

SELECTION RULES

The two comparative mechanisms, the magnetic quadrupole transition and the spin-orbit electric dipole transition have slightly different selection rules. For the case of $\Delta S = \pm 1$ transitions which we are interested in here the selection rules for the magnetic quadrupole transition are just like those of the electric dipole transition, or

$$\Delta L = 0, \pm 1, \text{ but } L = 0 \leftrightarrow 0; \text{ parity change, } (60)$$

while those for the spin-orbit electric dipole transition are

$$\Delta L = 0, \pm 1, \pm 2; \text{ parity change, } (61)$$

in the case of atoms with L - S coupling. Thus, for example, $^1S \leftrightarrow ^3S$ and $^2S \leftrightarrow ^4D$ transitions can only be explained by the spin-orbit electric dipole transition.

Transitions with parity no change cannot be explained by either of them, and we have to go to the magnetic octupole transition or the spin-orbit magnetic dipole transition. Their selection rules for $\Delta S = \pm 1$ transitions are

$$\Delta L = 0, \pm 1, \pm 2, \text{ but } L = 0 \leftrightarrow 0; \\ \text{parity no change for magnetic octupole, } (62)$$

$$\Delta L = 0, \pm 1, \pm 2; \text{ parity no change for} \\ \text{spin-orbit magnetic dipole. } (63)$$

Selection rules for molecules can be found by finding those for the electric dipole and the electric quadrupole transitions. The selection rules for the magnetic quadrupole and the magnetic octupole transitions are the same as those respectively. For the benzene molecule, for example, the lowest triplet state $^3B_{1u}$ is known to be able to go to the ground state $^1A_{1g}$ by the spin-orbit electric dipole transition^{5,6} but we see that the magnetic quadrupole transition is forbidden for this transition. In the case of the naphthalene and anthracene molecules, on the other hand, the lowest triplet state is assumed¹⁰ to be $^3B_{2u}$, and the magnetic quadrupole transition is allowed from this state to the ground state $^1A_{1g}$. The lowest triplet state of the benzene molecule is observed¹¹ to have the lifetime of more than 300 sec, while in most aromatic molecules the triplet lifetime is accepted to be about 1 sec. This may be explained by the above conclusion, since our analysis on the hydrogen molecule showed that the magnetic quadrupole transition must be more important than the spin-orbit electric dipole transition in the case of large molecules.

¹⁰ R. Pariser, J. Chem. Phys. **24**, 250 (1956).

¹¹ D. P. Craig, J. M. Hollas, and G. W. King, J. Chem. Phys. **29**, 974 (1958).

Absolute Electron Excitation Cross Sections of Helium*

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The absolute apparent electron excitation functions of helium have been measured for the 3^1S , 4^1S , 5^1S , 6^1S , 3^1P , 4^1P , 3^1D , 4^1D , 5^1D , 6^1D , 3^3S , 4^3S , 5^3S , 3^3P , 3^3D , 4^3D , 5^3D , and 6^3D states at pressures sufficiently low so that the effects of radiation imprisonment and collisional excitation transfer can be neglected. Corrections due to polarization of the radiation and the cascading from the upper excited states have been applied to the experimental data and the true excitation functions obtained. The peak values and the shape of these excitation functions are compared with the results reported from other laboratories. Generally good agreement is found with the previous works where the collisional excitation transfer was properly reduced and allowance was made for the cascading effect. The experimental cross sections show satisfactory agreement with the theoretical values calculated by the Born approximation for the 1S and 1P states at high-electron energies, but are about four times larger than the theoretical values for 1D states. In the case of the triplet series, the experimental cross sections exceed the calculated values by factors of ten to one hundred or more. It is concluded that the population of the triplet states is produced mainly by processes other than direct excitation.

I. INTRODUCTION

RECENT studies of electron excitation of helium atoms indicate that some of the atomic states may be populated to a large extent by collisional excitation transfer and cascading in addition to the usual electron-

impact excitation process.^{1,2} The excitation transfer and its concomitant effect on cascading may be reduced and even eliminated if measurements of the excitation are made with the helium gas at low pressure, i.e., about 1μ or less. Furthermore the populations of the 1P states are affected by imprisonment of resonance radiation at pressures above a few tenths of a micron and therefore

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¹ R. M. St. John and R. G. Fowler, Phys. Rev. **122**, 1813 (1961).

² C. C. Lin and R. M. St. John, Phys. Rev. **128**, 1749 (1962).

measurements on them should be made below that onset pressure in order that the imprisonment mechanism not obscure the electron-impact excitation process. Cascading effects cannot be entirely removed by reduction of the gas pressure as excitation of the upper levels goes on at all pressures. Thus, in the determination of the electron impact excitation cross section, considerable care must be exercised in subtracting from the total observed (apparent) cross section the contributions from the various other excitation mechanisms. Indeed, the effects of collisional transfer¹⁻³ and imprisonment are partly responsible for the disagreement of the electron-excitation cross sections reported in the early literature as well as the discrepancy between them and theoretical cross sections.

With the recent improved experimental techniques it is possible to work at pressures low enough to suppress the effect of excitation transfer when observing all but the weakest transitions. In this paper we shall present the apparent excitation functions of 18 excited states of helium measured at low pressure. The cross sections for direct electron excitation are then obtained after the application of a series of corrections. The results of several experimental investigations will be compared. Additionally comparison of these cross sections with the theoretical values will be made and discussed.

II. EXPERIMENTAL METHOD

The apparatus for measuring the relative excitation functions has been described in a previous paper.⁴ Absolute values of the excitation functions were obtained by calibration against a standard lamp as previously described.^{4,5} The lamp was a tungsten ribbon filament pyrometer supplied and standardized by the General Electric Company. The lamp was operated at 3 temperatures in the range from 1400 to 1700°K and its emission calculated within a small wavelength interval for the wavelength of each transition observed. Emissivity tables for tungsten determined by Larrabee were used.⁶ The sensitivity of the detection system was determined with the three-lamp temperatures. The maximum deviation of the sensitivity from the mean value at a given wavelength was generally less than 5%.

The solid angle viewed by the monochromator was determined by the use of a small variable size circular diaphragm which acted as the aperture stop. Transition probabilities used in this paper for evaluating the density of a given excited state by means of observation of the intensity of light emitted from it are those tabulated by Gabriel and Heddle.⁷

³ C. C. Lin and R. G. Fowler, *Ann. Phys. (N. Y.)* **15**, 461 (1961).

⁴ R. M. St. John, C. C. Lin, R. L. Stanton, H. D. West, J. P. Sweeney, and E. A. Rinehart, *Rev. Sci. Instr.* **33**, 1089 (1962).

⁵ R. M. St. John, C. J. Bronco, and R. G. Fowler, *J. Opt. Soc. Am.* **50**, 28 (1960).

⁶ R. D. Larrabee, *J. Opt. Soc. Am.* **49**, 619 (1959).

⁷ A. H. Gabriel and D. W. O. Heddle, *Proc. Roy. Soc. (London)* **A258**, 124 (1960).

III. ANALYSIS

The equation relating population gain and loss rates per unit volume of the j th state of an atomic system is

$$Q(j)[I_e N(g)/eS] + \sum_i N(i)A(ij) + \text{transfer gain} \\ \text{Electron impact gain} \qquad \qquad \text{Cascade gain} \\ = N(j)A(j) + \text{transfer loss}, \qquad (1) \\ \text{Cascade loss}$$

where $Q(j)$ is the cross section for excitation by electron impact from the ground state to the j th state, I_e is the electron-beam current passing through the collision tube, S is the cross-sectional area of the electron beam, and e the electronic charge. The symbols $N(g)$ and $N(j)$ stand for the densities of the ground and j th states; $A(ij)$ is the probability of transition from the i th state to the j th state, while $A(j)$ is the total probability of transition from the j th state to lower states. In the above equation we have neglected the effect of imprisonment of radiation. This follows from the assumption that observations of 1P functions, which are directly affected by imprisonment, are to be made at pressures low enough that imprisonment is negligible.

At low pressure the transfer excitation terms in Eq. (1) can be neglected. When this is done, one obtains

$$Q(j)[I_e N(g)/eS] + \sum_i N(i)A(ij) = N(j)A(j). \quad (2)$$

It is customary to introduce the branching ratio B ,

$$B(jk) = A(j)/A(jk), \quad (3)$$

so that Eq. (2) can be rewritten as

$$Q(j)[I_e N(g)/eS] + \sum_i N(i)A(ij) = B(jk)N(j)A(jk). \quad (4)$$

Here $N(j)A(jk)$ is the rate at which energy is emitted in connection with transition $j \rightarrow k$ and is determined experimentally from the photomultiplier current $I_P(\theta, j)$ measured at an angle θ relative to the electron beam. Since the radiation generally is not isotropic, a polarization correction factor $f_P(\theta, j)$, is introduced so that $I_P(\theta, j)f_P(\theta, j)$ is proportional to the angular average of the light intensity and thus allows the determination of the entire light flux emitted from the collision chamber. Accordingly we have

$$N(j)A(jk) = C_1(j)I_P(\theta, j)f_P(\theta, j), \quad (5)$$

where $C_1(j)$ is a proportionality constant determined from the calibration procedure using the standard lamp. For the purpose of comparison with the previous data, we define $Q'(j)$ and $Q''(j)$ as

$$Q'(j) \frac{I_e N(g)}{eS} \equiv Q(j) \frac{I_e N(g)}{eS} + \sum_i N(i)A(ij), \quad (6)$$

$$Q''(\theta, j) \equiv Q'(j)/f_P(\theta, j) \\ = eSC_1(j)I_P(\theta, j)B(j)/I_e N(g). \quad (7)$$

All the factors making up $Q''(\theta, j)$ are obtained by experimental observation except $B(j)$ which is determined from the theoretical transition probabilities.⁷ In fact, $Q''(\theta, j)$ is the cross section which has been reported traditionally by observers of excitation functions. We shall call it the cross section uncorrected for polarization, cascade, and transfer effects; or simply the apparent cross section. Likewise, $Q'(j)$ can be regarded as the observed cross section which has been corrected for polarization but not for cascading and transfer effects, and is obtained from the experimental $Q''(j)$ cross section.

The polarization correction factor⁸ is

$$f_P(\theta, j) = \frac{1}{3} \{ [300 - P(j)] / [100 - P(j) \cos^2 \theta] \}, \quad (8)$$

where $P(j)$ is the percentage polarization.

IV. EXPERIMENTAL RESULTS

The apparent excitation functions of 18 states as measured directly from the automatic processing apparatus are shown in Fig. 1. The graphs represent relative values. After the calibration procedure described earlier was followed, the absolute values of the apparent cross sections were obtained; the peak values are listed in Table I.

The apparent excitation function of the 3^1P level displayed in Fig. 1 was recorded at a pressure of 5.9μ . The shape of this curve was quite independent of gas pressure. Data obtained at pressures as low as 0.1μ were used to evaluate the peak apparent cross section of $350 \times 10^{-20} \text{ cm}^2$ listed in Table I.

The excitation function obtained at 4025–6 Å represents the sum of two-line functions. These are 4026 Å ($5^3D \rightarrow 2^3P$) and 4025 Å ($7^1S \rightarrow 2^1P$). One can

obtain an excellent approximation to the excitation of the 7^1S level by extrapolation from the 3, 4, 5, and 6 levels of that family; application of the appropriate branching ratio yields the function of the 4025-Å line, with a maximum value of $1.1 \times 10^{-20} \text{ cm}^2$. This, when subtracted from the function representing the sum of the two excitation processes, yields the 4026-Å function which, in turn, yields the 5^3D apparent excitation function.

V. PREVIOUS WORKS

The apparent electron excitation functions of helium have been measured by Lees,⁹ Thieme,¹⁰ Yakhontova,¹¹ McFarland and Soltysik,¹² and Heddle and Lucas.¹³ Of these Lees, Thieme, and Yakhontova determined absolute cross sections. Additionally, Stewart and Gabathuler¹⁴ have determined the peak values of the cross sections of several helium levels. Gabriel and Heddle⁷ determined the cross sections for 108-eV electrons for a number of helium levels.

The observations by Thieme, Yakhontova, Heddle, and Lucas, Gabriel and Heddle, and Stewart and Gabathuler were at pressures low enough to greatly reduce transfer effects. Of these, Thieme and Stewart and Gabathuler, however, did not work at pressures low enough to eliminate imprisonment of resonance radiation, and thus their absolute determinations of the 3^1P cross sections are abnormally high. All observers worked at pressures low enough that light emission from 1^1S , 3^1S , and 3^1P states was linear with pressure. All observers cited, including the authors of this paper, observed the excitation chamber in a direction normal to the electron beams. Thus all apparent cross sections determined at low pressures are subject to the same corrections required for polarization and cascade.

Table II shows the peak absolute values of the apparent cross sections of helium levels as measured by the authors of the paper, Yakhontova, Stewart and Gabathuler, Lees, and Thieme.¹⁵ It also shows our values and those of Gabriel and Heddle at an electron energy of 108 eV.

TABLE I. Maximum values of the apparent excitation cross sections (low-pressure values).

Level	Transition observed (Å)	Maximum cross section Q^{11} (10^{-20} cm^2)
3^1S	(7281)	49
4^1S	(5047)	24
5^1S	(4438)	9.2
6^1S	(4170)	4.8
3^1P	(5016)	350
4^1P	(3965)	159
3^1D	(6678)	42
4^1D	(4922)	17.6
5^1D	(4387)	9.0
6^1D	(4144)	4.7
3^3S	(7065)	107
4^3S	(4713)	35
5^3S	(4121)	12.3
3^3P	(3889)	97
3^3D	(5876)	31
4^3D	(4471)	12.0
5^3D	(4026)	6.2
6^3D	(3821)	3.9

⁸ I. C. Percival and M. J. Seaton, Phil. Trans. Roy. Soc. (London) **A251**, 113 (1958).

⁹ J. H. Lees, Proc. Roy. Soc. (London) **A137**, 173 (1932).

¹⁰ O. Thieme, Z. Physik **78**, 412 (1932).

¹¹ V. E. Yakhontova, Vestn. Lening. Univ., Ser. Fiz. i Khim. **14**, 27 (1959). (Translation 951 by Atomic Energy Research Establishment, Harwell, Berkshire, England.)

¹² R. H. McFarland and E. A. Soltysik, Phys. Rev. **127**, 2090 (1962); **128**, 1758 (1962).

¹³ D. W. O. Heddle and C. B. Lucas, Proc. Roy. Soc. (London) **A271**, 129 (1963).

¹⁴ D. T. Stewart and E. Gabathuler, Proc. Phys. Soc. (London) **74**, 473 (1959).

¹⁵ Some of these experimenters published values for cross sections for excitation of a given line transmitted from a given level. By use of the branching factor one can readily obtain the cross section for excitation to the upper level involved. We used the transition probabilities of Gabriel and Heddle for determining the branching factors and thus obtained level cross sections as displayed in Table II. Stewart and Gabathuler listed both line and level cross sections. Due to the fact that they used branching factors differing from those produced by the Gabriel and Heddle transition probabilities, their level cross sections show some slight variation from those we list for them.

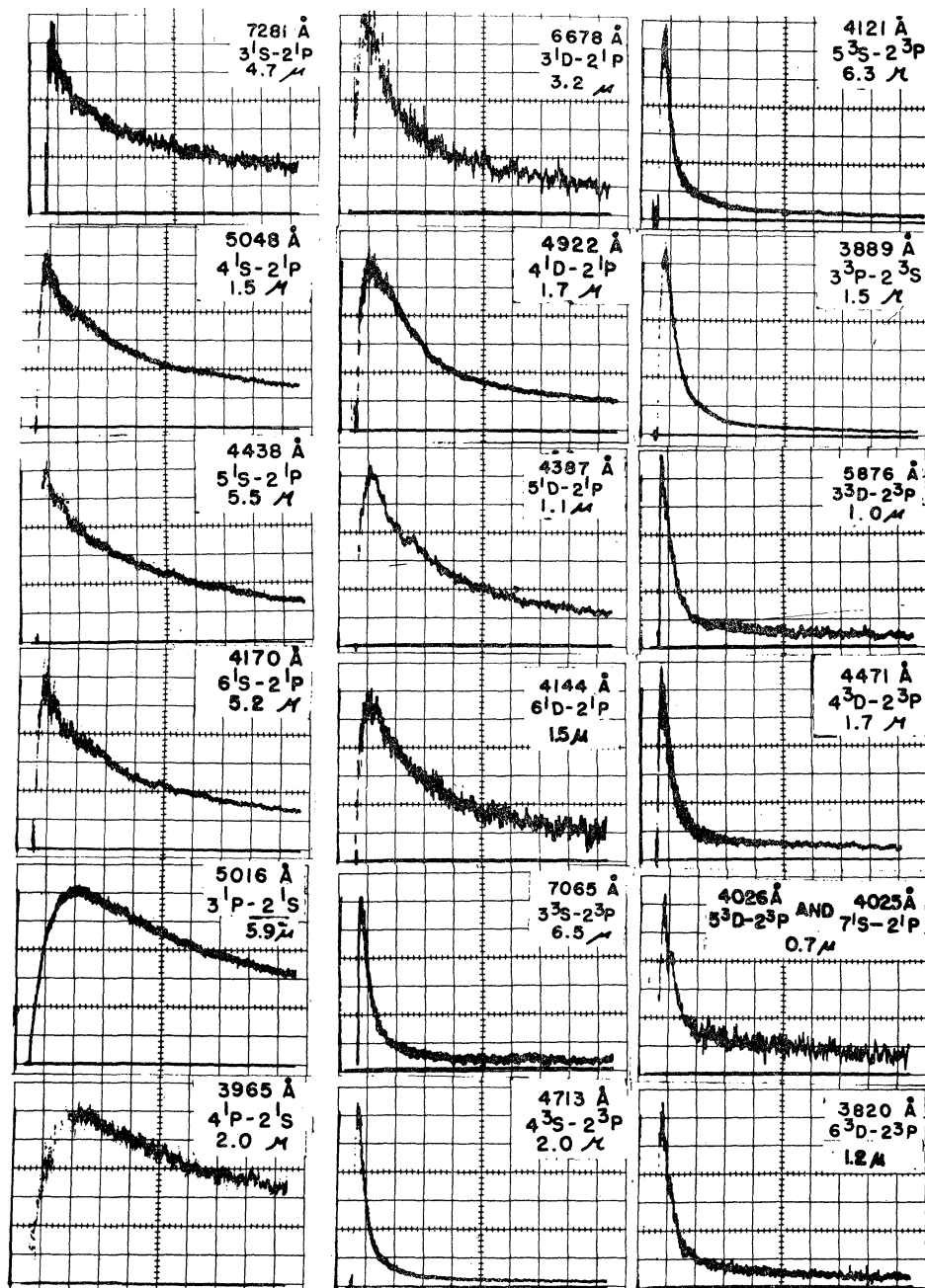


FIG. 1. Apparent excitation functions of 18 helium levels. Cross sections are relative; electron energy varies from 0 to 500 eV.

The measurements of Yakhontova are consistent with those reported herein. The ratio of Yakhontova's peak cross sections to ours averages 0.99 and each lies within the range of 0.83 to 1.16 with the exception of the 4^3S and 5^3D cross sections. In those cases the factors were 0.77 and 1.37. This rather good agreement throughout the levels including 1D , and 3D verifies that the pressures used in both investigations were below those which cause transfer effects.¹⁶

¹⁶ Yakhontova determined the absolute value of the peak cross section of lines from the 3 and 4^1P levels by operating at a gas

Stewart and Gabathuler do not quote directly the pressures used in their determinations of the apparent cross sections, but they were well aware of the pressure

pressure high enough to cause complete imprisonment (which would yield a value near that of the level cross section) and then determined the line cross sections (5016 and 3965 Å) by dividing by the appropriate branching factor. Due to a spreading of the beam with increasing imprisonment which is concomitant with increasing pressure, the measured line intensity will not increase as much as the branching ratio when imprisonment changes from a nil to its full value. Thus, the line cross sections given by Yakhontova were not converted back to level cross sections and hence are not tabulated in Table II.

TABLE II. Comparison of absolute values of apparent cross sections of helium obtained by several experimenters. All cross sections are expressed in units of 10^{-20} cm².

Level	This paper	Cross section at peak				Cross section at 108 eV	
		Yakhontova	Stewart and Gabathuler	Lees	Thieme	This paper	Gabriel and Heddle
3 ¹ S	49					31	36
4 ¹ S	24	20	27.5		28	15	16.5
5 ¹ S	9.2	7.7	10.0	5.9	16.5	6.1	7.0
6 ¹ S	4.8		6.1	2.8	9.5	3.0	4.0
3 ¹ P	350		4130	4360	3660	350	457
4 ¹ P	159		950	1270	1080	158	210
3 ¹ D	42					24	25
4 ¹ D	17.6	17.8	24	15.1	32	12	12
5 ¹ D	9.0	8.5	12.2	9.3	18.6	6.2	7.1
6 ¹ D	4.7	5.0	6.9		9.9	3.3	3.0
3 ³ S	107					10.2	15
4 ³ S	35	25	37	36	64	3.3	4.4
5 ³ S	12.3	12.7	17.2	8.6	40	1.17	1.44
3 ³ P	97	83	105	80	1890	15.3	11
3 ³ D	31	36	45		42	4.3	25
4 ³ D	12.0	12.4	18	15.2	23	1.64	4.6
5 ³ D	6.2	8.5	7.1			0.89	3.0
6 ³ D	3.9		4.3			0.53	1.5

effects, as they gave intensity versus pressure curves. Some of that data was obtained in the $2\text{-}\mu$ range, and we can assume the sensitivity of their equipment allowed them to obtain the maxima of the apparent cross sections at about that pressure. Their relative consistency with our data for ¹D and ³D indicates that they were able to minimize the transfer of excitation effects. Their values for 3¹P and 4¹P are very large and indicates an imprisonment effect as one expects as a pressure of $2\ \mu$. Disregarding the ¹P data, the ratio of their cross sections to ours averaged a 1.26 and varied within the limits of 1.06 to 1.50.

The data of Lees is in serious disagreement with our results for the 3¹P, due to his use of pressures in the $40\text{-}\mu$ range. His peak apparent cross sections for the ¹S, ¹D, ³S, ³D, and ³P levels compared to our values by a ratio averaging 0.86.

The data of Thieme compared to ours shows quite a variety of cross-section ratios; his extremely high value for excitation of the 3¹P level is at least in part due to imprisonment effects. His very large value for the 3³P level defies explanation other than through erroneous calibration procedures. Lees' and Thieme's data were obtained by photographic techniques and hence more subject to errors than the photoelectric data of the other investigators cited. The magnitudes of Thieme's data will be given no further consideration.

Gabriel and Heddle measured absolute values of the cross section for 17 helium levels at pressures apparently low for all except the ³D levels. The ratios of their apparent cross sections to those presented by the present authors averaged 1.12 for ¹S, ¹P, ¹D, ³S, and ³P levels, and lay within the range of 0.76 to 1.37. The ³D ratio varied up to 3.4 indicating a transfer fillin for the cross sections of Gabriel and Heddle.

A comparison of the shapes of the excitation functions

is presented in Table III. Each excitation function has been normalized to unity for an electron energy of 100 eV. Included are the data of Yakhontova, Lees, Thieme, McFarland and Soltysik, Heddle, and Lucas, and that presented in this paper. It can be seen that there is quite good agreement between the shape data presented herein and that of Yakhontova. This is the result of both sets of data being obtained under low-pressure conditions. The shapes of the ¹D and ³D curves of Lees are modified by the ¹P fillin due to his use of a relatively high gas pressure. The curves of Thieme are quite similar to those presented herein, a fact derived from the low-helium pressures used by him. McFarland and Soltysik obtained their functions with a gas pressure of 10 to 20 μ , and thus their curves show some transfer effects. The curves of Heddle and Lucas, while obtained at a pressure of about $1\ \mu$, do not show very good agreement with the curves of the other experimenters.

Another factor influencing the shape of an experimentally determined excitation function is that of the shape of the electron beam. If it should undergo any change with electron energy, the light detection system being used could change in sensitivity due to (a) a variation in the light-gathering ability of the optical system with change in the position of the light source and (b) a lack of homogeneity of the response of in the cathode of the photomultiplier. Care was exercised by the authors of this paper to maintain a cylindrical electron beam of constant diameter at all electron energies.

VI. POLARIZATION AND CASCADE CORRECTIONS

Values of the percentage polarization, $P(j)$, have been measured by McFarland and Soltysik¹² for varying pressure and electron energy for several of the transitions reported in this paper, and are used for making

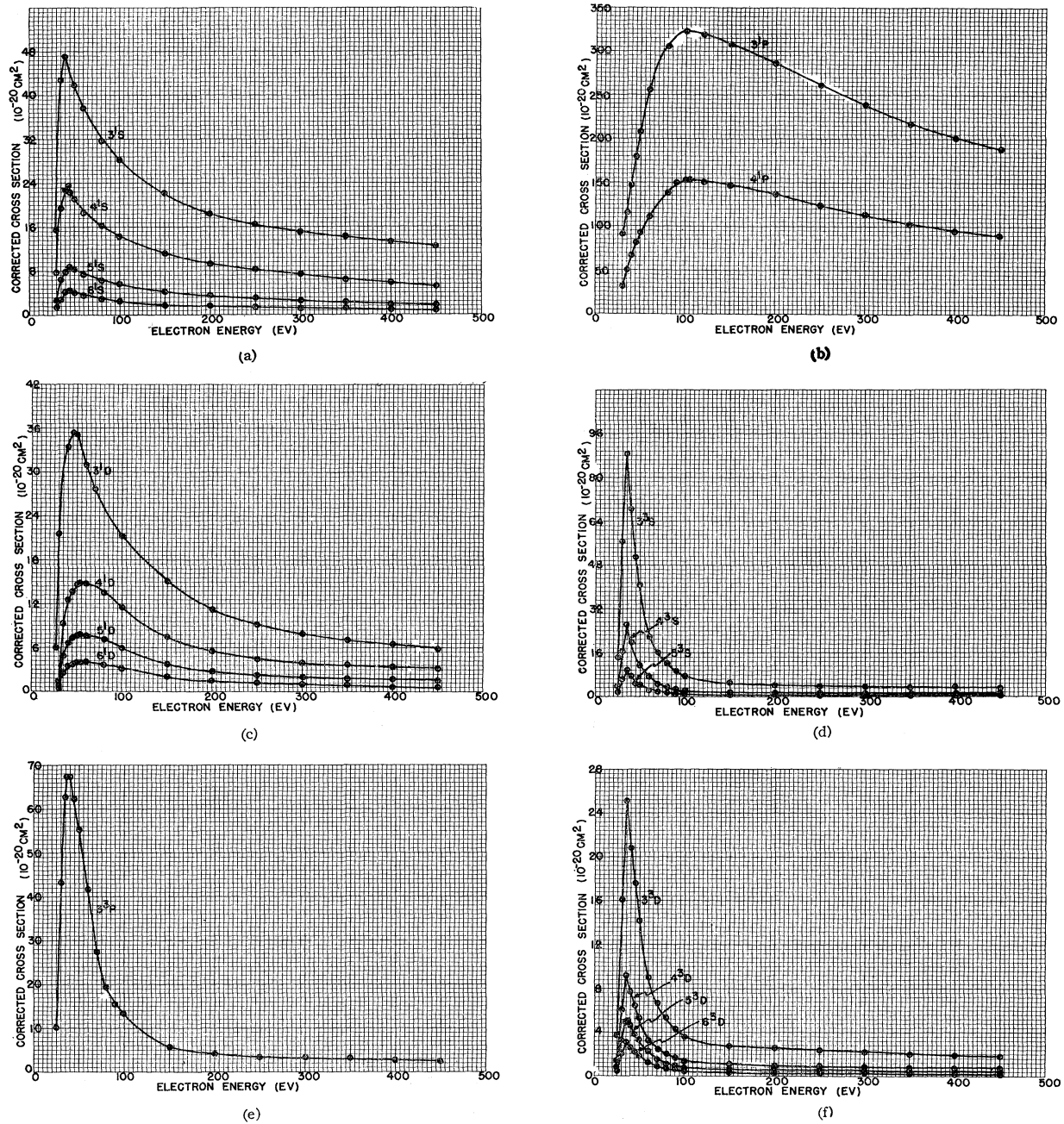


Fig. 2. Families of excitation function corrected for polarization and cascade effects. (a) Singlet S , (b) singlet P , (c) singlet D , (d) triplet S , (e) triplet P , (f) triplet D .

were nearly constant as a function of voltage. The 3^3S , 4^3S , and 5^3S functions of Q' were 20 to 30% due to cascade. The Q' curve of 3^3P was 30% due to cascade. The cascade correction for the 3^3D functions varied to 10 to 19%.

Fortunately, the errors which might be introduced by the extrapolations processes necessarily are small since the cascading from high states is small. That part of the population of a state coming from levels involved

in the extrapolation processes was 7% for the 3^1S state. The amounts falling to other low-level states by this process¹⁷ were as follows: 3^1P , 1%; 3^1D , 4%; 3^3S , 3%; 3^3P , 4%; 3^3D , 1%. There are additional uncertainties associated with the cascading from the F states. This point is discussed in Sec. VII.

¹⁷ Measurements of the $3P$ family were limited to $n=3$. The fall-off cross section with n was determined from the paper of Gabriel and Heddle which supplied cross section data for the 3, 4, and 5 states.

Frost and Phelps¹⁸ made determinations of cascade contributions. They estimated that no correction was necessary for the 1^1S and 1^1D curves. They obtained a 10% correction for the 3^1P and 4^1P levels at 100 eV. The triplet curves, at the peak of the excitation function, were populated by cascade as follows: 4^3S , 4%; 3^3P , 49%; 3^3D , 4^3D , 5^3D all 10%.

Gabriel and Heddle⁷ determined cascade corrections for electron energies of 108 eV. The 4^1S level population was 2% due to cascading. Higher 1^1S level populations were regarded as entirely caused by electron impact. Singlet P populations were assumed free of cascade effects. The 3^1D level was found to have 4% of its population due to cascade, but higher 1^1D unaffected by cascade. The triplets were populated by cascade as follows: 4^3S , 23%; 5^3S , 7%; 3^3P , 34%; 3^3D , 4%; 4^3D , 17%; 5^3D , 17%.

VII. COMPARISON WITH THEORY

The theory of excitation of helium atoms by electron impact has been treated rather extensively in the literature. Massey and Mohr¹⁹ calculated the excitation cross sections for the 2^1S , 3^1S , 2^1P , 3^1P , 4^1P , 5^1P , 3^1D , 4^1D , 5^1D and 4^1F states by the Born approximation and for the 2^3S , 3^3P , 4^3P , and 3^3D states using the Born-Oppenheimer approximation for incident electrons of various energies (60, 100, 200, and 400 eV). Curves for the theoretical excitation functions for the 3^1S , 3^1P , 4^1P , 4^1D , 5^1D and 2^3S states were also included in this work. Bates *et al.*²⁰ have given a critical analysis of the Born and Born-Oppenheimer approximation along with additional results of cross sections for some of the low- n states of He. As an improvement over the Born-Oppenheimer approximation, cross sections for the $1^1S \rightarrow 2^1S$, $1^1S \rightarrow 2^3S$, and $1^1S \rightarrow 2^3P$ transitions have been calculated by Massey and

TABLE IV. Comparison of observed and calculated cross sections for electrons of various incident energies. Observed cross sections are corrected for polarization and cascading. All cross sections are expressed in units of 10^{-20} cm².

Level	60 eV		100 eV		200 eV	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
3^1S	38	26	28	15	18.5	11
3^1P	260	340	320	270	290	190
4^1P	112	140	152	110	136	76
3^1D	31		21	4.4	11.1	2.5
4^1D	14.7	3.7	11.6	2.5	5.6	1.3
3^3S	21.5	1.3 ^a	7.6	0.60 ^a	4.1	0.13 ^a
3^3P	42	5.5	13.3	1.1	4.1	0.15
3^3D	9.0	0.13	3.5	0.03	2.6	0.004

^a The 3^3S calculated values are extrapolated from 2^3S calculations.

¹⁸ L. S. Frost and A. V. Phelps, Westinghouse (Pittsburgh) Research Report 6-94439-6-R3, 1957 (unpublished).

¹⁹ H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A140**, 613 (1932).

²⁰ D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, Phil. Trans. Roy. Soc. (London) **A243**, 93 (1950).

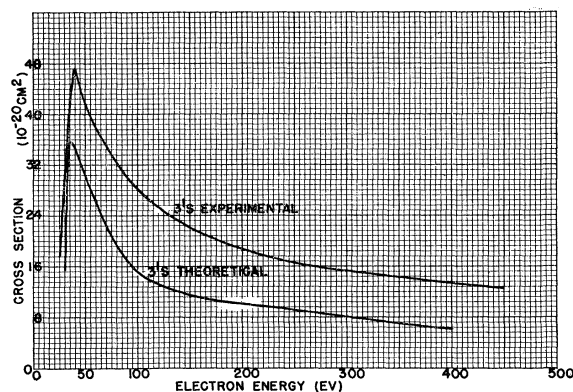


FIG. 3. Experimental and theoretical excitation functions of the 3^1S level. The experimental curve is corrected for polarization and cascade effects.

Moiseiwitsch²¹ using the method of exchange distorted waves (EDW). Unpublished calculations by Fox on the excitation cross sections of several 1^1S states were quoted in the paper of Gabriel and Heddle⁷ and by Seaton.²² In Table IV are listed observed and calculated (Massey and Mohr) excitation cross sections at electron energies of 60, 100, and 200 eV.

The theoretical and observed cross sections of the 3^1S level show good agreement. The calculated cross sections for the 1^1S states are subject to a higher degree of uncertainty than those of the other states, because the wave functions of the n^1S states were gotten by orthogonalization of the Slater-like orbitals. A small change of the effective nuclear charge, for instance, may result in a significant variation of the cross sections. Thus Massey and Mohr gave 15×10^{-20} cm² for the 3^1S cross section at 100 eV while the same cross section, according to the work of Fox,²³ is 46×10^{-20} cm². In the light of this, the experimental cross section may be considered to lie within the limits of the theoretical calculations. Figure 3 shows the comparison of the experimental and theoretical excitation functions of 3^1S .

Figure 4 shows the comparison between the theoretical and experimental excitation functions of 3^1P and 4^1P . The discrepancy at voltages below 100 eV is to be expected since the theoretical values were calculated by the use of the Born approximation. Analyses by Altschuler²⁴ and by Miller and Platzman²⁵ indicate that the use of approximate helium wave functions may lead to an error in the cross section as large as a factor of two or so. Thus the over-all agreement between the ob-

²¹ H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A227**, 38 (1954); **A258**, 147 (1960).

²² M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

²³ Fox's cross section of 3^1S were given for electron energy at 108 eV as 43×10^{-20} cm². The value at 100 eV is obtained by assuming the cross section to be inversely proportional to the energy of the colliding electron over this small range of energy.

²⁴ S. Altschuler, Phys. Rev. **87**, 992 (1952); **89**, 1093 (1953).

²⁵ W. F. Miller and R. L. Platzman, Proc. Phys. Soc. (London) **A70**, 229 (1957).

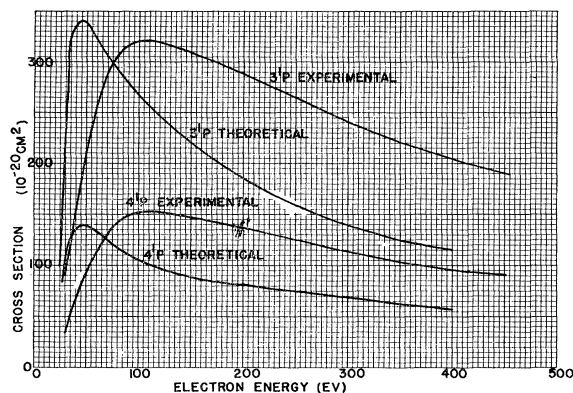


FIG. 4. Experimental and theoretical excitation functions of the 3^1P and 4^1P levels. The experimental curves are corrected for polarization and cascade effects.

served and calculated excitation cross sections for 3^1P and 4^1P should be considered as good as can be expected at this time.

The evaluation of the absolute cross sections Q from the experimental data for the 1D states is somewhat complicated by the fact that the amount of cascading from the 1F to the 1D states are not known, since no excitation measurements are available for the 1F states. We shall use the calculated value¹⁹ of $Q(4^1F)$ along with an n^{-3} dependence for the higher 1F states. The cascading from G to 1F will be neglected, since the populations of the G states are expected to be very small on account of the rapid decrease of the direct excitation cross sections with increasing values of L . Under these assumptions we have calculated $N(n^1F)$ and found that the $^1F \rightarrow ^1D$ cascading contributes less than 1% of the total population of the 1D state. This result remains essentially the same when the singlet-triplet mixing of the F states are taken into consideration.³ The absolute cross sections of 3, 4, 5, and 6 1D are then evaluated from the experimental data on Q'' (see Table I and Fig. 1). They are about four times larger than the theoretical values. At first, one might ascribe this discrepancy to the inaccuracy of our estimated populations of the F states. If we were to assume that $F \rightarrow ^1D$ cascading is entirely responsible for the deviation of the observed Q from the theoretical values, it would be necessary to increase the concentration of the atoms in the F states. This, in turn, would require cross sections for electron excitation of the 1F states to be 200 to 300 times as large as the theoretical values. The value of $Q(4^1F)$, for example, would have to be about $12 \times 10^{-20} \text{ cm}^2$, a seemingly unreasonable value. Our experimental results for the excitation cross sections of the 1D states therefore could not be brought into complete agreement with theory in a consistent manner.

Calculation by Fox as quoted by Seaton²² gives $Q(3^1D) = 7 \times 10^{-20} \text{ cm}^2$ at 108 eV as compared to $4 \times 10^{-20} \text{ cm}^2$ calculated by Massey and Mohr¹⁹ at 100 eV. The difference between these two values can be

taken as an indication of the degree of variation of the theoretical cross section (Born approximation) which can be expected from the use of different approximate helium wave functions. Seaton has pointed out the calculations by B II approximation show that the coupling between 3^1D and 3^1P is not important for the cross section of the 3^1D state. It is very unlikely then that the imperfection of the theory could account for the disagreement between the observed and calculated cross sections for 3^1D and 4^1D . Nor is it conceivable that errors in the experimental procedure could have caused the observed values to show this mismatch with the calculated cross sections. The measured apparent cross sections are proportional to the output current of the photomultiplier tube; thus, the relative values of the apparent excitation cross sections should be quite accurate. Of course the absolute experimental cross sections are subject to the errors of the light-intensity calibration as well as the cascade corrections. The amount of cascading populations in the 1P and 1D are quite small, i.e., less than 14% of the total populations. Errors in the calibration of the photomultiplier output should affect all the cross sections by a constant factor. This leads us to conclude that one cannot have simultaneous agreement between theory and experiment for the 3^1P , 4^1P , 3^1D , and 4^1D states.

For the 3^3P and 3^3D states the calculated cross sections are consistently smaller than the observed values. In fact, the discrepancy is too large to be ascribed to the errors in the theory or experiment or combination of both. In the case of the 3D states one is again faced with the problem of having to estimate the $F \rightarrow ^3D$ cascading. Calculations show that the contributions of $F \rightarrow ^3D$ cascading to the population of the n^3D states are less than 1%, i.e., completely negligible.

Finally for the 3S series, direct comparison between theory and experiment is more difficult since theoretical cross sections are available only for 2^3S , while our experimental results cover 3^3S , 4^3S , and 5^3S . In order to make any comparison it is necessary to extrapolate the experimental data with the assumptions that (i) the shape of excitation functions for all the n^3S states is identical, and (ii) the peak values of these functions follow the relation $n^{-\alpha}$ or $(n^*)^{-3}$ as was assumed by Phelps and Frost¹⁸ and by Gabriel and Heddle.⁷ Here, n^* is the effective quantum number such that the energy of the state is equal to a negative constant divided by $(n^*)^2$. The extrapolation procedure yielded experimental values of $Q(2^3S)$ equal to 180, 69, and 39×10^{-20} at 60, 100, 200 eV, respectively, for the $n^{-\alpha}$ relations, where $\alpha = 4.0$. Values of 140, 51, and 30×10^{-20} were obtained for the $(n^*)^{-3}$ relationship where $n^* = n - 0.30$. These are to be compared with the theoretical values of 5, 2.4, and $0.5 \times 10^{-20} \text{ cm}^2$ calculated by the Born-Oppenheimer approximation. Massey and Moisewitsch²¹ have shown that when the distortion of the plane wave is taken into consideration, the calculated

cross sections become much smaller at low voltages. Thus it is seen that the experimental cross sections for the 3S series are about 30 times the theoretical values. A comparison of the mismatch of theory and experiment of the 3S family with that of the 3P and 3D can best be made at the $n=3$ level. Since no theoretical cross sections are available for the 3^3S state they were extrapolated from $n=2$ to $n=3$ by use of the $(n^*)^{-3}$ relationship. These figures are to be found in Table IV. They are used only to provide an estimate of the theoretical values and to draw conclusions of qualitative nature.

An examination of Table IV reveals that the fraction of the observed cross section accounted for by theory is much smaller for the 3^3D state than for the 3^3S and 3^3P states. However, a more important consideration would seem to be that of the magnitude of the unaccounted for cross sections, i.e., $Q(\text{obs}) - Q(\text{theory})$. This value is of the same order of magnitude at a given electron energy for the three triplet states under comparison. Thus, the mechanism producing the excessive population in the triplet states does not preferentially populate any one state any more than the others.

VIII. CONCLUSIONS

The electron excitation cross sections for 18 excited states of helium have been determined by measuring the intensities of the radiation originated from these excited states at low pressure. Corrections have been made to allow for the cascading and polarization effects. The agreement between the observed and theoretical cross sections for the 3^1P , 4^1P , and 3^1S states is satisfactory. The experimental cross sections for 3^1D and 4^1D are about four times larger than the theoretical values. For the 3S , 3P and 3D states the experimental results far exceeds (a factor of 10 or more) the calculated cross sections.

The discrepancy in the cross sections of the triplet series with the calculated values is far too large to be explained by experimental uncertainty. Nor can one reasonably expect the Born-Oppenheimer approximation to produce cross sections which are ten to a hundred

times too small at electron energies above 60 or 100 eV. This is particularly true in view of the fact that the 1P and 1S cross sections calculated by the Born approximation do agree with the experimental values. Furthermore, calculations by Massey and Moseiwitsch²¹ show that the excitation cross sections obtained from the Born-Oppenheimer approximation and from the EDW method approach each other at electron voltages above 50 eV. One does not expect the use of more refined method of calculation will change the theoretical cross sections (above 50 eV) significantly. In the case of 3^1D and 4^1D although the disagreement between theory and experiment is less severe, it is very unlikely that the cumulative errors of the theoretical calculation and the experimental work including the associated analysis of the excitation data could account for the deviation of a factor of four.

The explanation which seems most plausible to us is that the observed population of the triplet states (and possibly, to some extent, of the 1D states) is produced mainly by processes other than direct excitation. Results of the measurements of the lifetime of the triplet states by Holtzberlein and Fowler²⁶ also point toward the same conclusion. Of course, the mechanism or mechanisms with which the triplet states are populated must have the correct linear behavior with respect to pressure and electron beam current. Efforts are being made to perform additional experiments to provide further evidence of this "anomalous" behavior of the triplet states as well as to search for the mechanisms which are responsible for the observed populations of these states.

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²⁶ T. M. Holtzberlein and R. G. Fowler, Paper B-1, Sixteenth Annual Gaseous Electronics Conference, Pittsburgh, 1963 (unpublished).