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Absorption Studies of Helium Metastable Atoms and Molecules

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The lifetimes of the metastable states of the helium atom and molecule in pure helium have been determined by using a time-sampling technique for the measurement of the time-varying optical absorption caused by the various metastables. The measured loss of helium singlet metastable atoms indicates destruction after diffusion to the wall, upon collisions with single atoms, and by conversion into triplet metastable atoms in collisions with thermal electrons. The triplet metastable atoms are destroyed upon diffusion and by collisions with two neutral atoms which result in the formation of molecules in the $2^3\Sigma_u{}^+$ state. These molecules have a natural lifetime of at least 0.05 second and are destroyed upon diffusion to the wall and by collisions with slow electrons or other metastables. The product of the diffusion coefficient and the helium atom density at 300°K is 1.5×10^{19} (cm^2/sec)(atom/cc) for the atomic metastables and 1.0×10^{19} (cm^2/sec)(atom/cc) for the molecular metastable. The cross sections for the destruction of the singlet atomic metastables are 3×10^{-14} cm^2 and 3×10^{-20} cm^2 for collisions with thermal (300°K) electrons and neutral atoms, respectively. The three-body combination coefficient for the conversion of triplet atomic metastables into molecular metastables is 2.5×10^{-34} cc^2 atom^{-2} sec^{-1} at 300°K.

I. INTRODUCTION

THE processes which determine the rates of destruction of helium metastable atoms in helium were originally studied by Ebbinghaus[1] and have been recently re-examined by Biondi[2] and by Phelps and Molnar.[3] In the latter paper, it is shown that the pressure and temperature variation of the lifetime of helium atoms in the triplet metastable state ($1s\ 2s\ {}^3S_1$) is consistent with the proposal that the metastables are destroyed upon diffusion to the wall of the absorption cell and by collisions with two neutral atoms. It was found that the rate of destruction of helium atoms in the singlet metastable state ($1s\ 2s\ {}^1S_0$) is strongly dependent upon the intensity of the pulsed discharge used to create the metastables. Recently, we have applied time sampling techniques to the measurement of the time-varying optical absorption[4] caused by the metastables and have obtained an increase in sensitivity of roughly two orders of magnitude. The purpose of the experiments described in this paper was to determine the collision processes responsible for the destruction of and conversion between the various metastable states from studies of the time variation of density of the metastables using the improved techniques. Except where otherwise indicated, the destruction of metastables as a result of collisions between pairs of metastables[2] will be assumed to be negligible. Quantitative studies of this process have proved to be quite difficult, but it is hoped that the results can be presented in a latter paper.

II. EXPERIMENT

The ac time sampling technique for the measurement of time-varying optical absorption is described in detail in reference 4. We will give a brief description of the principles of this technique using the block diagram of the apparatus shown in Fig. 1 and the wave forms shown in Fig. 2. The metastable atoms are created by periodically applying a short high-voltage pulse to the electrodes of the absorption cell so as to produce a discharge, Fig. 1(a). The metastables are detected by measuring the absorption of radiation emitted in transitions which terminate on the metastable state of the atom or molecule. The radiation is obtained from a helium source[5] and is collimated and passed through the absorption cell. The desired radiation is separated from the remainder of the helium spectrum by means of an interference filter and focused on the cathode of a photomultiplier. Corresponding to the changes in the metastable density, Fig. 2(b), there are changes in the number of photoelectrons produced at the cathode of the photomultiplier as shown by the dotted curve of Fig. 2(c). If the photoelectric current were amplified and presented on an oscilloscope, the technique described so far would be essentially the same as that used in recent studies.[3] The minimum measurable absorption is limited by the statistical fluctuations or "shot noise" in the number of photoelectrons leaving the photomultiplier cathode. While this noise can be reduced by decreasing the bandwidth of the oscilloscope amplifier, one is limited to a value determined by the bandwidth required to transmit the changing absorption signal. One solution to this problem is to operate the optical system for only a small portion of the afterglow and to average the resultant absorption signal over many cycles of the discharge. Such a time sampling system makes possible a large reduction in the band width of the detector and a consequent reduction in the shot

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[1] E. Ebbinghaus, Ann. Physik **7**, 267 (1930).

[2] M. A. Biondi, Phys. Rev. **82**, 543 (1951) and **88**, 660 (1952).

[3] A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1203 (1953).

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

[5] The radiation source used in these experiments was either a hot-cathode capillary discharge tube (reference 3) filled with helium to a pressure of 8 mm Hg or the "abnormal" cathode glow of a cold-cathode discharge tube filled to 20 mm. The capillary source emitted only atomic lines while the cold-cathode source emitted approximately equal intensities of atomic and molecular radiation.

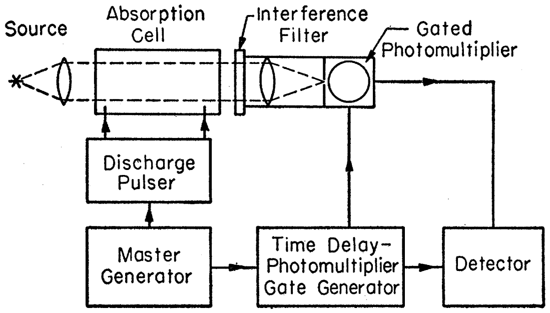

FIG. 1. Schematic of ac time-sampling apparatus for the measurement of time-varying optical absorption. The discharge pulser operates on alternate pulses from the master generator. The pulses from the master generator are delayed by a variable time-delay unit and then supplied to the photomultiplier gate generator and the synchronous rectifier of the detector unit.

noise without sacrificing the ability of the system to resolve changes in the absorption signal.[6] A simple system for "gating" the optical system is to use a continuous source and to apply a short high-voltage pulse to the dynodes of the photomultiplier.

We are now faced with the problem of measuring the small changes in photomultiplier current which are theoretically observable with the time-sampling techniques. One possibility is to "balance out" the signal corresponding to zero absorption either with the output of a second photomultiplier or with a dc signal.[6] A much more convenient technique is to gate the photomultiplier at twice the discharge frequency as shown by the solid curve of Fig. 2(c). Under these conditions, the current pulse immediately following the discharge is reduced as a result of the absorption by an amount large compared to that of the pulse occurring late in the afterglow. The fundamental component of this current waveform, Fig. 2(d), is directly proportional to the difference between the pulse heights and is separated from the undesired signal by means of a narrow-band amplifier and synchronous detector operating at a frequency equal to the repetition rate of the discharge. The variation of the amplitude of this ac signal with the time, t, between the discharge pulse and the first photomultiplier gate gives directly the time variation of the absorption caused by the metastables. The absolute fractional absorption can be obtained by making measurements under conditions in which the absorption is sufficient to cause observable changes in the average photomultiplier current.

The ac time-sampling technique described above provides a hundred-fold increase in sensitivity over methods which do not make use of time-sampling. This increased sensitivity makes it possible to make measurements at average metastable densities which are at least an order of magnitude lower than those previously studied.[3] Under these conditions, the measured absorption can be shown to be directly proportional to the metastable density so that the previous uncertainties as to the correction for nonlinear absorption are eliminated.[7] Measurements at lower metastable densities reduce the destruction of metastables due to collisions with electrons and other metastables. In addition, the increased sensitivity makes possible measurements of the absorption by metastables having low effective absorption coefficients, e.g., the helium metastable molecule.

The electron density present during the decay of the helium singlet metastables was calculated from measurements of the shift in the resonant frequency of a microwave cavity surrounding the absorption cell.[8] The arrangement of the microwave apparatus was the same as that described by Biondi[9] except that the discharge was initiated with a high-voltage pulse rather than with a pulse of microwave power from a magnetron. The vacuum system used in these experiments is typical of those used in this laboratory.[10] The ultimate pressure was 10^{-9} mm Hg or less, and the rate of rise of pressure in the isolated system was 10^{-9} mm Hg/min or less. The gas samples used to obtain the lifetimes of the atomic metastables were "reagent grade" helium obtained from Air Reduction Sales Company. Studies of the effect of known concentrations of neon on the lifetime of the molecular metastable showed that these samples contained neon concentrations of the order of two parts in 10^5. The neon was not removed by the pulsed discharge, as were small concentrations of other impurities, such as argon. The final studies of the molecular metastables were made with helium samples ob-

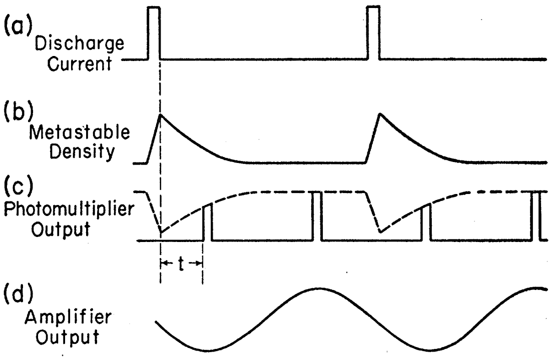

FIG. 2. Wave forms for ac time-sampling technique for the measurement of time-varying optical absorption.

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[6] The original experimental arrangements of Meissner and others were of this class by virtue of the use of a pulsed source of radiation. See reference 7. Apparently they were unable to reach the limit of sensitivity set by shot noise because of the difficulties in the measurement of small changes in intensity with photographic plates and the fluctuations in the source intensity under pulsed operation. D. J. Eckl, Can. J. Phys. **31**, 804 (1953) has overcome these particular difficulties by using two photomultipliers as detectors. One photomultiplier is used to "balance out" the signal due to the unabsorbed light.

[7] A. C. G. Mitchell and M. K. Zemansky, *Resonance Radiation and Excited Atoms* (University Press, Cambridge, 1934), Chap. IV.

[8] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[9] M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).

[10] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

tained by a careful evaporation of liquid helium. These samples contained less than two parts in 10^7 of neon.

All of the data presented in this paper were obtained at room temperature, i.e., 300±5°K. If we make the extreme assumption that all of the discharge energy appears as heat in the volume of the gas, the calculated temperature rise at the end of the discharge pulse is about 5°C for a helium pressure of one mm Hg and proportionately less at higher pressures.[3,11] Experimentally, there was no observable rise in the temperature of the absorption cell wall. Measurements of the metastable absorption as a function of the intensity of the source showed that the destruction of metastables as a result of excitation to radiating states was negligible.

III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

The experimental results will be presented in the order of decreasing energy of the metastable state involved. Such a presentation allows a more natural discussion of the conversion of one metastable state into another. Thus, Fig. 3 shows that the decay in the absorption of the 5016 A line by the 2^1S metastables is accompanied by an increase in the absorption of the 3889 A line by 2^3S metastables. This observation suggests that atoms in the 2^1S state are being converted into atoms in the 2^3S state. Studies of the decay of the 2^1S density, to be discussed below, show that under the conditions of this experiment the rate of 2^1S destruction is determined by the density of electrons present during the afterglow. Accordingly, we propose that the metastables are converted according to the reaction

$$\mathrm{He}(2^1S)+e\rightarrow\mathrm{He}(2^3S)+e+0.79\text{ ev}.$$

This qualitative picture leads us to consider solutions to the differential equations governing the metastable behavior. It is assumed that the decay 2^1S metastable density, S, is determined by their loss due to diffusion, to collisions with neutral atoms, and collisions with thermal electrons. The differential equation expressing this is

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

where D_S is the diffusion coefficient for the 2^1S metastables, $\nu(N)$ is the frequency of destruction of the 2^1S metastables as a result of collisions with neutral atoms, N, and β is the frequency per electron for the conversion of 2^1S metastables into 2^3S metastables by thermal electrons of density, n.

If we assume that the 2^1S density is distributed in the fundamental diffusion mode and that the time and spatial variation of the electron density can be neglected, the solution to Eq. (1) is

$$S=S_0e^{-\nu_St}, \tag{2}$$

where

$$\nu_S=D_S/\Lambda^2+\nu(N)+\beta n \tag{3}$$

and Λ is the diffusion length[12] for the absorption cell. The assumption that the electron density is essentially constant during the 2^1S decay is shown to be valid by simultaneous microwave measurements of the time variation of the electron density. The electron density is found to change by less than 20 percent. An analytical solution of Eq. (1) for a cosinusoidal spatial distribution of the electrons can be obtained for the one dimensional case in terms of Mathieu functions. This investigation shows that the cross section calculated from the central electron density is low by about 20 percent. Accordingly, the corrected value of β from the plot of ν_S *vs* n in Fig. 4 will be taken as 3.5×10^{-7} cc/electron-sec and corresponds to an average cross section for 300°K electrons of 3.0×10^{-14} cm^2. Since the collision which converts a 2^1S metastable into a 2^3S metastable is an exchange collision, the principal contribution to the cross section at low electron energies is expected to be due to electrons with zero angular momentum.[13] In this case theory shows that the maximum allowable cross section for conversion by thermal electrons is 4×10^{-14} cm^2.

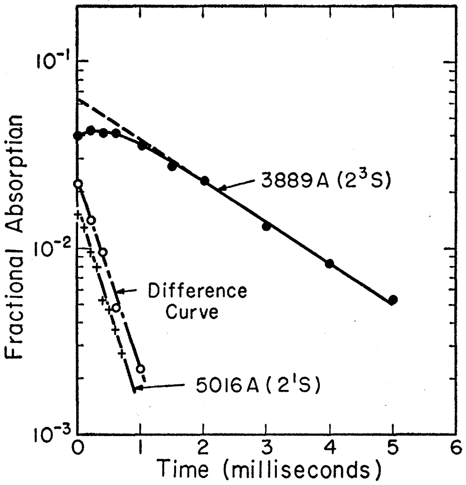

FIG. 3. Time variation of absorption of 5016 A and 3889 A lines by helium singlet (2^1S) and triplet (2^3S) metastables for a pressure of 1.5 mm Hg and $\Lambda^2=0.053$ cm^2. The initial triplet metastable density was approximately 10^{11} metastables/cc.

The differential equation governing the triplet metastable density, T, is

$$\partial T/\partial t=D_T\nabla^2T-AN^2T+\beta nS, \tag{4}$$

where D_T is the diffusion coefficient for the 2^3S metastables and AN^2 is the frequency for the destruction of the 2^3S metastables in collision with two neutral atoms.[3] The solution to Eq. (4) under the assumption of a spatial distribution given by the fundamental diffusion

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[11] E. H. S. Burhop, Proc. Phys. Soc. (London) **A67**, 276 (1954).

[12] The diffusion length, Λ, for a cylindrical absorption cell is given by $1/\Lambda^2=(\pi/L)^2+(2.4/R)^2$, where L and R are the length and radius of the cylinder.

[13] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), Chap. III.

mode and using Eq. (2) is

$$T=(T_0+T_S)e^{-\nu_T t}-T_S e^{-\nu_S t}, \tag{5}$$

where

$$\nu_T=D_T/\Lambda^2+AN^2 \tag{6}$$

and

$$T_S=\beta n S_0(\nu_S-\nu_T)^{-1}.$$

Equation (5) shows that the time variation of the 2^3S metastable density is given by the difference between two exponentials. This means that a straight line fitted to a semilogarithmic plot of the 3889 A absorption data at late times will have a slope of ν_T so long as $\nu_S>\nu_T$. The difference between this straight line and the measured curve should give a straight line whose slope is ν_S, i.e., it should be parallel to the 2^1S decay curve. Figure 3 shows that this is indeed the case. Furthermore, when the measured absorption values for the 2^1S metastables are multiplied by the ratio of the theoretical absorption coefficients,[14] as has been done in Fig. 3, the difference density curves agree in magnitude with predictions of Eq. (5) to within 20 percent.

In principle, the pressure variation of the destruction frequency for the 2^1S metastable can be determined by extrapolating the data given in Fig. 4 to zero electron density. However, at the lower electron densities the scatter in the data is usually large enough to obscure small variations in ν_S with pressure. So far, the only usable data on the pressure variation of ν_S was obtained by adding a low-voltage (<1000 volts) pulse lasting for about one millisecond to the breakdown spark in such a way as to terminate the discharge with a very low current and electron density but with a measurable metastable density.[15] Figure 5 shows the pressure variation of ν_S when taken under conditions such that the electron density was less than 10^8 electron/cc. The smooth curve is fitted to the data on the assumption that 2^1S metastables are destroyed by diffusion and by collisions with single neutral helium atoms. Within the accuracy of this data, the diffusion coefficient agrees with that obtained for the 2^3S metastable and is $D_S=440\pm50$ cm²/sec at 1 mm or $D_SN=1.4\pm0.2\times10^{19}$ (cm²/sec)(atom/cc) at 300°K. The average cross section for the volume destruction of the 2^1S metastables is 3×10^{-20} cm². This value agrees with rough estimates of the cross section expected for the destruction of metastables by collision induced radiative transitions.[2,16] Measurements of the absorption by 2^3S metastables under these conditions failed to show the buildup at early times which would be expected if the collision of a 2^1S metastable with a neutral atom resulted in the formation of a 2^3S metastable.

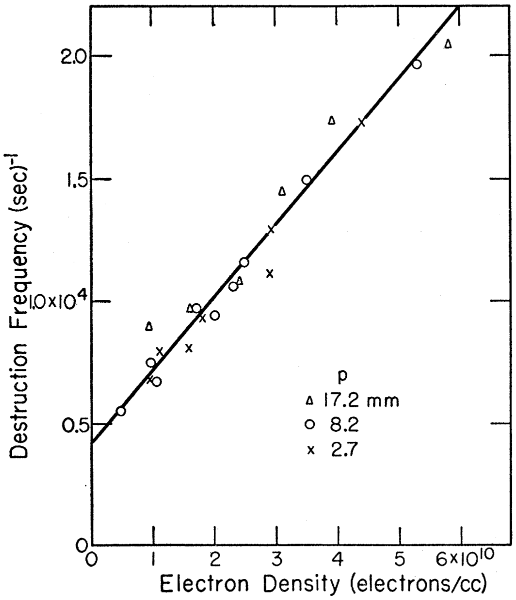

FIG. 4. Measured destruction frequency for helium singlet metastables as a function of the central electron density at various pressures and 300°K. $\Lambda^2=0.053$ cm².

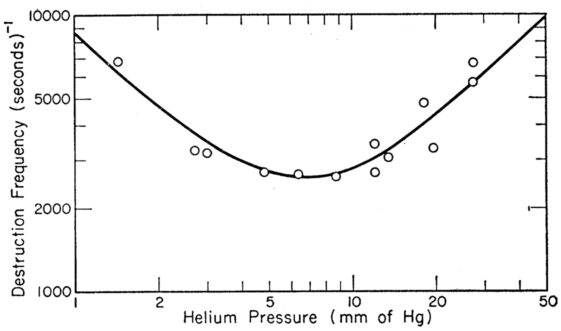

FIG. 5. Measured destruction frequency for helium singlet metastables as a function of helium pressure at 300°K under conditions of negligible electron density. $\Lambda^2=0.053$ cm².

The pressure variation of the destruction frequency for the 2^3S metastable for two absorption cells is shown in Fig. 6. The smooth curves represent fits to the experimental data of Eq. (6) using a single diffusion coefficient. The diffusion coefficient for the 2^3S metastables at 300°K is 470 ± 25 cm²/sec at 1 mm of $D_TN=1.51\pm0.08\times10^{19}$ (cm²/sec)(atom/cc). The value for the three-body combination coefficient is $A=0.26\pm0.03$ sec^{-1} mm^{-2} $=2.5\times10^{-34}$ cc² atom^{-2} sec^{-1} at 300°K. These coefficients are at the upper limit of the experimental error estimated for the previous results.[3] The difference may result from the presence of nonlinear absorption

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[14] D. R. Bates and A. Damgaard, Trans. Roy. Soc. (London) **A242,** 101 (1949).

[15] Calculations of the energy dissipated by the discharge show that the maximum temperature rise in the gas due to this pulse is about equal to that for the breakdown pulse.

[16] The destruction of 2^1S metastables by collision induced radiation was proposed by J. L. Nikerson, Phys. Rev. **47,** 707 (1935), in order to explain the presence of a band of continuous radiation near 600 A. The presence of a sharp band edge at a wave number 385 cm^{-1} larger than that of the 602 A forbidden line was interpreted as indicating the existence of a maximum in the difference in the potential energy curves for the $2^1\Sigma$ and $1^1\Sigma$ states. Such **a** maximum is predicted from theory in reference 17.

resulting from the relatively large metastable densities required with the less-sensitive techniques used in the earlier work. The small increase in the experimental points above the smooth curve at intermediate pressures is believed to be due to small amounts of neon present in the helium samples used but, in some cases, may indicate a small loss due to collisions of metastables with other metastables or slow electrons. The experimental value for the 2^3S diffusion coefficient is in good agreement with the value of $D_TN=1.29\times10^{19}$ (cm²/sec) (atom/cc) at 300°K calculated from the theoretical diffusion cross section data given by Buckingham and Dalgarno.[17] Although these diffusion measurements are not a very sensitive means for observing the effects of the reflection of metastables from the walls, the fit of the low pressure data to an inverse pressure dependence suggests the reflection coefficient for the metastables at the glass walls is less than 20 percent.[18] The combination coefficient for the three-body collisions is considerably lower than the corresponding coefficients for similar three-body reactions such as the destruction of argon[3] and mercury[18] metastables. As pointed out previously,[3,11] this low value is consistent with the existence of a long-range repulsive interaction such as that calculated[17] for the metastable states of the helium molecule.

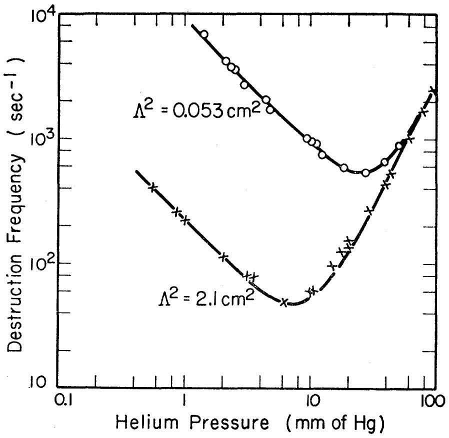

FIG. 6. Measured destruction frequency for helium triplet metastables as a function of helium pressure at 300°K for absorption cells with $\Lambda^2=0.053$ and $\Lambda^2=2.1$ cm².

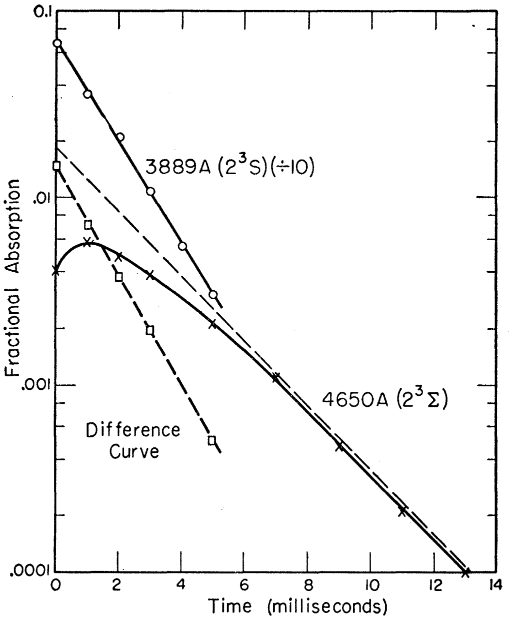

FIG. 7. Time variation of absorption of 3889 A line and 4650 A band by helium triplet atomic (2^3S) and molecular metastables ($2^3\Sigma$) at 300°K for $\Lambda^2=0.050$ cm² and a helium pressure of 16 mm Hg. The initial 2^3S density was approximately 1.5×10^{11} metastables/cc. The measured values of the 3889 A absorption have been increased by a factor of 2.8 in order to correct for an apparent partial reversal of the 3889 A line by the cold-cathode cource.

The loss of the 2^3S metastables in three-body collisions with neutral helium atoms suggests that the process results in the formation of an excited triatomic molecule which may radiate before dissociation, dissociate into the neutral atoms, or form a vibrationally stable diatomic molecule by giving up sufficient kinetic energy to one of the neutral atoms. In the latter case, the potential energy curves calculated by Buckingham and Dalgarno[17] for the $2s\sigma\ ^3\Sigma_u^+$ and $2s\sigma\ ^1\Sigma_u^+$ states indicate that the diatomic molecule should be formed in a high vibrational level of the $2^3\Sigma$ state. If the selection rule forbidding intercombination radiation is sufficiently well obeyed[19,20] the $2^3\Sigma$ molecules will give up their vibrational energy to neutral atoms and reach the lowest vibrational level where they may be detected by measuring the absorption of the 4650 A band of the $3^3\Pi_g\rightarrow2^3\Sigma_u$ system.[21]

The solid curves of Fig. 7 show the measured fractional absorption for the 3889 A line and the 4650 A band at a pressure of 16 mm in an absorption cell with $\Lambda^2=0.050$ cm². These curves are interpreted as showing that as the 2^3S metastables are destroyed there is a buildup in the concentration of the $2^3\Sigma$ metastables as a result of the reaction $\mathrm{He}(2^3S)+2\mathrm{He}\rightarrow\mathrm{He}_2(2^3\Sigma)+\mathrm{He}$. We propose that under the conditions of this experiment the $2^3\Sigma$ metastables are destroyed upon diffusion to the

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[17] R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) **A213**, 327 and 506 (1952).

[18] A. O. McCoubrey, Phys. Rev. **93**, 1249 (1954).

[19] R. Meyerott, Phys. Rev. **90**, 671 (1949). This paper is one of many which give evidence for the existence of a metastable helium molecule. However, the potential energy curve obtained for the ground state of the helium molecule is very difficult to reconcile with the potential energy curve obtained from theory and atomic beam experiments. See, e.g., I. Amdur, J. Chem. Phys. **17**, 844 (1949).

[20] The potential energy curve crossing proposed in reference 11 seems unlikely in view of the failure of the calculated curves to cross (reference 17, p. 338) and the fact that the lowest vibrational level of the $2^1\Sigma$ state is known to be higher than that of the $2^3\Sigma$ state by 0.29 electron volt (reference 21).

[21] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 536. G. H. Dicke and E. S. Robinson, Phys. Rev. **80**, 1 (1950).

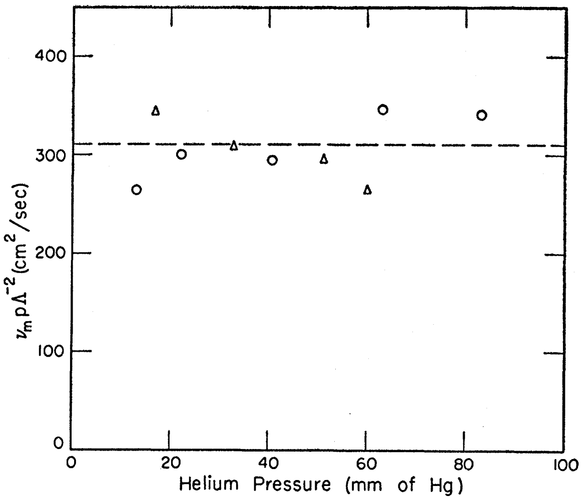

FIG. 8. $\nu_M p\Lambda^{-2}$ for $2^3\Sigma$ metastables as a function of helium pressure for $\Lambda^2=0.050$ cm^2(Δ) and $\Lambda^2=0.015$ cm^2(0). Since $\nu_M p\Lambda^{-2}=D_M p$, its average value (dotted line) is the diffusion coefficient at 1 mm and 300°K. The large scatter in the data is indicative of the difficulties in making measurements at sufficiently low densities to avoid the effects of collisions with slow electrons or other metastables.

wall of the absorption cell. The differential equation governing the time variation of the $2^3\Sigma$ density, M, is

$$\partial M/\partial t=D_M\nabla^2M+AN^2T, \tag{7}$$

where D_M is the diffusion coefficient for the $2^3\Sigma$ metastables. Because of the relatively long times and high pressures involved in the studies of the $2^3\Sigma$ buildup we have neglected the time required to dissipate the vibrational excitation energy. One can also neglect the second term in the solution for the 2^3S density given Eq. (5). If we assume a fundamental diffusion mode, the solution to Eq. (7) is

$$M=(M_0+M_T)e^{-\nu_M T}-M_T e^{-\nu_T t}, \tag{8}$$

where

$$\nu_M=D_M/\Lambda^2 \quad \text{and} \quad M_T=AN^2(T_0+T_S)(\nu_T-\nu_M)^{-1}.$$

Equation (8) shows that a straight line fitted to a semilogarithmic plot of the $2^3\Sigma$ absorption data at late times will have a slope equal to ν_M. In addition, the difference between this straight line and the measured curve should be a straight line with the same slope as the 2^3S decay curve, i.e., the difference curve and the 2^3S curve should be parallel. Figure 7 shows that this is indeed the case. The curves can be made to agree in magnitude with theory provided that the ratio of the integrated absorption coefficient for the 3889 A line is 15 times the average absorption coefficient for the 4650 A band.* This ratio contains a factor of 10 to 15 for the ratio of the integrated to average absorption coefficient for the 4650 A band resulting from the distribution of the emission and absorption over a number of transitions involving the various rotational levels of the molecule.[21] In view of our lack of knowledge of the relative values for the integrated absorption coefficients and the uncertainties involved in correcting the measured fractional absorption values for differences in line breadth and fine structure, we conclude that the experimental results are consistent with our hypothesis of complete conversion of the 2^3S metastables to $2^3\Sigma$ metastables in three-body collisions.

Figure 8 shows the results of a series of measurements of the destruction frequency for the $2^3\Sigma$ metastables as a function of pressure in absorption cells with $\Lambda^2=0.050$ cm^2 and 0.015 cm^2. The dashed curve is fitted to the data on the assumption that the metastables are lost by diffusion with a negligible volume loss. The diffusion coefficient obtained from these experiments at 300°K is $D_M=310\pm50$ cm^2/sec at 1 mm or $D_MN=1.0\pm0.2\times10^{19}$ (cm^2/sec)(atom/cc). In order to enhance any volume destruction which might be present, the time variation of the $2^3\Sigma$ density was measured in an absorption cell with $\Lambda^2=2.1$ cm^2 at pressures up to 97 mm. Since Fig. 9 shows that the final decay of the absorption is not exponential with time, it appears that the $2^3\Sigma$ metastables are being destoryed by collisions with slow electrons or other metastables. The expected contribution of diffusion to the destruction frequency is 1.5 sec^{-1}, so that the destruction frequency of 23 sec^{-1} indicated by the final slope of the $2^3\Sigma$ decay sets an upper limit to the volume destruction which is one hundred times lower than the volume destruction of the 2^3S metastables. This result and similar data at lower pressures show that the natural lifetime of the $2^3\Sigma$ metastable state is at least 0.05 sec.

IV. SUMMARY AND DISCUSSION

The results of the measurements of the destruction frequency for the metastable states of helium are summarized in Table I. The agreement between the theoretical and experimental diffusion coefficients for the triplet atomic metastable is as good as can be expected in view of the uncertainties in the energy of interaction for the $2^3\Sigma$ state. Because of the similarities in the in-

TABLE I. Diffusion coefficients and volume loss at 300°K.

Metastable state	Diffusion coefficients at 300°K (DN in (cm^2/sec) (atoms/cc))	Volume loss at 300°K
2^1S	1.4×10^{19}	linear: $\langle\sigma v\rangle_{\text{Av}}=6\times10^{-15}$ cc atom^{-1} sec^{-1}
2^3S	$1.151\pm0.08\times10^{19}$	quadratic: $A=(2.5\pm0.3)\times10^{-34}$ cc^2 atom^{-2} sec^{-1}
$2^3\Sigma$	$1.0\pm0.2\times10^{19}$	natural lifetime>0.05 sec

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* *Note added in proof.*—An interferometric study by L. S. Frost shows that the effective temperature of the cold-cathode source is essentially the same as that of the capillary source. This means that the correction factor for the 3889 A absorption in Fig. 7 should have been 1.8 instead of 2.8. The ratio of the integrated absorption coefficient for the 3889 A line to the average absorption coefficient for the 4650 A band is then 10 instead of 15.

teraction curves for the $2^1\Sigma$ and $2^3\Sigma$ states, it is not surprising that their diffusion coefficients are equal to within the experimental error. The indication that the diffusion coefficient for the metastable molecule is smaller than that for the metastable atom is reasonable in view of the larger size of the molecule and the fact the effects of excitation transfer on the diffusion cross section are small.[17]

If the two-body collision destruction of the 2^1S metastables is the result of collision-induced radiation, and if the height of the interaction energy curve is as large as calculated by Buckingham and Dalgarno,[17] then the cross section indicated by our data is surprisingly large. Rough estimates of the probability for collision-induced radiation[2] give cross sections of the order of the observed value only in the absence of a significant repulsive interaction. If the interaction energy for the $2^1\Sigma$ state follows the calculated curve, only one in 10^4 of the thermal collisions could result in an approach to distances of the order of five atomic units where an appreciable radiative transition probability might be expected. This difficulty would not be present if the height of the potential maximum were of the order of that suggested by Nickerson.[16] It should be possible to determine the "activation" energy involved in this process by measuring the variation in the average cross section with the gas temperature.

The low value for the three-body combination coefficient for the conversion of 2^3S metastables into $2^3\Sigma$ metastables as compared to the values for mercury[18] and argon[3] appears to de due to a repulsive interaction for the 2^3S atom and two neutral atoms similar to that found for the $2^3\Sigma$ and $2^1\Sigma$ states of the diatomic molecule. However, there is no reliable theory available for the calculation of three-body combination coefficients. The agreement between the experimental value and the estimates based on the Thompson "recombination" theory[11] and the calculated $2^3\Sigma$ interaction would appear to be fortuitous since the approach of the third helium atom may have a strong effect on the interaction energy of the system. The absence of an appreciable three-body destruction for the $2^3\Sigma$ metastable suggests that the three-body interaction is repulsive or, at most, weekly attractive. It is of interest to note that the process of the conversion of an atomic metastable into a diatomic molecular metastable, which we postulate on the basis of direct measurements of optical absorption by the metastables, has been proposed by McCoubrey to explain the production of band fluorescence in mercury[18] and by Colli to explain the time dependence of photoelectric current pulses in a coaxial discharge tube filled with argon.[22]

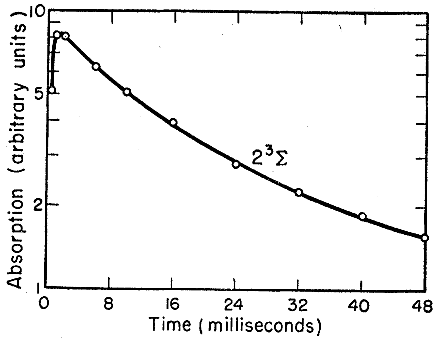

FIG. 9. Time variation of absorption by $2^3\Sigma$(4650 A) metastables for a helium pressure of 97 mm Hg and $\Lambda^2=2.1$ cm². The maximum $2^3\Sigma$ density was approximately 2×10^{10} metastables/cc.

The measurement of the cross section for the conversion of 2^1S metastables into 2^3S metastables by thermal electrons is probably the first measurement of a "superelastic" cross section for electrons of such low energy. In view of the approach of the experimental value to the possible theoretical maximum it would be very interesting to determine the variation of this cross section with electron energy. This could be done most easily by varying the temperature of the gas.

The author wishes to express his appreciation for many valuable discussions of these problems with his associates in the Atomic Physics Group. He is especially indebted to Mr. J. L. Pack for the design of the electronic components of the time-sampling apparatus.

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[22] L. Colli, Phys. Rev. **95**, 892 (1954).