Collisional Excitation Transfer to the $4\,^1D$ State in Helium by Multiple State Mechanism*

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The electron-excitation function of the $4\,^1D$ state of helium has been measured at various pressures by means of an automatic processing system. The peak of the curve shifts gradually from 50 eV to 100 eV as the pressure is increased due to the collision transfer from the ^1P states. The transfer can be explained by the multiple state mechanism. Based on this theory the calculated population of the $4\,^1D$ state at 7.4×10^{-2} mm pressure agrees quite well with experiments. The observed amount of transfer from n ^1P states to $4\,^1D$ and to $4\,^3D$ are of the same order of magnitude as predicted by the theory. The results of this work provide strong support for the multiple state transfer process.

I. INTRODUCTION

IT has been known for many years that the secondary peak in the electron-excitation function of the $3\,^3D$ state of helium at high pressures is related to the transfer of excitation by collision from a singlet to a triplet state. Lees and Skinner[1] suggested that the reaction

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

is responsible for the singlet-triplet transfer. However, direct transfer processes of this type violate the Wigner spin conservation rule which is expected to hold for states with low principal quantum number.[2] Furthermore, in order to account for the experimental observations quantitatively, it is necessary to assume a cross section as large as 4.5×10^{-14} cm^2 which is 30 times larger than the kinetic value. To overcome this difficulty, St. John and Fowler[3] suggested that the increased population of the $3\,^3D$ is not due to the direct transfer from $3\,^1P$, and proposed a multiple state transfer to explain the anomalously large singlet-triplet transfer. A theoretical justification and approximate calculations of the transfer cross sections have been given by Lin and Fowler.[4] In this multiple state scheme it has been shown that the helium atoms, which are excited to the high $n\,^1P$ states, transfer primarily to the nF states by colliding with a normal atom.[3,4] Since the spin-orbit coupling constants become larger than the exchange integrals for the F states, the Russell-Saunders coupling scheme breaks down with the result of a substantial singlet-triplet mixing in these states. Because of the mixed singlet and triplet "character," the atoms in the nF states then can cascade to the $3\,^3D$. Thus, through the intermediary of the "mixed" nF states, an atom might transfer from an $n\,^1P$ to $3\,^3D$ without violating the Wigner rule. The transfer cross sections relating to the $3\,^3D$ state calculated by the multiple state theory are in good agreement with the experimental values.

According to the multiple state transfer theory, part of the atoms in the nF states will cascade to the $n\,^1D$ series. This effect would result in a pressure-dependent transfer between the ^1P states and an $n\,^1D$ state. The effect should manifest itself in the form of a curve with a broad maximum at 100 eV (^1P) being added to the curve characteristic of the $n\,^1D$ state at low pressures. The latter curve has a rather broad maximum at 50 eV. Due to the broadness of the maxima of these curves, and their separation of only 50 eV, their sum tends to show but a single maximum whose location depends upon the relative amplitudes of the two curves.

In this paper, we shall report some measurements of the excitation function of the $4\,^1D$ state. The results are interpreted by means of the multiple state process. It is shown that the excitation transfer from the ^1P states to the $4\,^1D$ state observed in this work offers additional support of the multiple state theory.

II. EXPERIMENTAL METHOD AND RESULTS

Attempts were first made to detect the pressure-dependent peaking of the excitation function of the $4\,^1D$ state by measuring the intensities of the $4\,^1D\rightarrow 2\,^1P$ (4922 Å) radiation[5] at various excitation voltages with the apparatus used for the previous work in this laboratory.[3,6] Because of the fluctuations in the photomultiplier output, the results were rather ambiguous. For this experiment, we have constructed a system which automatically processes optical excitation data with a filter device to suppress the background noise. The use of this apparatus not only improves the experimental sensitivity but also replaces the rather tedious point-by-point data gathering procedure by a continuous recording.

* Supported by the Air Force Office of Scientific Research.

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

[2] E. Wigner, Nachr. Ges. Wiss. Gottingen 375 (1927); H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), p. 427.

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

[4] C. C. Lin and R. G. Fowler, Ann. Phys. (New York) **15**, 461 (1961).

[5] The frequency of the $3\,^1D\rightarrow 2\,^1P$ is somewhat too low to be detected accurately by a photomultiplier having an S-13 type response.

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

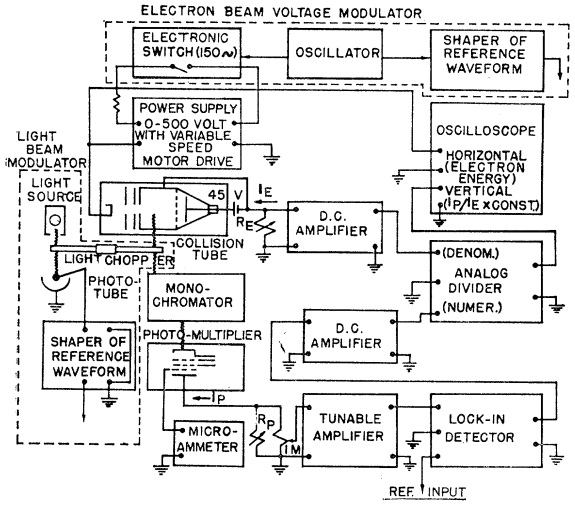

FIG. 1. Collision tube, detection system, and data processing system. Only one modulation system is used at a time.

In Fig. 1 is shown a block diagram of the collision tube, the detection system, and the data processing system. Details of the structure of the collision tube can be found in reference 6. The power supply of the electron beam is swept over the range of 0–500 V by means of a variable speed (period from 1 to 20 min) motor drive to give a tracing of the excitation function. In order to suppress photomultiplier noise and background current, the photomultiplier output is modulated at a rate of 150 cps. The modulation process can be accomplished either by chopping the light beam passing from the excitation chamber to the monochromator or by turning the electron beam voltage on and off 150 times per second while the voltage supply is being slowly swept through its entire range. Both schemes are included in Fig. 1, although only one modulation unit is used at a time.

The modulated photomultiplier output is amplified and detected by a lock-in detector[7] of very small bandwidth which is synchronized by a reference voltage generated by the modulating devices. The detected output is further amplified and fed to the numerator input of an analog divider. The denominator input of this divider is connected to a voltage which is proportional to the electron beam current. The analog divider then delivers a signal proportional to the ratio of the photomultiplier current to the electron beam current which is fed to the oscilloscope to give a continuous trace of the excitation function. Absolute values of the excitation function can be obtained by calibration against a standard lamp.[8]

The excitation function for $4\,^1D$ at various pressures is reproduced in Fig. 2. It is seen that the peak gradually shifts from 50 to 100 eV as the pressure increases. At low pressure, the total excitation cross section has a rather wide peak at 50 eV. Thus, when the contributions of the $n\,^1P$ states to the $4\,^1D$ state are included at higher pressure, only a shift of the peak (rather than two maxima as in the case of $3\,^3D$) is observed. The form of the excitation function at high pressure can indeed be fitted quite well into the sum of two curves, one having the shape of the $4\,^1D$ curve (low pressure) and the other the shape of an $n\,^1P$ curve.

From the absolute calibration the number of atoms in the $4\,^1D$ state is found to be $3.5\times10^5/\text{cm}^3$ at a pressure of 7.4×10^{-2} mm and electron beam current 100 μA and electron energy of 100 eV. This number will be compared with the calculated value in the next section.

III. CALCULATIONS

The theoretical analysis of the population of the $3\,^3D$ state has been made in two different ways. St. John and Fowler[3] assumed the cross sections for the collision transfer $n\,^1P \rightarrow n\,^3F$ to have the empirical form of either k_2n^2 or k_4n^4. From the experimental value of the density of atoms in the $3\,^3D$ state, it is possible to determine k_2 and k_4. In a more rigorous treatment given subsequently,[4] the collision cross sections for $n\,^1P \rightarrow nF$ are calculated by the semiclassical method developed by Stueckelberg.[9] These then give the

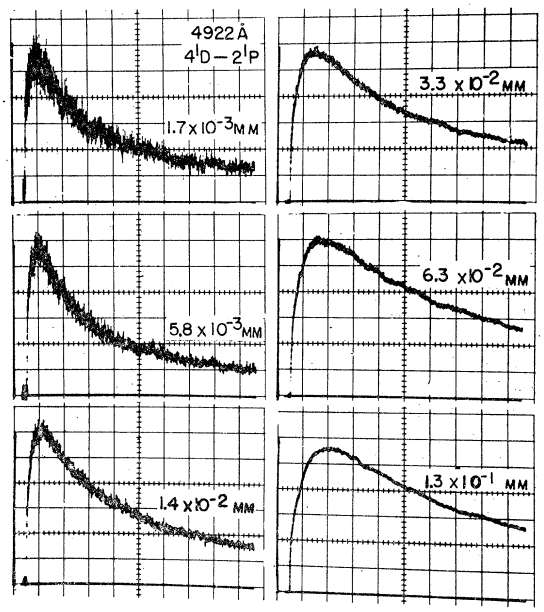

FIG. 2. Excitation function of $4\,^1D$ for pressures ranging from 1.7×10^{-3} to 1.3×10^{-1} mm. Ordinates represent the apparent cross section; the maximum value of the cross section for each pressure is given in Table II. Abscissas represent electron energy, 0–500 eV.

[7] See, for example, E. A. Rinehart, R. H. Kleen, and C. C. Lin, J. Mol. Spectroscopy **5**, 458 (1960).

[8] 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).

[9] E. C. G. Stueckelberg, Helv. Phys. Acta. **5**, 370 (1932); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collision* (Oxford University Press, New York, 1949), 2nd ed., p. 150.

TABLE I. Observed and calculated population density of helium atoms in the D states (in units of atoms/cm^3). Pressure $=7.4\times10^{-2}$ mm Hg; electron beam current $=100\,\mu$A; electron energy $=100$ eV.

States	Density observed	Density calculated
$4\,^1D$	3.5×10^5	3.5×10^5
$3\,^3D$	2.3×10^5	3.7×10^5
$4\,^3D$	1.8×10^5	2.5×10^5

concentrations of the atoms in the various nF states from which the population of the $3\,^3D$ state is found. In this paper we shall follow the latter approach.

The equation which relates the population and depopulation rates of the $4\,^1D$ state is

$$Q(4\,^1D)\frac{I_eN(g)}{eS}+\sum_{n=5}^{\infty}N(nF)A(nF\rightarrow 4\,^1D)$$

$$+\sum_{n=5}^{\infty}N(n\,^1P)A(n\,^1P\rightarrow 4\,^1D)=N(4\,^1D)A(4\,^1D), \quad (2)$$

where $Q(4\,^1D)$ is the direct excitation cross section, $N(j)$ is the number of atoms per cm^3 in the jth state, $A(i\rightarrow j)$ is transition probability from state i to j, and $A(j)$ is the total transition probability from the jth state to all the lower levels. The cross sectional area of the electron beam is S, the electron current is I_e, and the electronic charge is e. When use is made of data taken at pressures low enough that transfer and imprisonment effects are negligible, Eq. (2) can be used for determining $Q(4\,^1D)$ as follows: The right-hand member of the equation is measured experimentally. Transition probabilities used were those compiled by Gabriel and Heddle.[10] In order to compute the densities $N(n\,^1P)$, use was made of the measured cross section for the $3\,^1P$ state[6] along with the assumption of an n^{-3} dependence for higher states. In the case of the nF states, no direct measurements of cross sections have been made; thus, we have resorted to an extrapolation from the data of the S, P, and D states reported by Thieme.[11] In this way $Q(4\,^1D)$ was determined to be 3.1×10^{-20} cm^2.

We are now in a position to calculate the population density of $N(4\,^1D)$ from Eq. (2) at the pressure of 7.4×10^{-2} mm. Here, the values of $N(nF)$ and $N(n\,^1P)$ are no longer proportional to the gas pressure because of the transfer and imprisonment effects. The atomic densities $N(nF)$ have been calculated in the earlier work.[4] Using an equation analogous to that of Eq. (2′) of reference 3, we can determine $N(n\,^1P)$. From the value of $Q(4\,^1D)$ given in the previous paragraph, $N(4\,^1D)$ is obtained as 3.5×10^5 cm^{-3} at 7.4×10^{-2} mm pressure. The exact agreement between this theoretical value and the experimental value given in Sec. II must be regarded as somewhat fortuitous in view of the approximate nature of the theory as well as the uncertainty in some of the excitation cross sections used in the cascade computation.

[10] A. H. Gabriel and D. W. O. Heddle, Proc. Roy. Soc. **A258**, 124 (1960).

[11] O. Thieme, Z. Physik **78**, 412 (1932).

IV. TRIPLET D STATES

Populations of the $3\,^3D$ and $4\,^3D$ states were experimentally measured and theoretically determined by the methods outlined in previous sections. These results and those of the $4\,^1D$ state are summarized in Table I. The figures for the $3\,^3D$ state vary slightly from those given in reference 4 but are believed to be more accurate due to an improvement in technique.

Figure 3 shows the excitation function of the $3\,^3D$ state of helium at pressures ranging from 1.7×10^{-3} to 0.13 mm. Figure 4 shows similar data for the $4\,^3D$ state. Absolute values of the maximum of the excitation function for each pressure are given in Table II for the $4\,^1D$, $3\,^3D$, and $4\,^3D$ states.

V. DISCUSSION

The agreement between theory and experiment on the population of the helium atoms in the various D states, as shown in Table I, is quite satisfactory. It is concluded that the appearance of a peak at 100 eV in each excitation function at high pressure can be explained successfully by the multiple state transfer

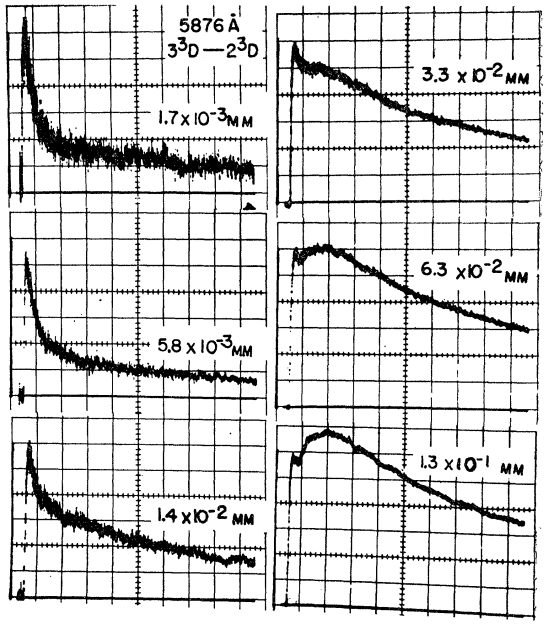

FIG. 3. Excitation function of $3\,^3D$ for pressures ranging from 1.7×10^{-3} to 1.3×10^{-1} mm. Ordinates represent the apparent cross section; the maximum value of the cross section for each pressure is given in Table II. Abscissas represent electron energy, 0–500 eV.

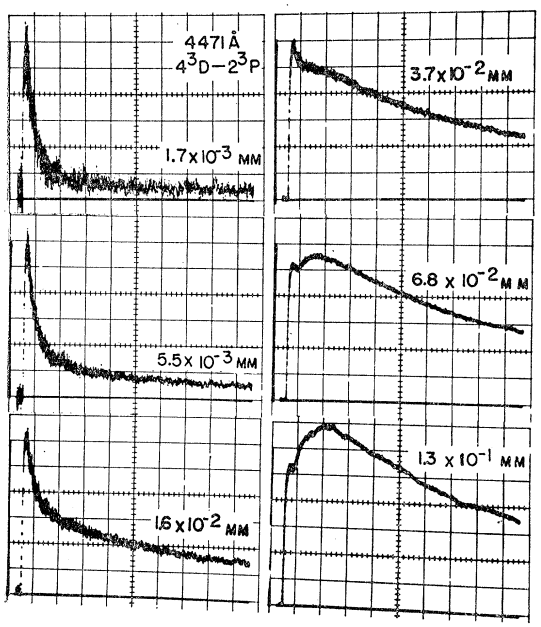

FIG. 4. Excitation function of $4\,^3D$ for pressures ranging from 1.7×10^{-3} to 1.3×10^{-1} mm. Ordinates represent the apparent cross section; the maximum value of the cross section for each pressure is given in Table II. Abscissas represent electron energy, 0–500 eV.

mechanism. Of particular interest is that experimentally the amount of transfer of $n\,^1P\rightarrow 4\,^1D$ and of $n\,^1P\rightarrow 4\,^3D$ are of the same order as is predicted by the theory.[4] A large part of the difference between the observed values of $N(j)$ between $4\,^1D$ and $4\,^3D$ in Table I is due to the fact that the direct excitation cross section for $4\,^1D$ is considerably greater than $4\,^3D$. To demonstrate this point we have found, by extrapolating from the low-pressure data, that at 7.4×10^{-2} mm pressure the observed population density of $4\,^1D$ would have been 1.3×10^5 cm^{-3} if there were no collision transfer. The corresponding quantity for $4\,^3D$ is 0.22×10^5 cm^{-3}.

Our results, therefore, lend a strong support to the multiple state mechanism. If one were to assume that the transfer is due to direct processes as in Eq. (1), it would be difficult to understand why the two reactions

$$\mathrm{He}(1\,^1S)+\mathrm{He}(4\,^1P)\rightarrow\mathrm{He}(1\,^1S)+\mathrm{He}(4\,^1D), \quad (3)$$

$$\mathrm{He}(1\,^1S)+\mathrm{He}(4\,^1P)\rightarrow\mathrm{He}(1\,^1S)+\mathrm{He}(4\,^3D), \quad (4)$$

should have about the same cross sections when one of them violates the Wigner spin rule but not the other. For instance, the Coulomb interactions between the electrons and nuclei of one helium atom with the other provide the necessary transition matrix elements for the first reaction to take place. On the other hand, to effect *direct* collision transition from $4\,^1P$ to $4\,^3D$ one has to invoke the interatomic spin-orbit coupling, i.e., the interaction of the spin of the np electron in the excited atom with the orbital motion of the electrons

TABLE II. Maximum values of apparent cross sections shown in the excitation functions of Figs. 2, 3, and 4.

$4\,^1D$		$3\,^3D$		$4\,^3D$	
Pressure (mm Hg)	Cross section (cm²)	Pressure (mm Hg)	Cross section (cm²)	Pressure (mm Hg)	Cross section (cm²)
1.7×10^{-3}	9.3×10^{-20}	1.7×10^{-3}	19.5×10^{-20}	1.7×10^{-3}	5.8×10^{-20}
5.8×10^{-3}	9.9×10^{-20}	5.8×10^{-3}	23.0×10^{-20}	5.5×10^{-3}	6.4×10^{-20}
1.4×10^{-2}	12.4×10^{-20}	1.4×10^{-2}	27.1×10^{-20}	1.6×10^{-2}	7.5×10^{-20}
3.3×10^{-2}	15.2×10^{-20}	3.3×10^{-2}	28.6×10^{-20}	3.7×10^{-2}	9.3×10^{-20}
6.3×10^{-2}	19.4×10^{-20}	6.3×10^{-2}	34.0×10^{-20}	6.8×10^{-2}	10.6×10^{-20}
1.3×10^{-1}	22.0×10^{-20}	1.3×10^{-1}	47.0×10^{-20}	1.3×10^{-1}	17.3×10^{-20}

in the normal atom. These two types of interactions should yield cross sections which are vastly different.

At first thought it might seem that the shift of the peak of the excitation function in the $4\,^1D$ state could be explained by cascading from the directly excited ^1P states. The imprisonment effect of the ^1P states might account for the pressure dependence of the location of the peak. The rate of gain of the $4\,^1D$ state due to this process is

$$\sum_{n=5}^{\infty} N(n\,^1P)A(n\,^1P\rightarrow 4\,^1D).$$

Calculations show, however, that this amounts to only 5% of the experimental value. Another argument which rules out this explanation is that no 100 eV peaking is observed in the excitation function of the $4\,^1S$ state which should receive more cascading from ^1P states since the transition probabilities of $n\,^1P\rightarrow 4\,^1S$ transitions are much larger than those of the corresponding $n\,^1P\rightarrow 4\,^1D$ transitions.

Finally, one might wish to examine the amount of $4\,^1D$ population as contributed by the direct transfer process from $4\,^1P$ to $4\,^1D$, as shown in reaction (3), which has been neglected in our analysis. In fact, direct transfer of excitation of this sort has been used by Gabriel and Heddle[10] to explain the pressure-dependent population of the ^1D states. Although our experiments do not discriminate between the direct transfer process and the multiple state mechanism, the results here suggest that the contribution from the former is small compared to that from the latter. If we assume complete single-triplet mixing in all the F states, both the $4\,^1D$ and $4\,^3D$ states would be fed by the nF states through cascading at the same rate. Since the total transition probability of the $4\,^3D$ state to all the lower states is 31.1×10^6 sec^{-1} and that of $4\,^1D$ is 26.4×10^6 sec^{-1}, the ratio of the population of $4\,^1D$ to $4\,^3D$, which results from the multiple state transfer process, is 1.18. The actual amount of the singlet-triplet mixing can be estimated from the relative magnitude of the spin-orbit coupling constant to the exchange integral. Using the numerical values of these quantities given in reference 4, we obtain the mixing ratio of $5\,^1F$ to $5\,^3F$ as 1.19. This number will become closer to unity for the higher nF states. Using, however, a mixing ratio of 1.19 for

all the nF states, a ratio of 1.67 would result for the population of the $4\,^1D$ to $4\,^3D$ state due to the multiple state transfer process. The actual value of the population ratio should thus lie between 1.18 and 1.67. To compare this with our experimental data we first subtract from the measured atomic densities of $4\,^1D$ and $4\,^3D$ the amount of population produced by direct excitation and cascading from the P states. In this manner we obtain 1.4 as the ratio of the population of $4\,^1D$ vs $4\,^3D$ due to collisional excitation transfer only. The close agreement here indicates that the multiple transfer process is responsible for the major part of the pressure-dependent population of the $4\,^1D$ state.

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Complex Refractive Index of an Ideal Monatomic Gas*

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The main results of some previous work of the author on this subject are rederived in a more rigorous fashion. In particular, no appeal is made to perturbation theory or to the author's "damping operator" formalism, and closer attention is paid to the question of proper averaging over configurations of absorbers. All effects due to translational motion of absorbers are neglected, but the dipolar "resonance" interactions are included. It is shown that the formal results of the previous work, which permit a detailed calculation of the absorption line shape, are valid under the following assumptions: (a) The average optical behavior of the gas is describable in terms of a refractive index; (b) there is no correlation between the positions of different absorbers, i.e., the gas is ideal. However, it is also shown that the cutoff procedure for handling a divergent integral which appears in the theory must be modified. The modified cutoff procedure leads to a large increase in the theoretically predicted linewidth, in qualitative agreement with experiment.

I. INTRODUCTION AND SUMMARY

In a previous pair of papers,[1] the author has presented a theory of the complex refractive index of an ideal monoatomic gas. The treatment ignored effects of translational motion of the absorbers (atoms), but included the dipolar "resonance" interactions between different absorbers. The formalism used was that of "damping operators," previously introduced by the author.[2] The calculated formula for the linewidth was in agreement with previous theories,[3] but not with recent experiments.[4]

There are two possible grounds on which the results of A and B might be questioned. First, there is the "damping operator" formalism itself. This formalism, while not particularly difficult, is nevertheless unfamiliar to most physicists, and might be regarded with suspicion by some on that account. A more solid basis for skepticism is the fact that the development of the formalism[2] depends on a number of rearrangements of the perturbation theory expansion for the true stationary state; it follows that the basic equations for the damping operators have been rigorously derived only for the case where the perturbation expansion converges absolutely, though the author feels that they are probably valid under more general conditions.

The second ground for doubt concerns the question of averaging. To make this clear, we note that in the quantum mechanical formalism the phenomenological Maxwell equations are supposed to be obeyed in some sense by those matrix elements of the various field operators which correspond to creation or destruction of a "dressed" photon. For example, the refractive index $\rho(\nu_\lambda)$ is defined by

$$4\pi\langle 0|P_i(\mathbf{r})|\tilde{\lambda}\rangle=[\rho^2(\nu_\lambda)-1]\langle 0|E_i(\mathbf{r})|\tilde{\lambda}\rangle, \qquad (1)$$

where $|0\rangle$ is the ground state (no absorbers excited, no photons present), and $|\tilde{\lambda}\rangle$ is a dressed photon state. $P_i(\mathbf{r})$ and $E_i(\mathbf{r})$ are the operators for the i-component of dipole moment density and electric field, respectively, at the point $\mathbf{r}$. (For further details on notation, see Secs. A-II and A-IV.) The matrix elements appearing on both sides of Eq. (1) are to be interpreted as averages of some kind; and in the case of a gas with translational motion neglected, the average should be over all allowed spatial configurations of the absorbers. Once this average is taken, there is no need for the customary further averaging over a "physically small" region; the necessary "smoothing out" is already accomplished

* This work was supported in part by the U. S. Air Force Office of Scientific Research, through Contract No. AF 49(638)-940.
[1] C. A. Mead, Phys. Rev. **120**, 854, 860 (1960), hereafter denoted by A and B, respectively. Equations from these papers will be referred to by expressions such as (A-3) meaning Eq. (3) of A; sections will be similarly denoted; e.g., Sec. B-II is Sec. II of B.
[2] C. A. Mead, Phys. Rev. **112**, 1843 (1958).
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[4] J. Tomiser, Acta Phys. Austriaca **8**, 198 (1953); **8**, 276 (1954); **8**, 323 (1954); **9**, 18 (1954). H. Moser and H. Schultz, Ann. Physik **7**, 243 (1959).