New Process of Excitation Transfer in Helium*

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Precise observations have been made on light emission from low triplet levels of helium gas traversed by a monoenergetic electron beam, with varying helium pressure and electron energy. In the past it has been customary to assign this triplet excitation to direct transfer from ^1P states in flagrant violation of the Wigner rule and seemingly excessive cross sections for the transfer have been inferred.

A new process of excitation transfer is proposed which minimizes the conflict with the Wigner rule by reducing the sizes of the cross sections required to values close to the gas-kinetic cross section. It is hypothesized that many ^1P states, including those with large quantum number n, transfer excitation energy to neighboring triplet states having closely corresponding principal quantum numbers. The triplet states thus formed in turn populate low-level triplet states by radiative transitions. It is found that states lying between $n=4$ and $n=15$ would play the dominant role in the transfer process.

Satisfying qualitative explanations of several additional excitation-transfer-process phenomena are derived from this new multiple-state-transfer process.

I. INTRODUCTION

THE primary purpose of this paper is to suggest a new explanation of the transfer of excitation by collision from a singlet state to a triplet state in a gas such as helium and to show that it is consistant with some experimental observations. In this type of gas the Wigner spin conservation rule[1] is expected to be of great importance. This rule states that the total angular momentum of electron spin is conserved in a collision involving two gas atoms. In general, this rule is expected to apply best when the angular momenta of an atom have LS coupling. Helium atoms with both electrons close to the nucleus show strong LS coupling. States of helium in which one electron is in its lowest state and the other a highly elevated state do not show as strong LS coupling. Therefore a collision involving such an atom would not be expected to adhere so strongly to the Wigner rule.

The reactions which usually have been proposed to account for the transfer of excitation energy may be exemplified by the following:

$$\mathrm{He}(1\,^1S)+\mathrm{He}(n\,^1P)\rightarrow\mathrm{He}(1\,^1S)+\mathrm{He}(n\,^3D). \quad (1)$$

In such a reaction only thermal kinetic energies are available to trigger the process, and since the triplet levels lie between 19.8 and 24.6 ev above the ground state, only one atom may emerge from the collision in an excited state even though a collision of the second kind may have occurred. The production of only one triplet means that the total spin angular momentum of the system has been changed by $h/2\pi$ and the Wigner spin conservation rule violated. Large transferred populations are experimentally observed in states as low as the $3\,^3D$ state where the violation of the Wigner rule would be extreme. It is our contention that, in place of direct transfer between low lying levels, a process is active in which many ^1P levels transfer excitation to a corresponding multiplicity of nearby levels in other series, the Wigner rule being presumed to be less restrictive for levels lying near the continuum. These indirectly excited atoms then degrade to lower levels by radiative transitions. It is from these lower levels that the observed visible light is subsequently emitted.

II. EARLY INVESTIGATIONS

Transfer of excitation in helium has been investigated by Lees and Skinner[2,3] and by Wolf and Maurer.[4,5] The experimental method of Lees[2] was to pass an electron beam through a collision chamber filled with helium gas. He observed the radiation emitted from the beam path and its immediate vicinity. Prominent features of his observations included similarities between light emitted from ^1P states and light emitted from ^3D states at pressures slightly above the very lowest used. The light from ^1P states originated from outside the electron beam channel as well as from the channel at high pressures. This spreading effect increased with pressure and was attributed to the imprisonment of resonance radiation ($n\,^1P\rightarrow 1\,^1S$). Light from ^3D levels also exhibited this spreading to a remarkable degree, with the relative spreading increasing with n. Imprisonment of this radiation by the normal helium atoms is impossible, since intercombination lines of helium are observed neither from absorption nor emission. Lees and Skinner[3] postulated that this phenomenon was brought about by the ^1P excitation spreading out from the channel by the imprisonment process with the ^1P atoms subsequently forming ^3D atoms by a process such as given in Eq. (1). This is quite possible energetically as an $n\,^3D$ level is separated only a few thousands of an

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[1] E. Wigner, Nachr. Ges. Wiss. Göttingen, p. 375 (1927).

[2] J. H. Lees, Proc. Roy. Soc. (London) **A137**, 173 (1932).

[3] J. H. Lees and H. W. B. Skinner, Proc. Roy. Soc. (London) **A137**, 186 (1932).

[4] W. Maurer and R. Wolf. Zeits. Phys. **92**, 100 (1934).

[5] R. Wolf and W. Maurer, Zeits. Phys. **115**, 410 (1940).

electron volt from the equivalent $n\,^1P$ level. However, it violates the Wigner spin conservation rule to a dramatic degree, and is repeatedly cited as a major proof of the weakness of the rule.[6]

A second type of observation by Lees[2] also seemed to demand transfer of excitation from ^1P to ^3D states. This was the gradual growth with pressure of a peak in the uncorrected excitation function curve of a ^3D level that corresponded rather closely in energy to the peak in a ^1P excitation function. Lees and Skinner[3] calculated that the cross section for transfer from the $3\,^1P$ state to the $3\,^3D$ state would have to be about 4.5×10^{-14} cm^2, a value 30 times larger than the gas-kinetic value.

Wolf and Maurer[5] used an experimental arrangement consisting of two chambers, each filled with helium. The first was the collision chamber through which the electron beam passed and excited the helium gas. The second chamber was adjacent to this, but isolated in such a way that no electrons could be shot into it. However, radiation from the first chamber could enter it. The radiation from the first chamber, in being absorbed by the gas in the second chamber, produced fluorescent light in the second chamber. This light was observed in a direction perpendicular to the direction of the radiation from the first chamber. The spectrum of the fluorescent light showed not only lines of the principal singlet series ($n\,^1P\rightarrow 2\,^1S$), but also lines whose initial levels were ^3D, ^1D, ^3P, ^3S, and ^1S. The lines originating from the ^1D and ^3D levels were the most intense of the unexpected lines.

Wolf and Maurer attributed the presence of these lines to an excitation transfer process in which the $n\,^1P$ excitation was directly transformed into $n\,^3D$, $n\,^1D$, etc. states by collision. See Eq. (1). The cross sections calculated for transfer to ^1D and ^3D states were 10 or more times as large as the gas-kinetic cross section even for $n=3$. Transfer into other states was at a considerably lower rate and the values calculated for these transfer cross sections were approximately equal to the gas-kinetic value of 1.5×10^{-15} cm^2. All of these explanations involved not only violation of the Wigner rule, but a preferential violation, in that the cross sections needed invariably were very large.

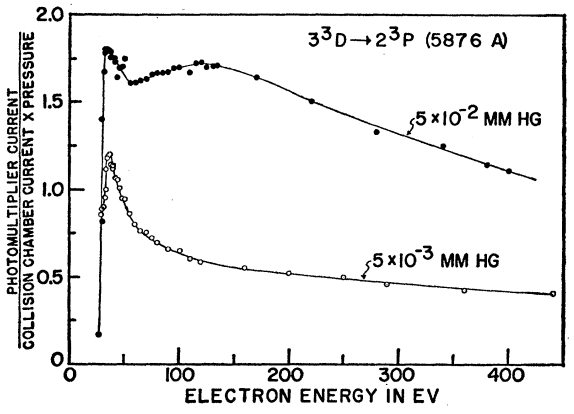

FIG. 1. Photomultiplier current per unit electron current per unit pressure vs electron energy. Transition from $3\,^3D$ to $2\,^3P$. Pressures are 5×10^{-3} and 5×10^{-2} mm.

[6] E. J. B. Wiley, *Collisions of the Second Kind* (Edward Arnold and Company, London, 1937), p. 30. P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 47.

III. NEW DATA

The experimental results obtained at this laboratory will now be discussed and an interpretation given which is based on the multiple state transfer process. The experimental apparatus is described in detail in an earlier paper.[7] Briefly, a beam of monoenergetic electrons was passed through a collision chamber containing helium atoms. The excited atoms emitted radiation which was filtered and detected by a photomultiplier. The electron energy and pressure were varied. The electron beam current could also be changed, but the light output from the collision chamber was exactly proportional to the current. This indicated that any excitation process involved an atom being struck by only one electron, rather than being struck successively by several electrons. For this reason, light yields are expressed for unit electron beam currents.

The ratio I_{pm}/pI_c, photomultiplier current to the product of pressure times electron beam current, as a function of electron beam energy is shown in Fig. 1 for two pressures for the $3\,^3D\rightarrow 2\,^3P$ transition. At the lower pressure a single sharp peak occurs at about 38 ev. The curve monotonically and smoothly decreases at higher energies. This type of curve has the shape generally expected of a triplet excitation function and will be considered to be solely due to direct excitation of ground-state helium atoms by electron impact. However, high ^3P and ^3F levels, also directly excited by electron impact, feed the $3\,^3D$ level by the cascade

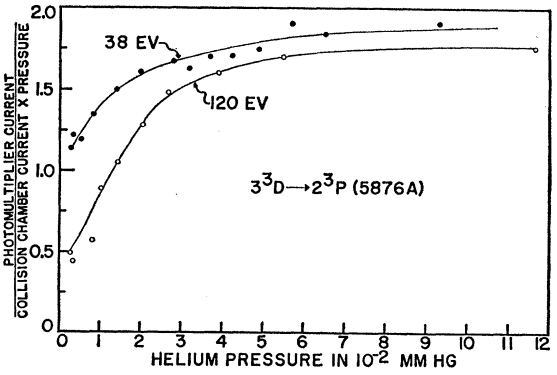

FIG. 2. Photomultiplier current per unit electron current per unit pressure vs pressure. Transition from $3\,^3D$ to $2\,^3P$. Electron energies are 38 and 120 ev.

[7] R. M. St. John, C. Bronco, and R. G. Fowler, J. Opt. Soc. Am. **50**, 28 (1960). Philip Smith, Phys. Rev. **36**, 1293 (1930).

process; their effects must be removed when an absolute calculation of the excitation cross section of the $3\,^3D$ level is made. The density of atoms in the $3\,^3D$ state per microampere photomultiplier current was 1.54×10^{2} per cm^3 with one μa electron current.

At a high pressure the curve shows a broad secondary maximum with its peak at 120 ev, as shown in Fig. 1. The value of I_{pm}/pI_c increases in the pressure range of 4×10^{-3} to 7×10^{-2} mm, with the change for electron energies of 38 and 120 ev shown in Fig. 2. The 38-ev curve increases by 57% while the 120-ev curve increases by 350% in this pressure range. At pressures greater than 7×10^{-2} mm, I_{pm}/pI_c increases very slowly with pressure for the two cases.

Figures 3 and 4 show the data obtained for the $3\,^3P\rightarrow2\,^3S$ (3889A) and $4\,^3S\rightarrow2\,^3P$ (4713A) transitions. These transitions show single sharp maxima at about 35 ev. The high pressure curves exhibit a very slight increase of I_{pm}/pI_c at and near 120 ev. This increase is very minor, however, compared to the increase exhibited by the transition from the $3\,^3D$ level.

The increase in the light output per unit pressure from the $3\,^3D$ state at elevated pressure appears to be due to excitation of this level by transfer from ^1P states. The ^1P states have direct excitation functions with a broad maximum near 120 ev. Figure 5 shows the excitation function of the $3\,^1P$ level of helium,[7] the ionization function of helium,[7] and the difference of the curves of Fig. 2. The latter is proportional to the radiation from the $3\,^3D$ level due to transfer of excitation.

In addition to the fact that the shape of the broad maximum of an uncorrected ^3D excitation function nearly matches that of the ^1P function, its pressure dependence is noticeable similar. The light emission per unit pressure from the $3\,^1P$ state begins rising at $p=3\times10^{-4}$ mm and again levels off at a pressure of 5 or 6×10^{-2} mm. See Fig. 5 of reference 7. The light emission per unit pressure from the $3\,^3D$ state begins increasing at a pressure of 4×10^{-3} mm and becomes nearly constant again at about 7×10^{-2} mm. The increase in light from the $3\,^3D$ state should set in at a higher pressure than that for the ^1P state since a buildup of ^1P concentration is required before an appreciable increase in transfer of excitation may be effected. At the high-pressure end of the curves, the density of normal atoms will be great enough that transfer of excitation energy back and forth from singlet to triplet will become copious; under these conditions the density of $3\,^3D$ atoms will be almost entirely dependent on the density of ^1P atoms. Since the curves of light emission from the ^1P and $3\,^3D$ states are so similar at high pressures, one can thus justify in a second manner that major contribution to the $3\,^3D$ population comes from ^1P states.

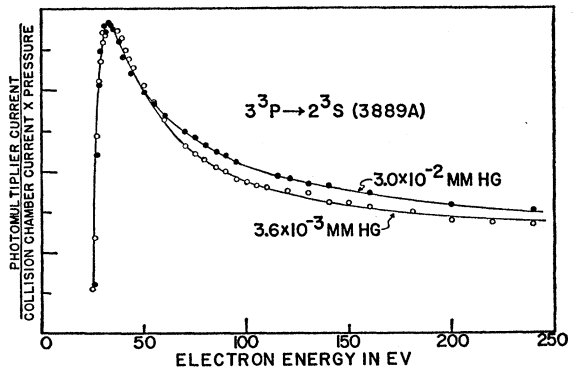

FIG. 3. Photomultiplier current per unit electron current per unit pressure vs electron energy. Transition from $3\,^3P$ to $2\,^3S$. Pressures are 3.6×10^{-3} and 3.0×10^{-2} mm.

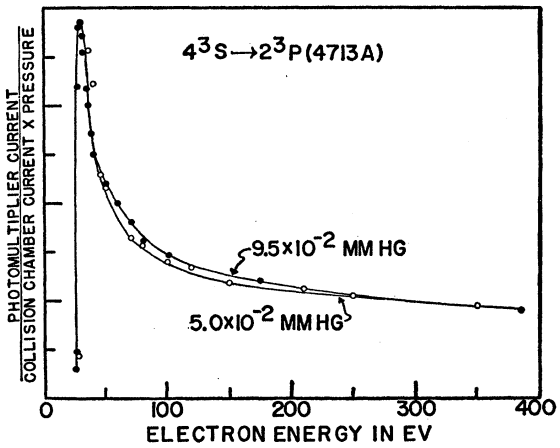

FIG. 4. Photomultiplier current per unit electron current per unit pressure vs electron energy. Transition from $4\,^3S$ to $2\,^3P$. Pressures are 5.0×10^{-2} and 9.5×10^{-2} mm.

IV. MULTIPLE STATE TRANSFER

As stated before, several investigators have attempted explanation of the broad maximum by postulating a transfer of excitation from the ^1P level

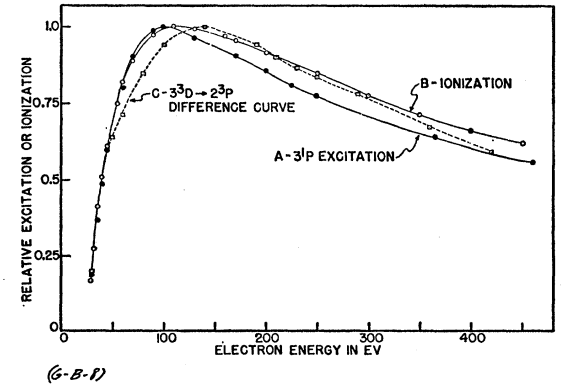

FIG. 5. A. Excitation function of helium $3\,^1P$ level. B. Ionization function of helium. C. Difference in excitation curves at $3\,^3D$ level; the low pressure curve is subtracted from the high pressure curve (see Fig. 1).

nearest the triplet level which yielded the observed light.

There is another and more plausible explanation of the pressure-dependent broad hump which appears in the ^3D transition curves. Atoms in the $1\,^1S$ state (ground state) are excited to the many upper levels by electron impact. At very low pressures these concentrations are depleted by radiative transitions; at high pressures both radiative losses and transfer gains and losses can occur. The singlet P concentrations become very large with increased pressure due to imprisonment of resonance radiation and hence, through the transfer process, can cause a buildup of certain triplet concentrations. The manifold triplet levels thus populated can feed triplet levels beneath them through radiative transitions. Of all the transitions from a particular level, the one with the largest probability is the one in which the l value of the terminal level is one less than that of the initial level and the n value of the terminal level is the smallest in that series of terminal levels. Transition probabilities to other levels in this family become smaller as n increases. Thus, the lower that the level of a family being fed by cascade lies in the energy diagram, the more its population will be augmented despite the fact that considerable transfer is occurring at higher levels.

The cross section for transfer of excitation is expected to increase with n in a complicated fashion. Three physical quantities will mainly determine the variation. First, the gross physical size of the atom may increase as n^4 since the atomic radius increases as n^2. Second, the closeness of resonance between the $n\,^1P$ and an nth triplet level of any series will increase for larger n values. The third effect arises from the spin conservation rule. It is reasonable to expect that the Wigner rule would become less dominant as n increases because of the decreased quantum mechanical exchange interaction between the spins of the excited and inner electrons of the excited atom. The exact dependence of the last two factors is unknown and no speculations concerning them will be made here. Results of calculations based on two dependences on n are presented in the next section. It will be seen that the choice of cross-section dependence has only a mild influence on the distribution of active states required. The purpose of presenting results of calculations based on n^2 and n^4 cross sections is to bring out this fact. The n^4 cross-section dependence, however, seems to be the most acceptable from a physical point of view.

The data presented in Sec. III indicates that ^3D levels are not fed to any significant amount by the direct transfer process, but by cascade from ^3F levels. Figure 4 shows that the $4\,^3S$ level is little affected by transfer, whether by direct transfer from $4\,^1P$ or indirectly through $n\,^1P$ to $n\,^3P$ transfer. Figure 3 shows that the $3\,^3P$ level is little affected by transfer whether by direct transfer, or indirectly through $n\,^1P$ to $n\,^3S$ or $n\,^1P$ to $n\,^3D$ transfer. Figure 1 shows the $3\,^3D$ level

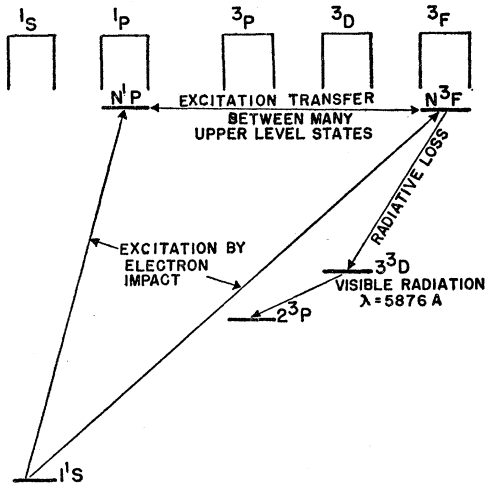

FIG. 6. Helium energy level diagram showing excitation by electron impact, transfer, and radiative transitions.

much affected by transfer, either directly from $3\,^1P$ or indirectly through $n\,^1P$ to $n\,^3P$ or $n\,^1P$ to $n\,^3F$ transfer. The first two of these three possibilities were eliminated by the previous citations, and thus only transfer via the ^3F levels seems feasible. A quantum mechanical development by Lin and Fowler[8] to be reported in a subsequent paper points to a selection rule wherein transfer transitions involving $\Delta l=2$ are favored over others.

V. CALCULATIONS

An analysis of the transfer of excitation through many levels follows. Figure 6 shows the energy level diagram of helium. Atoms in the $1\,^1S$ state (ground state) are excited by electron impact to the many upper levels. For electron energies at 120 ev, the singlet excitations are near their peak while triplet excitations have declined from their peaks. The excited $n\,^1P$ state atoms, in colliding with ground state atoms, will produce $n\,^3F$ atoms.

The cross sections for excitation transfer between two states will be assumed to be inversely proportional to the statistical weights of the states. Thus

$$Q_t(n\,^1P\rightarrow n\,^3F)=[G(n\,^3F)/G(n\,^1P)]Q_t(n\,^3F\rightarrow n\,^1P)=bQ_t,$$

where

$$Q_t=Q_t(n\,^3F\rightarrow n\,^1P) \quad \text{and} \quad b=[G(n\,^3F)/G(n\,^1P)]=7.$$

In the absence of exact knowledge it will be assumed that the cross section for transfer Q_t will be equal to k_2n^2 or k_4n^4. Here k_2 and k_4 are constants and n is the principal quantum number. It is hoped that this range of functions assumed for the cross section will encompass the actual function.

[8] This development was presented in part at the 13th Gaseous Electronics Conference in Monterey, California October 12–15, 1960.

The triplet state atoms are formed by electron impact and transfer of excitation. They may lose their excitation energies either by radiative or collisional transfer processes. The latter process may return the triplet atoms to singlet states or possibly to additional triplet states. The latter transfer possibility will be neglected in these calculations.

The constants k_2 or k_4 in the cross section for transfer of excitation must be evaluated to give the transfer cross sections the values required by the experimentally determined intensity of light emission from the low-level triplet state. Our measurements are of the light emitted from the $3\,^3D$ state and therefore we will confine our calculations and remarks to the process whereby that particular low-level state is populated.

The following equations are those which relate the various population and depopulation rates of the involved states. $n\,^1P$ state:

$$\underset{\substack{\text{electron}\\\text{impact gain}}}{Q(n\,^1P)\frac{I}{e}\frac{N}{S}}+\underset{\substack{\text{transfer}\\\text{gain}}}{NN(n\,^3F)Q_t\bar{c}}+\underset{\substack{\text{regained by}\\\text{imprisonment}}}{f_nN(n\,^1P)A(n\,^1P\rightarrow 1)}=\underset{\substack{\text{transfer}\\\text{loss}}}{NN(n\,^1P)bQ_t\bar{c}}+\underset{\substack{\text{radiative loss}\\\text{except to ground}}}{N(n\,^1P)A'(n\,^1P)}+\underset{\substack{\text{radiative loss}\\\text{to ground}}}{N(n\,^1P)A(n\,^1P\rightarrow 1)}, \quad (2)$$

where f_n is the fraction of resonance quanta which are absorbed in the collision chamber, $A(n\,^1P\rightarrow 1)$ is the transition probability from the $n\,^1P$ state to the $1\,^1S$ state, and $A'(n\,^1P)$ is the sum of all transition probabilities from the $n\,^1P$ state except that to the $1\,^1S$ state.

If $(1-f_n)=g_n$, the fraction of the resonance quanta which escape from the collision chamber, the equation for the $n\,^1P$ state becomes:

$$\underset{\substack{\text{electron}\\\text{impact}}}{Q(n\,^1P)\frac{I}{e}\frac{N}{S}}+\underset{\substack{\text{transfer}\\\text{gain}}}{NN(n\,^3F)Q_t\bar{c}}=\underset{\substack{\text{transfer}\\\text{loss}}}{NN(n\,^1P)bQ_t\bar{c}}+\underset{\substack{\text{net radiative}\\\text{loss}}}{[g_nA(n\,^1P\rightarrow 1)+A'(n\,^1P)]N(n\,^1P)}.$$

Letting $g_nA(n\,^1P\rightarrow 1)+A'(n\,^1P)=A(n\,^1P)$, the total transition probability for the $n\,^1P$ state, the $n\,^1P$ equation becomes:

$$Q(n\,^1P)\frac{I}{e}\frac{N}{S}+NN(n\,^3F)Q_t\bar{c}=NN(n\,^1P)bQ_t\bar{c}+A(n\,^1P)N(n\,^1P). \quad (2')$$

$n\,^3F$ state:

$$\underset{\substack{\text{electron}\\\text{impact gain}}}{Q(n\,^3F)\frac{I}{e}\frac{N}{S}}+\underset{\substack{\text{transfer}\\\text{gain}}}{NN(n\,^1P)bQ_t\bar{c}}=\underset{\substack{\text{transfer}\\\text{loss}}}{NN(n\,^3F)Q_t\bar{c}}+\underset{\substack{\text{radiative}\\\text{loss}}}{N(n\,^3F)A(n\,^3P)}. \quad (3)$$

$n\,^3P$ state:

$$\underset{\substack{\text{electron}\\\text{impact gain}}}{Q(n\,^3P)\frac{I}{e}\frac{N}{S}}=\underset{\substack{\text{radiative}\\\text{loss}}}{N(n\,^3P)A(n\,^3F)}. \quad (4)$$

$3\,^3D$ state:

$$\underset{\substack{\text{electron}\\\text{impact gain}}}{Q(3\,^3D)\frac{I}{e}\frac{N}{S}}+\underset{\substack{\text{gain by cascade}\\\text{from }^3F}}{\sum_{n=4}^{\infty}N(n\,^3F)A(n\,^3F\rightarrow 3\,^3D)}+\underset{\substack{\text{gain by cascade}\\\text{from }^3P}}{\sum_{n=4}^{\infty}N(n\,^3P)A(n\,^3P\rightarrow 3\,^3D)}=\underset{\substack{\text{radiative}\\\text{loss}}}{N(3\,^3D)A(3\,^3D)}. \quad (5)$$

The $3\,^3D$ state equation may be rewritten as follows:

$$\sum_{n=4}^{\infty}N(n\,^3F)A(n\,^3F\rightarrow 3\,^3D)=N(3\,^3D)A(3\,^3D)-Q(3\,^3D)\frac{I}{e}\frac{N}{S}-\sum_{n=4}^{\infty}N(n\,^3P)A(n\,^3P\rightarrow 3\,^3D). \quad (5')$$

In these equations the cascading into the nth level from a higher level is neglected, and the direct transfer of excitation from $3\,^1P$ to $3\,^3D$ is assumed negligible. When the equations of the nth state are solved in terms of the density of the ^3F series member one obtains:

$$N(n\,^3F)=\frac{\dfrac{[Q(n\,^1P)+Q(n\,^3F)]INb}{eSA(n\,^1P)}+\dfrac{Q(n\,^3F)I}{Q_teS\bar{c}}}{1+b\dfrac{A(n\,^3F)}{A(n\,^1P)}+\dfrac{A(n\,^3F)}{NQ_t\bar{c}}}.$$

In these expressions, I is the electron current and N is the density of normal atoms. The results which follow are for a helium pressure of 5×10^{-2} mm. S is the electron beam cross section and is determined by the geometry of the electron gun. $\bar{c}$ is the mean relative velocity of helium atoms at room temperature; a value of 1.78×10^5 cm/sec was used. The value of $N(3\,^3D)$ was determined by comparing the light output from the collision chamber with that from a standard lamp. A symbol such as $A(n\,^3F)$ represents the sum of probabilities for transitions out of the $n\,^3F$ state. The transi-

tion probabilities are theoretical.[9,10] Values involving $n>8$ are extrapolated from the tabulated values. The excitation cross sections from the ^1P states are based on the data of St. John, Bronco, and Fowler for the $3\,^1P$ state.[7] An n^{-3} dependence is assumed.[11] The values thus obtained are in good agreement with those of Thieme.[12] The cross sections for direct excitation to the $n\,^3F$ states by electron impact are approximations which were obtained by extrapolation from Thieme's data on ^3S, ^3P, and ^3D states. The expression used herein is:

$$Q(n\,^3F)=(2.0\times10^{-18}/n^3)\text{ cm}^2.$$

At pressures low enough that transfer of excitation is negligible (i.e., when the secondary peak on the excitation function is negligible), one may determine $Q(3\,^3D)$. This value is used in the $Q(3\,^3D)(IN/eS)$ term when higher pressures are used. At 120 ev, $Q(3\,^3D)$ is 6.0×10^{-20} cm^2. This value is not to be regarded as having great accuracy, as the cross sections for excitation by electron impact to the ^3F level are approximations only. Had the excitation to the ^3F levels been considered negligible, with the $3\,^3D$ state filled by direct excitation and cascading from ^3P states, the cross section would have been approximately one and one half times as large as the value given here. However, the actual value of $Q(3\,^3D)$ is of very minor importance in determining the transfer cross sections; only the total populating effects of direct excitation to the $3\,^3D$ level and direct excitation to the low ^3F levels are of importance.

The values of g_n for use in this analysis were, for the first set of calculations, determined from the results of Phelps.[13] The effective radius of the collision chamber was assumed to be 1.0 cm, a value slightly smaller than the actual radius. The imprisonment of resonance radiation is greatest for radiation emitted from low ^1P states; imprisonment effects cease to exist when the n value of the resonance level exceeds 14. Such results will be called "partial imprisonment" results.

A second set of quantitative calculations was made in which it was assumed that imprisonment of all resonance radiation was complete ($g_n=0$). These yield "complete imprisonment" results. The basis of this assumption is derived from an inspection of the data shown in Fig. 2. The photomultiplier current per pressure vs pressure has virtually reached a saturation value at a pressure of 0.05 mm. This suggests that the slight increase in density of ^3F atoms per gas density noted as higher pressures is due to the increased number of ^3F levels which are near saturation rather than due to the compounded effect of an increase in the imprisonment of the ^1P atoms and an increase in the number of ^3F states which are near saturation.

TABLE I. Calculated cross sections in cm^2 for transfer of excitation from an $n\,^1P$ state to an $n\,^3F$ state.

	Complete imprisonment		Partial imprisonment	
n	$1.54\times10^{-18}n^4$	$5.9\times10^{-17}n^2$	$4.7\times10^{-18}n^4$	$14\times10^{-17}n^2$
4	0.39×10^{15}	0.94×10^{15}	1.2×10^{15}	2.24×10^{15}
5	0.96×10^{15}	1.48×10^{15}	2.9×10^{15}	3.5×10^{15}
6	2.0×10^{15}	2.1×10^{15}	6.1×10^{15}	5.0×10^{15}
7	3.7×10^{15}	2.9×10^{15}	11.3×10^{15}	6.9×10^{15}
8	6.3×10^{15}	3.8×10^{15}	19.2×10^{15}	9.0×10^{15}
9	10.1×10^{15}	4.8×10^{15}	31×10^{15}	11.3×10^{15}
10	15.4×10^{15}	5.9×10^{15}	47×10^{15}	14.0×10^{15}
11	22.5×10^{15}	7.1×10^{15}	69×10^{15}	16.9×10^{15}
12	32.0×10^{15}	8.5×10^{15}	97×10^{15}	20.1×10^{15}
13	44.0×10^{15}	10.0×10^{15}	134×10^{15}	23.8×10^{15}
14	59.1×10^{15}	11.6×10^{15}	179×10^{15}	27.8×10^{15}
15	77.9×10^{15}	13.3×10^{15}	238×10^{15}	31.5×10^{15}

VI. RESULTS OF CALCULATIONS

The above equations and data yield cross sections for transfer from $n\,^1P$ to $n\,^3F$ of $1.4\times10^{-16}n^2$ and $4.7\times10^{-18}n^4$ cm^2 for the partial imprisonment assumption. The reverse transfer from $n\,^3F$ to $n\,^1P$ with partial imprisonment have cross sections of $2.0\times10^{-17}n^2$ and $6.8\times10^{-19}n^4$ cm^2. Calculations based on the assumption of complete imprisonment of radiation yield cross sections of transfer from $n\,^1P$ to $n\,^3F$ of $5.9\times10^{-17}n^2$ and $1.54\times10^{-18}n^4$ cm^2, and cross sections for the reverse transfer of $8.5\times10^{-18}n^2$ and $2.2\times10^{-19}n^4$ cm^2. The forward cross sections are tabulated as a function of n in Table I. The results of the partial imprisonment calculations almost certainly represent an upper limit on the transfer cross sections. Even in this case, the cross sections of low states have values near the gas-kinetic value of 1.5×10^{-15} cm^2, and are in harmony with the Wigner rule.

In Eq. (5′) the right-hand members are experimentally determinable while the left side is composed of a series of functions of the transfer cross section. Each left side member is a measure of the amount its respective $n\,^3F$ state contributes to the $3\,^3D$ population through both transfer and electron impact. When each left-side member is evaluated with $N\rightarrow0$ (no transfer of excitation), it is a measure of the contribution of the $n\,^3F$ state due to electron impact alone. Subtraction of these values yields the transfer contribution of the nth term. The transfer contribution of each term expressed as a percent of the entire amount transferred, is plotted in Fig. 7 for each form of the transfer cross section for the partial imprisonment calculation. States with n between 4 and 15 handle more than 95% of the transferred excitation. In both cases, states above $n>15$ contribute little to the populating of the $3\,^3D$ level.

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For states of $n>15$, the transfer contribution is very nearly equal for both dependences and is proportional to n^{-4}. In this high n range the summation was replaced by an intergration process. Figure 8 shows the transfer contributions of the various n levels for the complete imprisonment case. States with n between 4 and 15 handle more than 90% of the transferred excitation.

It is seen that the n dependence of the transfer cross section may vary within rather wide limits, and still allow the cross section for any state of low n value to be of an acceptably small size. The authors feel that a cross section initially proportional to n^4, but saturating at a constant value or even decreasing for large n, is probably the most nearly like the actual cross section. For n values great enough to cause atoms to overlap one another (if their physical size were that given by the transfer cross section), the cross section dependence on n might be expected to break down and the cross section itself become as small as that of the incident normal atom. In this realm of n it is more a case of a neutral atom colliding with an electron than with an excited atom.

The physical fact accounting for the fact that the transfer contribution of the high n states is insensitive to the cross-section dependence on n is that the cross section is high for any of the dependences assumed. A large cross section causes the high triplet states to be saturated; this being the case transfer transitions back and forth from the high triplet and singlet states heavily outnumber radiative transitions.

Up to this point two calculations have been made for the proposed multiple state transfer process, which might be regarded as giving lower bounds on the process. Thus, despite the uncertainty which exists about selection rules, collision cross sections, and transition probabilities when the principal quantum number is so large ($n>15$) that the classical orbital dimensions of the atom exceed the interatomic distances, all rules and formulas found for small n have been extrapolated boldly. Still a third calculation was performed which has the nature of an upper bound on the theory; it was assumed that no selection rules at all operate except the rule that direct electron excitation from the $1\,^1S$ state to the triplet states is substantially less probable (owing to the need for exchange) than to the upper singlet states. This rule is a result of the original structure of the $1\,^1S$ state and will be assumed to be retained for large n.

In making this third calculation we assumed that the collision process can be treated as a collision between a free electron (the excited orbital electron) and the neutral colliding $1\,^1S$ atom and hence is independent of n for transfers between non-degenerate levels. Furthermore it was assumed that imprisonment of resonance radiation emitted from the levels with $n>15$ is negligible for a pressure of 5×10^{-2} mm. The result of the calculation is that only the states with n values between 15 and 24 are needed to explain the observed onset of transfer at a pressure of 6×10^{-3} mm, and the observed saturation of transfer at 5×10^{-2} mm, and that a transfer cross section as small as $8\times10^{-19}n^2$ cm^2 between levels of n^2-fold degeneracy will account for the amount of transfer observed. Further tests of this

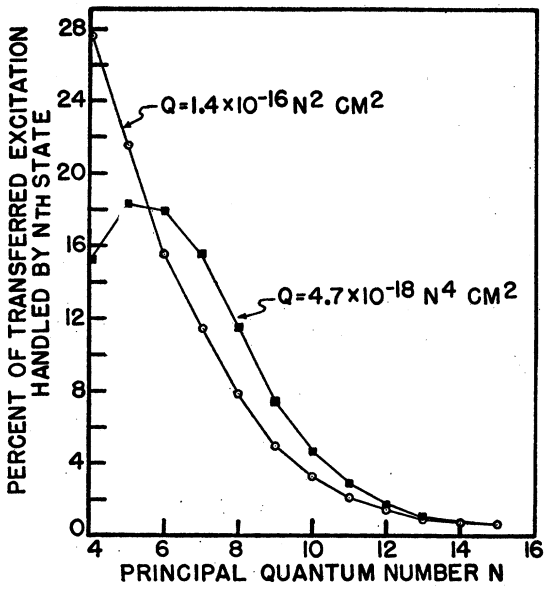

FIG. 7. Percent of transferred excitation handled by nth state in populating the $3\,^3D$ level; partial imprisonment of resonance radiation.

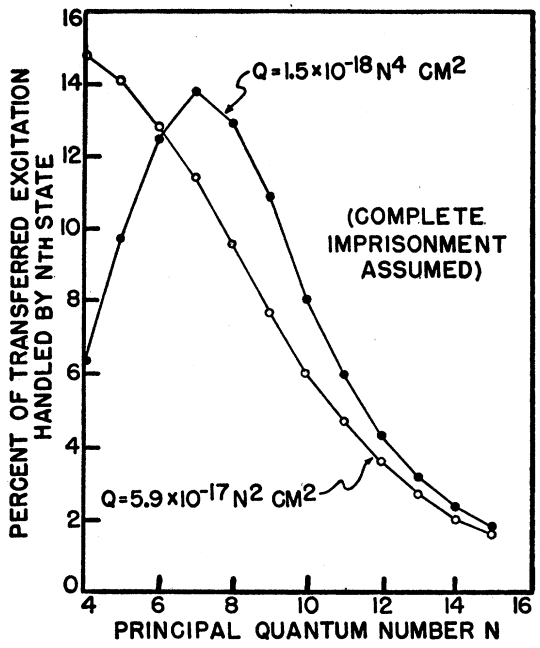

FIG. 8. Percent of transferred excitation handled by nth state in populating the $3\,^3D$ level; complete imprisonment of resonance radiation assumed.

new theory would be desirable. Since the transfer through the upper states should be strongly dependent upon the cutoff of large n values by ionizing collisions, which in turn depends on the gas temperature, it is a deduction that the proposed process should be strongly temperature dependent, and experiments to test this are now in process.

Two pieces of experimental evidence exist which indicate that the third process may be preferable to the other two. First, when the transfer cross section curve is obtained by subtracting the measured direct excitation to the $3\,^3D$ state from the gross excitation, it is found that in respect to its shape and the location of its maximum, it resembles more the ionization cross section curve than the direct cross section for $3\,^1P$. (See Fig. 5.) It would be anticipated that cross-section curves for quantized states near the ionization level would trend toward the ionization curve in shape and hence transfer through the high states should bear out this resemblance. Second, the third process is independent of imprisonment effects in the pressure range examined and will allow a faster saturation of the gross excitation curve with increasing pressure than the first process. The experimental curve (see Fig. 2) seems to indicate that the transfer effect is in fact nearly saturated at 5×10^{-2} mm.

We thus conclude that by invoking the transfer process through the upper states the apparent violations of the Wigner rule at least can be minimized if the selections rules are merely extrapolated, and can be removed if the selection rules do not hold. Effort is now being directed to the theory of the high quantum states in the presence of perturbations to endeavor to refine the process proposed.

VII. APPLICATION TO EARLY RESULTS

The multiple state excitation transfer explanation can account for all observed experimental results mentioned to this point in this paper. Qualitative explanations of a number of points will be given.

Lees noted that both the relative spreading of a line originating from a ^3D level and the size of the broad peak relative to the narrow "triplet" peak of the excitation function of this line increased with n. The narrow peak is caused by direct excitation into the triplet states and this varies inversely as n^3. The broad peak is dependent on high level ^3F states radiating into the $n\,^3D$ level. The probability for a transition such as this varies inversely approximately as n^2. This combination of effects will cause the broad peak to drop more slowly than the narrow peak as n increases. Also the diffuse part of the beam, having its real origin in the imprisoned resonance radiation, will by the same reasoning, dominate the direct excitation portion as n increases.

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