PHYSICAL REVIEW VOLUME 128, NUMBER 1 OCTOBER 1, 1962

Cross Sections for the De-Excitation of Helium Metastable Atoms by Collisions with Atoms*

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(Received February 1, 1962)

The lifetimes of metastable helium atoms He(2 ^3S) and He(2 ^1S) were measured by a time-resolved optical absorption technique in the afterglow of a pulsed helium discharge at 10-mm pressure with small concentrations of various impurity gases added. The following de-excitation cross sections in units of 10^{-16} cm^2 have been determined for He(2 ^3S): Ne—0.28, Ar—6.6, Kr—10.3, Xe—13.9, N$_2$—6.4, and H$_2$—6.0. The uncertainties are estimated to be ±20% for the rare gases and ±50% for the molecular gases. He(2 ^1S) cross sections were measured to be Ne—4.1, Ar—55, Kr—64, and Xe—103, all times 10^{-16} cm^2. The neon cross section is believed reliable to ±20% but the remaining singlet cross sections may be too high by as much as a factor 2 or 3. The cross sections refer to de-excitation by ionizing collisions except in the case of neon where neon excitation occurs. Competing destruction processes render the singlet cross-section analysis somewhat uncertain except in the case of neon.

I. INTRODUCTION

THE lifetimes of He(2 ^3S) and He(2 ^1S) metastable atoms were measured in helium containing known small concentrations of Ne, Ar, Kr, Xe, H$_2$, and N$_2$. The metastable atom concentrations were determined by an optical absorption technique developed by Phelps.[1,2] Except in the case of Ne, the ionization potential of the impurity gas is lower than the excitation energy of either metastable and the process studied is the ionization of an impurity atom in a collision with a metastable, the so-called Penning effect. The purpose of the experiments described in this paper was to determine the cross sections for these de-excitation reactions.

II. EXPERIMENT

The experimental apparatus is essentially the same as that developed by Phelps[1,2] and is shown in diagrammatic form in Fig. 1. Metastable concentration following a pulsed discharge was determined from the fractional absorption due to the triplet He(2 ^3S) or singlet He(2 ^1S) metastable using the 3889- or 5016-Å spectral lines, respectively. The gas is contained in a Pyrex tube having internal molybdenum wire electrodes. The tube is pulsed at 15 cps with a breakdown voltage pulse of variable duration and a detecting photomultiplier is gated at 30 cps at a selected time after the breakdown pulse, alternate photomultiplier gating pulses being in the early and late afterflow. At the late afterglow pulse time the absorption is essentially zero so that the photomultiplier output has a 15-cps fundamental whose amplitude is proportional to fractional absorption and hence, for small fractional absorption, to metastable concentration. This scheme is indicated in Fig. 2. The signal was amplified by a sharply tuned amplifier and then ordinarily fed to a synchronous detector which was capable of integrating the output over a period of as long as 60 sec.

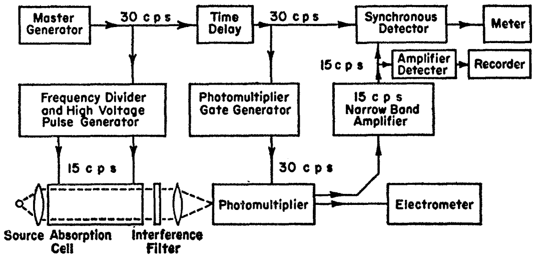

FIG. 1. Absorption measuring system.

A critical factor in these experiments was the control and determination of the impurity concentration in the absorption cell. We believe that the wide discrepancies in the previously published values for Penning cross sections probably derive from uncertainties in the impurity gas concentration. Figure 3 shows the cell filling system. The portion of the system in the oven is baked at 400°C for two 12-h periods while being evacuated with a Varian Vac-Ion 5-liter/sec pump. Between bakeouts the internal cell electrodes and the barium getter wires are outgassed with an induction heater. After the second bakeout the barium getters are flashed with the induction heater. The ultimate vacuum is around 10^{-8} mm of Hg. Grade A bottled helium containing approximately 3×10^{-5} parts neon was leaked through liquid nitrogen cooled charcoal trap 1 (see Fig. 3) into cataphoresis tube 1 where remaining rare gas impurities are removed to charcoal trap 2 by running the cataphoresis tube at 50-mA current. This quite pure helium was allowed to leak into the second cataphoresis tube and cell chamber. A further cataphoresis process was carried out in tube 2 at 50 mA and the pressure adjusted. A 10-mA cataphoresis current was also run from one electrode of the absorption cell to the anode of tube 2. Slightly lower destruction frequencies (reciprocal lifetimes) were obtainable by seal-

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* This research was supported by the Propulsion Sciences Division, Air Force Office of Scientific Research.

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[1] A. V. Phelps and J. L. Pack, Rev. Sci. Instr. **26**, 45 (1955).

[2] A. V. Phelps, Phys. Rev. **99**, 1307 (1955).

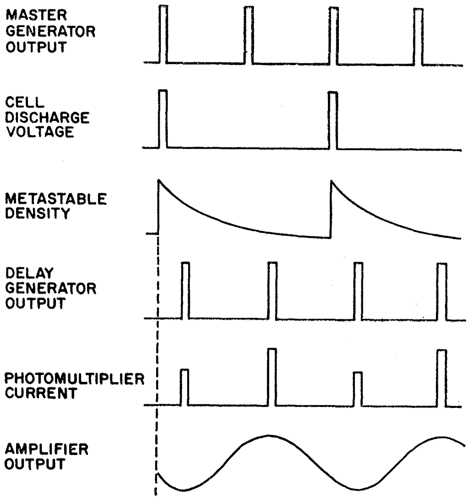

FIG. 2. Absorption system wave forms.

ing off the cell rather than using the valves, however, this greatly limited the flexibility of the system. The reproducibility of measurement for pure helium for repeated fillings was approximately 5% in the destruction frequencies.

The introduction of a small known amount of impurity into the pure helium is greatly complicated by the strong tendency for even rare gases to be adsorbed onto the clean glass surfaces, thereby falsifying the impurity concentration. The method used here was to measure the pressure of the impurity after it was introduced, so that all of the atoms which were going to attach themselves to the wall would not be considered. The impurity was leaked through trap 3, whose composition and temperature were dependent upon the type of impurity, until the oil manometer indicated a few mm Hg pressure. The impurity was leaked through the variable leak 5 into both the cell and impurity chambers. The pressure was read on the ion gauge, operating at 1-mA grid current to reduce the pumping action of the gauge. Immediately upon reaching the desired pressure both ion gauge and leak were turned off. The impurity was allowed to equilibrate with the surfaces, then pumped down to 10^{-2} mm or lower with the Vac-Ion. The impurity chamber alone was then refilled to a specific pressure near the original one. Following this the cell chamber was filled with pure helium as discussed above and finally the pure helium and impurity were allowed to diffuse together by opening valve 4. The relative chamber volumes were calibrated to allow final pressure determinations of both helium and impurity.

The ionization gauge used was a Westinghouse WL-5966 which was calibrated against a McLeod gauge using nitrogen gas. The relative gauge sensitivities used were those given by Schulz[3] for He, Ne, Ar, H_2, and N_2, also obtained on a WL-5966 gauge. The relative sensitivities for Kr and Xe were taken from Dushman and Young.[4] The data of these two sources agree very well for He, Ne, and Ar. Sensitivities supplied by the Vacuum-Electronics Corporation in private correspondence agree well for the rare gases. For H_2 there is a 33% discrepancy and for N_2 a 22% discrepancy between references 3 and 4 but for other reasons, to be discussed, the H_2 and N_2 cross sections could not be reliably measured anyway.

Xe was found to be slowly adsorbed by the barium getter which was therefore removed for these measurements. Ne was the only gas which showed almost no tendency to be pumped by the ionization gauge. For N_2 and H_2 the barium getters and charcoal trap 3 were removed. When the pulsed discharge was operated, both N_2 and H_2 were found to be rapidly "cleaned up." N_2 also disappeared rapidly when only external electrodes were used. For this reason it was only possible to get a fractional absorption measurement for a single delay time for each filling of these gases. The data are correspondingly less reliable. Measurements on both CO_2 and O_2 were attempted but they cleaned up so rapidly as to give no evidence of their presence.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

The differential equations governing singlet (S) and triplet (T) metastable decay are given by Phelps[2] as

$$\partial S/\partial t = D_S\nabla^2 S - \nu(N)S - \beta n_e S, \tag{1}$$

$$\partial T/\partial t = D_T\nabla^2 T - AN^2 T + \beta n_e S, \tag{2}$$

where D's are diffusion coefficients, β is the frequency per electron for conversion of $2\,{}^1S$ metastables into $2\,{}^3S$ metastables by thermal electrons of concentration n_e in the process

$$\mathrm{He}(2\,{}^1S) + e \rightarrow \mathrm{He}(2\,{}^3S) + e + 0.79\ \mathrm{eV}, \tag{3}$$

$\nu(N)$ represents the frequency of destruction of singlets by collisions with neutral atoms N. AN^2 represents the loss of triplets in collision with two neutrals, pre-

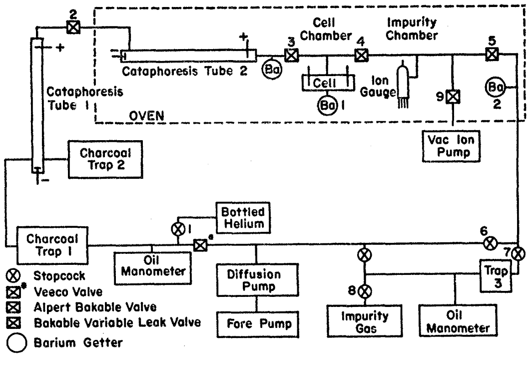

FIG. 3. Cell filling system.

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[3] G. J. Schulz, J. Appl. Phys. **28**, 1149 (1957).

[4] S. Dushman and A. H. Young, Phys. Rev. **68**, 278 (1945).

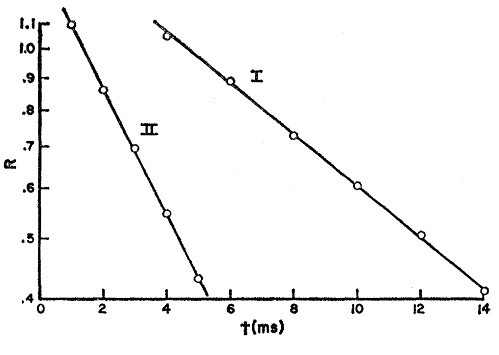

FIG. 4. Sample curves of 3889Å He(2 ^3S) fractional absorption R vs time; Curve I, pure helium, 10 mm pressure; Curve II, same with 1.0×10^{12} atoms/cm^3 krypton added.

sumably via

$$\mathrm{He}(2\,^3S)+2\mathrm{He}\rightarrow \mathrm{He}_2(2\,^3\Sigma)+\mathrm{He}. \qquad (4)$$

When impurity atoms are added we can write (1) and (2) as

$$\partial S/\partial t=-\nu_S{}^0 S-\langle\sigma_S V\rangle n_i S-\beta n_e' S, \qquad (1')$$

$$\partial T/\partial t=\nu_T{}^0 T-\langle\sigma_T V\rangle n_i T, \qquad (2')$$

where σ's are the impurity destruction cross sections in question, V's relative velocities, and n_i the impurity concentration. Superscripts null denote destruction frequency in pure helium, n_e' is the additional number of electrons in the afterglow as a result of addition of the impurity. It will be shown that this may not be negligible. A corresponding term could also be added to (2′) but since the singlet lifetimes are very short compared to triplet lifetimes and since only relative concentrations are of concern, such a term would not enter the following analysis. From Eq. (2′), it can be seen that

$$\ln(T/T_0)=-(\nu_T{}^0+\langle\sigma_T V\rangle n_i)t,$$

so that the change in slope of a log concentration vs time curve due to addition of impurity yields directly the quantity $\langle\sigma_T V\rangle n_i$, from which a velocity-averaged cross section σ_T is calculated. (The gas temperature in the cell is not measurably increased by the pulsed discharge.) The singlet destruction cross sections have been similarly calculated utilizing Eq. (1′), neglecting n_e', the additional electron density due to the addition of impurity gas. The estimated validity of this assumption is discussed in detail below.

In pure helium the measured threebody coefficient 0.31 ± 0.03 agrees well with Phelps[2] value 0.26 ± 0.03 sec^{-1} mm^{-2}. The diffusion coefficient $D_T=560(\pm50)$ cm^2/sec is larger than Phelps' value 470 ± 25 cm^2/sec. We suspect that our diffusion may not be in the pure fundamental mode, therefore, indicating a larger diffusion rate by admixture of second diffusion mode even though the log concentration-time curves do not exhibit significant deviations from linearity. Since this loss mechanism is not variable with impurity concentration, it does not affect the impurity cross-section determinations. A different electrode arrangement is being built in an attempt to remove this effect. The circular wire electrodes herein used had an unfortunate similarity to the second diffusion mode configuration. The cylindrical cell had an i.d. of 4.66 cm, length 9.64 cm with electrodes of 3.80-cm diam spaced 7.00 cm apart, giving a squared diffusion length $\lambda^2=0.857$ cm^2. Measurements were made at 10 mm Hg pressure which gave the minimum triplet destruction frequency in pure helium, 95.3 sec^{-1}. This is the pressure at which diffusion loss just balances volume destruction for this size cell and is, therefore, insensitive to slight variations in helium gas pressure and most sensitive to destruction frequency changes by impurity effects. Using Phelps values for the constants in Eq. 1, observed singlet destruction for pure helium corresponds to an electron concentration of $\sim3\times10^9$ cm^{-3}. Phelps found n_e to vary by less than 20% during the singlet decay. The electron concentration can be varied by varying discharge pulse conditions which gives a variation in ν_S, while ν_T does not so vary, in agreement with Phelps observation. Figure 4 shows a typical 3889-Å absorption curve with and without impurity. Table I gives the experimental results and other known experimental cross sections.

TABLE I. Helium metastable destruction cross sections.

Gas	Ionization potential (eV)	σ_{Ti} (10^{-16} cm^2)	Other reported values				σ_{Si} (10^{-16} cm^2)		σ_i [f]
Ar	15.76	6.6	3.8[a]	0.9[b]	$\sim$10[c]	0.3[d]	55	12[a]	6.6[g]
Kr	14.00	10.3					64		16.5
Xe	12.13	13.9			$\sim$10[c]		103		20.2
N_2	15.51	6.4			$\sim$10[c] ( )				6.1
H_2	15.6	6.0							1.7
Ne	21.56	0.28	0.37[e]	0.22[a]			4.10		
CO_2									14.5
C_2H_4									13.1

[a] A. V. Phelps, Westinghouse Research Laboratories Scientific Paper 6-94439-6-P3, 1957 (unpublished).
[b] M. A. Biondi, Phys. Rev. **88**, 660 (1953).
[c] F. D. Colegrove and P. A. Franken, Phys. Rev. **119**, 680 (1960).
[d] A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1202 (1953).
[e] A. Javan, W. R. Bennett, Jr., and D. R. Herriott, Phys. Rev. Letters **6**, 106 (1961).
[f] W. P. Jesse and J. Sadauskis, Phys. Rev. **100**, 1755 (1955).
[g] Since Jesse and Sadauskis give only relative cross sections, these data are all relative to our argon cross section.

An approximate calculation of metastable densities indicated that 1% absorption of 3889 Å corresponded to about 4×10^9 triplets/cm^3 and 1% absorption of 5016 Å corresponded to about 1.4×10^9 singlets/cm^3. The maximum metastable concentrations in the measureable afterglow then were each around 5×10^9/cm^3.

In the case of Ne, the Ne emission spectrum could be observed for as long as 30 msec as shown in Fig. 5 and yielded the same slope at late times as the 3889 Å absorption, indicating one Ne photon emitted per He($2\,^3S$) destroyed (or at least a constant ratio).

Only in the case of neon is a reliable He($2\,^1S$)-impurity destruction cross section deduced from the measured destruction frequency. This is because the mechanism of singlet loss frequency due to superelastic collisions with electrons is of comparable magnitude to the other terms in Eq. (1) and the electron concentration in the afterglow may be strongly perturbed by the ionizations by metastables. An estimate of additional ionization caused by metastable destruction before the singlet lifetime is measured can be made as follows:

$$dn_e'/dt \cong \sigma(n_T+n_S)\bar{V}n_i$$

or

$$\delta n_e'/n_i \cong 10^{-15}\times(10^{10})\times10^5\times\delta t \cong \delta t/\mathrm{sec};$$

for $\delta t \sim 100\,\mu$sec, the approximate time before singlet lifetime measurements are made,

$$\delta n_e'/n_i \cong 10^{-4}.$$

For $n_i=10^{12}$/cc, $\delta n_e' \approx 10^8$ cm^{-3}. An impurity $\sim10^{12}$/cc increases the destruction frequency of singlets by ~1000 sec^{-1}. Using Phelps' β in Eq. (1), 10^8 electrons/cc gives a change in destruction frequency $3.5\times10^{-7}\times10^8 \approx 35$ sec^{-1}. If this estimate is seriously low then the singlet cross sections may be substantially smaller than given in Table I. Another experimental approach is being undertaken in an attempt to eliminate this uncertainty.

An analysis of the cross sections reported in this paper in terms of a simple kinetic theory model, suggested by the relative insensitivity of the cross sections to the particular impurity involved, is given in the following paper.[5]

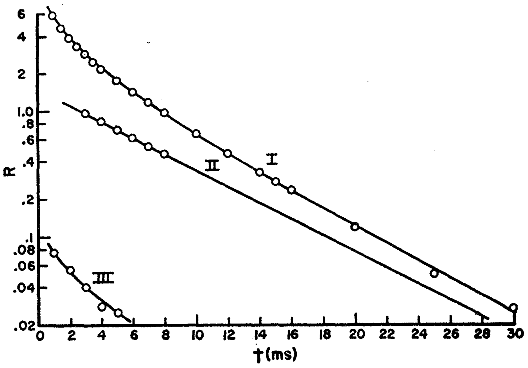

FIG. 5. Comparison of neon emission and He($2\,^3S$) absorption. Curve I, neon emission (arbitrary units) vs time; curve II, fractional absorption (R) of 3889Å by He($2\,^3S$) vs time; curve III, 3889Å emission (arbitrary units) vs time.

Our attention has been called to the work of Jesse and Sadauskis[6] on ionization by alpha particles in mixtures of gases. They interpreted their results in terms of relative cross sections and compared with Biondi's helium triplet-argon cross section, now known to be too low. A renormalization of their data to our argon Penning cross section for the triplet helium metastable has been included in Table I. Their cross sections show remarkably good agreement with the triplet cross sections in Table I although they were presumably measuring largely singlet metastable cross sections according to their own view. It may very well be that the ratio of singlet to triplet cross sections for various impurity gases will turn out to be essentially constant, however, definitive statements concerning singlet cross sections certainly must await improved measurements. The process of ionization in relatively high-pressure gas mixtures analyzed by Jesse and Sadauskis is, of course, extremely complicated, involving uncertainties in ratios of singlet and triplet metastables, molecule formation, and other processes. In view of the reasonable agreement of the data of Jesse and Sadauskis, one might expect that their Penning cross sections for helium triplets with CO_2 and C_2H_4, suitably normalized in Table I, are reasonably reliable.

Note added in proof. Since completion of this work, it has been learned that Penning cross sections have been measured in an atomic-beam experiment [W. P. Sholette and E. E. Muschlitz, Jr., J. Chem. Phys. (to be published)]. The triplet helium metastable Penning cross sections for Ar, Kr, Xe, and N_2 agree with those reported here within 15%. The H_2 cross section reported by Sholette and Muschlitz is only 43% of the value reported in this paper. Sholette and Muschlitz are also able to measure destruction cross sections in O_2 and CO. In every case except H_2, Sholette and Muschlitz find the helium singlet metastable Penning cross section to be equal to the triplet cross section, whereas we find the singlet cross section to be substantially larger. We can offer no explanation of this difference at present, however, in view of the considerably less metastability of the singlet it would be very surprising if the singlet cross sections were not larger.

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[5] Eldon E. Ferguson, following paper [Phys. Rev. **127**, 210 (1962)].

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