from Eq. (3):

$$\langle\sigma v\rangle = 4\pi\left(\frac{M^*}{2\pi kT}\right)^{3/2}\int_0^\infty \sigma \exp\left(-\frac{M^* v^2}{2kT}\right) v^3\, dv$$

$$= 14.59(\mu^2\mu_E^2/\hbar)^{2/5}\left(\frac{2kT}{M^*}\right)^{3/10} \tag{6}$$

with M^* being the reduced mass of the colliding partners. The calculated cross section, σ_{cal}, is obtained as $\langle\sigma v\rangle(2kT/M^*)^{-1/2}$. The calculated results for $He(3\,^1P) + X \rightarrow He(1\,^1S) + X^+ + e^-$ at $600\ ^{+200}_{-100}$°K are given in Table I. A value, 0.0433 a.u., is used for μ^2 between the ground state and the excited state $3\,^1P$ of helium.[14] The values of σ_{ph} have been deduced from experimental photoionization cross sections.[20-25]

Table I shows that the present measurements of the total deexcitation cross sections are larger than σ_{cal}. The difference is significantly large for Xe. The associative ionization

$$He(3\,^1P) + X \rightarrow HeX^+ + e \tag{7}$$

may contribute to the total deexcitation cross sections. Munson *et al.*[26] mass spectrometrically observed all of the heteronuclear ions (HeX^+) in helium-X gas mixtures excited by low-energy electrons and they obtained a rough estimate of the ratio of cross sections for associative ionization to Penning ionization to be of the order of 0.1 to 0.5. Hotop *et al.*[27] obtained the ratio for associative to Penning-ionization cross sections for He($2\,^1S$) and He($2\,^3S$) at 320°K to be, in Ar: 0.21 and 0.15, in Kr: 0.13 and 0.17, and in Xe: 0.02 and 0.11. Considering these measurements we may conclude that most of the difference between the present experimental results and theoretical values for Ne, Ar, and Kr can be attributed to the contribution from associative ionization. The large difference for Xe is not explained by that process.

There are two other possible effects that can be considered to explain the difference for xenon. One is that the He($3\,^1P$) atom is also removed by collisional deexcitation transfer:

$$He(3\,^1P) + X \rightarrow He^* + X + KE. \tag{8}$$

It is characteristic of this process[13] that such exchanges of internal and kinetic energy (KE) are only probable for energy differences in those cases where the He* state considered is another singlet state in close energy resonance with the original He($3\,^1P$). The following reaction is the only important collisional deexcitation mechanism under the present conditions,

$$He(3\,^1P) + X \rightarrow He(3\,^1D) + X + KE. \tag{9}$$

At present, to our knowledge, there has been no measurement of the cross section for process (9). In pure helium the cross section for $He(3\,^1P) + He \rightarrow He(3\,^1D) + He + KE$ has been measured to be in the range $(3-35)\times10^{-16}$ cm^2 by Bakos and Szigeti,[28] Frish and Ionikh[29] and Wellenstein and Robertson.[30] Experiments have been carried out on He-Xe and He-Kr mixtures as a function of Xe and Kr pressure with observation of the 6678-Å emission from the $3\,^1D$-$2\,^1S$ transition in He. Over the pressure range for which the change in He($3\,^1P$) lifetime was significant as shown in Fig. 4, no increase in 6678-Å ($3\,^1D$-$2\,^1S$) intensity was observed. Since the population of the He($3\,^1D$) following one excitation pulse is small compared to that of He($3\,^1P$) reaction (9), if of primary importance, would

noticeably change the He($3\,^1D$) population. We conclude that this reaction under those conditions is a secondary effect.

The second possible process is that the calculation, assuming rectilinear relative motion, is not a good approximation in the case of xenon. Because of the large polarizability of xenon, the van der Waal's force between He($3\,^1P$) and xenon atoms is large and this attraction may play an important role such that the relative trajectory is strongly curved inward. Rectilinear motion is a good approximation for Ne, Ar, and Kr in which the polarizabilities are smaller than in Xe. The differences between the observed and calculated cross sections may be a fruitful field of further theoretical analysis together with additional experimental results.

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[1]E. E. Ferguson and H. S. Schlüter, Planet. Space Sci. 9, 701 (1963).

[2]W. R. Bennett, Jr., Appl. Opt. Suppl. 2, 3 (1965).

[3]J. Dutton and J. M. Powell, J. Phys. B 4, 1506 (1971).

[4]W. P. Jesse and J. Sadauskis, Phys. Rev. 100, 1755 (1955).

[5]The present state of knowledge regarding chemi-ionization reactions by metastable-state atoms has recently been reviewed by R. D. Rundel and R. F. Stebbings, in *Case Studies in Atomic Collision Physics*, edited by M. R. C. McDowell and E. W. McDaniel (North-Holland, Amsterdam, 1972), Vol. 2, p. 547. See also Radiat. Res. 59, 337 (1974).

[6]S. Kubota, J. Phys. Soc. Jpn. 29, 1017 (1970).

[7]C. E. Melton, G. S. Hurst, and T. E. Bortner, Phys. Rev. 96, 643 (1954).

[8]K. A. Bridgett, T. A. King, and R. J. Smith-Saville, J. Phys. E 3, 767 (1970).

[9]C. Davies and T. A. King, J. Phys. E (to be published).

[10]K. A. Bridgett and T. A. King, in *Proceedings of the International Conference on Optical Pumping and Atomic Line Shape*, edited by T. Skalinski (Panstwowe Wydawnictwo Naukowe, Warsaw, 1969), pp. 359–368.

[11]S. Kubota, C. Davies, and T. A. King, J. Phys. B (to be published).

[12]This energy is lower than the energy level of He($3\,^1P$), i.e., 23.09 eV. Since the energy spread of the electrons from the gun is about 0.2 eV, He($3\,^1P$) states are excited by the electrons which are the high-energy tail of the electron energy distribution.

[13]W. R. Bennett, Jr., Ann. Phys. (N. Y.) 18, 367 (1962).

[14]W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, NSRDS-NBS-4 (U. S. GPO, Washington, D. C., 1966), Vol. 1.

[15]W. R. Bennett, Jr., P. J. Kindlmann, and G. N. Mercer, Appl. Opt. Suppl. 2, 34 (1965).

[16]K. Katsuura, J. Chem. Phys. 42, 3771 (1965).

[17]T. Watanabe and K. Katsuura, J. Chem. Phys. 47, 800 (1967).

[18]M. Mori and H. Fujita, J. Phys. Soc. Jpn. 20, 432 (1965).

[19]M. Mori, J. Phys. Soc. Jpn. 21, 979 (1966).

[20]J. A. R. Samson, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1966), Vol. 2, p. 177.

[21]A. Pery-Thorne and W. R. S. Garton, Proc. Phys. Soc. Lond. 76, 833 (1960).

[22]J. A. R. Samson, J. Opt. Soc. Am. 54, 420 (1964).

[23]O. P. Rustgi, J. Opt. Soc. Am. 54, 464 (1964).

[24]O. P. Rustgi, E. I. Fisher, and C. F. Huller, J. Opt. Soc. Am. 54, 745 (1964).

[25]H. E. Blackwell, G. S. Bajwa, G. S. Shipp, and G. L. Weissler, J. Quant. Spectrosc. Radiat. Transfer 4, 239 (1964).

[26]M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Chem. Phys. 67, 1942 (1963).

[27]H. Hotop, A. Niehaus, and A. L. Schmeltekopf, Z. Phys. 229, 1 (1969).

[28]J. Bakos and J. Szigeti, J. Phys. B 1, 1115 (1968).

[29]S. E. Frish and Yu. E. Ionikh, Opt. Spectrosk. 25, 9 (1968) [Opt. Spectrosc. 25, 171 (1968)].

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