THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 138, No. 2A 19 APRIL 1965

Theory of the Excitation of the 4686-Å Line of He^+ by Electron Impact*

EDWARD T. P. LEE AND CHUN C. LIN†
Department of Physics, University of Oklahoma, Norman, Oklahoma
(Received 16 November 1964)

The cross sections for the production of He^+ ion in the $4S$ state by single-electron collisions with neutral helium atoms in the ground state have been calculated by the Born approximation at various incident-electron energies from 200 to 450 eV. These cross sections range from 8.2×10^{-21} to 6.6×10^{-21} cm^2. By using the ionization-excitation cross sections of the $4P$ and $4D$ states calculated by Dalgarno and McDowell and by extending their calculations to $4F$, the cross sections of the excitation of the $n=4 \rightarrow n=3$ transitions of He^+(4686 Å) have been computed. It was found that the transition $4S \rightarrow 3P$ contributes about 90% of the total radiation of the various members of the $n=4 \rightarrow n=3$ group. The theoretical cross sections of the 4686-Å radiation agree with the experimental values to within 15%. It is concluded that the observed 4686-Å radiation can be ascribed mainly to direct ionization-excitation to the $n=4$ states of He^+ by single-electron impact, and no evidence is found for any indirect excitation mechanism which is responsible for a significant portion of the population of the $4S$ state of He^+.

INTRODUCTION

RECENTLY, the production of excited ionized helium atoms by electron impact has been observed by the optical method.[1,2] In these experiments the intensity of the transition $n=4 \rightarrow n=3$ (4686 Å) of He^+ which resulted from a beam of electrons passing through a container of helium was measured. Because of the near L degeneracy in He^+, the observed radiation is the total intensity of the five transitions $4S \rightarrow 3P$, $4P \rightarrow 3S$, $4P \rightarrow 3D$, $4D \rightarrow 3P$, and $4F \rightarrow 3D$. If the emission of the 4686-Å radiation is believed to result primarily from direct ionization-excitation induced by electron impact, the cross section of the 4686-Å radiation can be calculated from the ionization-excitation cross sections of the $4S$, $4P$, $4D$, and $4F$ states of He^+. Calculations for the $4P$ and $4D$ states have been made by Dalgarno and McDowell.[3] In the paper of St. John and Lin,[1] it was assumed that the ionization-excitation cross section of the $4S$ state of He^+ lies somewhere between those of $4P$ and $4D$ as suggested in Ref. 3. Using a cross section of the $4S$ state estimated in this manner, we found that the $4S \rightarrow 3P$ transition alone constitutes about half of the total intensity of all the $n=4 \rightarrow n=3$ lines. This happens because the $4S$ state cascades only to $3P$ and $2P$ with an intensity ratio of 3:4, whereas the majority of the atoms in $4P$ cascade to $1S$, leaving a small fraction of the population for the $4P \rightarrow 3S$ and $4P \rightarrow 3D$ transitions. The ionization-excitation cross section for $4F$ can be well expected to be much smaller than that of $4D$, and the $4F \rightarrow 3D$ transition should be quite insignificant compared to the other members of the 4686-Å group.

Because of the importance of the $4S \rightarrow 3P$ transition in its contribution to the intensity of the 4686-Å radiation, we have calculated the ionization-excitation cross sections for the $4S$ state of He^+ by the Born approximation. Also, the ionization-excitation calculations of Dalgarno and McDowell have been extended to include the $4F$ state. The theoretical cross sections for the 4686-Å radiation are then determined and compared with the experimental results. In the case of the excitation of the triplet states of the neutral helium atoms, St. John, Miller, and Lin[4] have found that the observed cross sections are much larger than the theoretical values, leading to the conclusion that the observed population of the triplet states in their discharge experiment is produced mainly by processes other than

* Supported by the U. S. Air Force Office of Scientific Research, Grant AF-AFOSR-252-63.
† Alfred P. Sloan Foundation Fellow.
[1] R. M. St. John and C. C. Lin, J. Chem. Phys. **41**, 195 (1964).
[2] R. H. Hughes and L. D. Weaver, Phys. Rev. **132**, 710 (1963).
[3] A. Dalgarno and M. R. C. McDowell, in *The Airglow and the Aurorae*, edited by E. B. Armstrong and A. Dalgarno (Pergamon Press, Inc., New York, 1956), p. 340.
[4] R. M. St. John, F. L. Miller, and C. C. Lin, Phys. Rev. **134**, A888 (1964).

direct excitation. It is therefore of interest to see if the observed intensity of the 4686-Å radiation can be ascribed mainly to direct ionization-excitation processes.

II. EXCITATION OF THE 4S STATE OF He^+

Let us denote the radius vectors of the two atomic electrons and the colliding electron by $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}$; the energies and wave functions of the initial and final states of the atomic states by E_i^0, E_f^0, $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$, and $\Psi_f(\mathbf{r}_1,\mathbf{r}_2)$; and the wave vectors of the incident and scattered electron by $\mathbf{k}_i$ and $\mathbf{k}_f$. According to the Born approximation, the differential cross section for the ejection of an electron with momentum between κ and $\kappa+d\kappa$ into the solid angle $d\sigma$ by an electron which is scattered into $d\omega$ is, in atomic units,[3,5,6]

$$I_\kappa d\sigma d\omega d\kappa=(k_f/4\pi^2k_i)\left|\int V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r})\Psi_i(\mathbf{r}_1,\mathbf{r}_2)\Psi_f^*(\mathbf{r}_1,\mathbf{r}_2)\times\exp(i\mathbf{K}\cdot\mathbf{r})d\tau_1d\tau_2d\tau\right|^2 d\sigma d\omega d\kappa\,, \quad (1)$$

where

$$V=\frac{1}{|\mathbf{r}-\mathbf{r}_1|}+\frac{1}{|\mathbf{r}-\mathbf{r}_2|}-\frac{2}{r}\,, \quad (2)$$
$$\mathbf{K}=\mathbf{k}_i-\mathbf{k}_f.$$

The wave function for the ground state of the helium is taken as the product of two hydrogenic wave functions with effective charge Z, i.e.,

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=\phi_{1s}(Z|\mathbf{r}_1)\phi_{1s}(Z|\mathbf{r}_2)\,. \quad (3)$$

We have omitted the spin part of the wave function, since within our approximation of neglecting exchange effect, the interaction potential is devoid of spin coordinates. The effective charge is chosen as $Z=1.69$ in accordance with the work of Massey and Mohr.[6] The final state of the atom consists of an electron of He^+ in the (nl) state with nuclear charge $Z'=2$ and an unbound electron with momentum $\boldsymbol{\kappa}$. The wave function for this system is

$$\Psi_f(\mathbf{r}_1,\mathbf{r}_2)=(1/\sqrt{2})[\phi_{nl}(Z'|\mathbf{r}_1)\psi_\kappa(\mathbf{r}_2)+\phi_{nl}(Z'|\mathbf{r}_2)\psi_\kappa(\mathbf{r}_1)]\,. \quad (4)$$

Following Massey and Mohr,[6] we shall approximate ψ_κ, the wave function of the ionized electron, by the continuum wave function in a Coulomb field[7] of charge Z'' which is denoted by φ_κ, or

$$\psi_\kappa^*(\mathbf{r})\simeq\varphi_\kappa^*(Z''|\mathbf{r})=\frac{1}{2\pi}\left[\frac{\kappa Z''}{1-\exp(-2\pi Z''/\kappa)}\right]^{1/2}\times[\Gamma(1-iZ''/\kappa)]^{-1}\exp(i\kappa r)\times\int_0^\infty u^{-iZ''/\kappa}\exp(-u)J_0\{(4i\kappa\xi u)^{1/2}\}du\,, \quad (5)$$
$$\xi=r+(\mathbf{r}\cdot\boldsymbol{\kappa})/\kappa\,.$$

The choice of Z'' is rather difficult; in their calculation of ionization cross section of helium, Massey and Mohr[6] used $Z''=1.69$ so as to make Ψ_f orthogonal to Ψ_i. This value will be adopted for our calculations. The integral involving V can now be decomposed into

$$\begin{aligned}\mathcal{B}(i,f)&=\int\Psi_iV\Psi_f^*e^{i\mathbf{K}\cdot\mathbf{r}}d\tau d\tau_1d\tau_2\\&=(4\pi/K^2)\int[\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)]\times\Psi_i(\mathbf{r}_1,\mathbf{r}_2)\Psi_f^*(\mathbf{r}_1,\mathbf{r}_2)d\tau_1d\tau_2\\&=(8\pi/\sqrt{2}K^2)\left[\int\exp(i\mathbf{K}\cdot\mathbf{r}_1)\phi_{1s}(Z|\mathbf{r}_1)\times\phi_{nl}^*(Z'|\mathbf{r}_1)d\tau_1\int\phi_{1s}(Z|\mathbf{r}_2)\varphi_\kappa^*(Z''|\mathbf{r}_2)d\tau_2\right.\\&\quad\left.+\int\exp(i\mathbf{K}\cdot\mathbf{r}_1)\phi_{1s}(Z|\mathbf{r}_1)\varphi_\kappa^*(Z''|\mathbf{r}_1)d\tau_1\times\int\phi_{1s}(Z|\mathbf{r}_2)\phi_{nl}^*(Z'|\mathbf{r}_2)d\tau_2\right]. \quad (6)\end{aligned}$$

For $l=0$, the orthogonality between Ψ_i and Ψ_f indeed requires $Z''=Z$, thus the above integral becomes

$$[\mathcal{B}(i,f)]_{l=0}=(4\sqrt{2}\pi/K^2)\times\int\exp(i\mathbf{K}\cdot\mathbf{r}_1)\phi_{1s}(Z|\mathbf{r}_1)\varphi_\kappa^*(Z''|\mathbf{r}_1)d\tau_1\times\int\phi_{1s}(Z|\mathbf{r}_2)\phi_{ns}(Z'|\mathbf{r}_2)d\tau_2. \quad (7)$$

When $l\neq0$, the angular dependence of ϕ_{nl} makes Ψ_f orthogonal to Ψ_i, and the condition of $Z''=Z$ is no longer necessary. In fact, for $l\neq0$, the use of $Z''=Z$ leads to vanishing cross sections as may be seen from Eq. (6). The choice of Z'' for these cases has been discussed by Dalgarno and McDowell.[3]

The expression given in (7) is now used to calculate the excitation cross sections of the 4S state of He^+. The procedure of integration has been outlined by several authors[5,6,8] and will not be detailed here. The

[5] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), 2nd ed.

[6] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A140**, 613 (1933).

[7] A. Sommerfeld, Ann. Physik **11**, 257 (1931).

[8] P. Swan, Proc. Phys. Soc. (London) **A68**, 1157 (1955).

total cross sections have been calculated for several energies of the incident electron by integrating I_κ in Eq. (1) over σ, ω, and κ. The results are summarized in Table I. These cross sections will be denoted by $Q(\mathrm{He}^+,4S)$. The peak value of the cross section occurs at about 230 eV.

Since the choice of Z'' for the continuum wave function is somewhat arbitrary, it is interesting to investigate this point in some detail and attempt to estimate how sensitively the calculated cross sections depend on this parameter. We have calculated the values of Z'' for the particular wave functions φ_κ which give the same cross sections $Q(\mathrm{He}^+,4P)$ and $Q(\mathrm{He}^+,4D)$ at 405 eV as those reported by Dalgarno and MacDowell.[3] They are

$$Z''=1.45\,, \quad \text{for} \quad 4P\,,$$
$$Z''=1.53\,, \quad \text{for} \quad 4D. \tag{8}$$

To get an estimate on the variation of the calculated cross sections with respect to Z'', we shall compute $Q(\mathrm{He}^+,4S)$ for $Z''=1.45$. However, in the case of $l=0$, if Z'' is chosen to be different from Z, the wave functions of the initial and final states are not orthogonal to each other when the approximation described in Eq. (5) were adopted. To avoid this difficulty we shall orthogonalize the continuum function with respect to $\phi_{1s}(Z|\mathbf{r})$, i.e., we construct[9]

$$\psi_\kappa(\mathbf{r})=\alpha\varphi_\kappa(Z''|\mathbf{r})+\beta\phi_{1s}(Z|\mathbf{r})\,, \tag{9}$$

and select the coefficients so that ψ_κ is orthogonal to $\phi_{1s}(Z|\mathbf{r})$. The cross sections are then obtained from (7) upon replacing φ_κ by ψ_κ as given in the preceding equation. Corresponding to $Z''=1.45$, the value of the excitation cross section to the $4S$ state of He^+ at 405 eV is 8.7×10^{-21} cm^2. This amounts to a variation of 25% from the calculated value listed in Table I.

III. EXCITATION OF THE 4F STATE OF He^+

For excitation to states of He^+ with $l\neq0$, the second term in the right-hand side of Eq. (6) vanishes, and $\mathcal{B}(i,f)$ becomes

$$[\mathcal{B}(i,f)]_{l\neq0}=(4\sqrt{2}\pi/K^2)\times\int\exp(i\mathbf{K}\cdot\mathbf{r}_1)\phi_{1s}(Z|\mathbf{r}_1)\phi_{nl}(Z'|\mathbf{r}_1)d\tau_1\times\int\phi_{1s}(Z|\mathbf{r}_2)\varphi_\kappa(Z''|\mathbf{r}_2)d\tau_2. \tag{10}$$

The cross sections for the $4P$ and $4D$ state of He^+ have been calculated by Dalgarno and McDowell,[3] and their method of calculation will be extended to $4F$. Since we do not have the value of Z'' for $4F$, we shall use those of $4P$ and $4D$ as a guide. For $Z''=1.45$ and 1.53, the calculated cross sections at 405 eV are 1.6×10^{-23} and 0.7×10^{-23} cm^2, respectively; thus we shall take $Q\simeq1\times10^{-23}$ cm^2. Fortunately, as will be seen in the following section, the contribution from the $4F$ state to the total cross section of the excitation of the 4686-Å line is exceedingly small; even a variation in $Q(\mathrm{He}^+,4F)$ by a factor of 10 would hardly alter the cross sections of the 4686-Å radiation. The theoretical cross sections of $\mathrm{He}^+(4F)$ at five different energies are included in Table I.

[9] D. R. Bates, A. Fundaminsky, and H. S. W. Massey, Phil. Trans. Roy. Soc. London **A243**, 93 (1950).

TABLE I. Cross sections (in 10^{-21} cm^2) for simultaneous excitation and ionization of He by electron impact.

	Incident electron energy (in eV) 200	270	340	405	450
$Q(\mathrm{He}^+,4S)$[a]	8.1	8.2	7.6	6.9	6.6
$Q(\mathrm{He}^+,4P)$[b]	2.9	3.1	2.9	2.8	2.7
$Q(\mathrm{He}^+,4D)$[b]	0.68	0.69	0.66	0.62	0.57
$Q(\mathrm{He}^+,4F)$[c]	0.01	0.01	0.01	0.01	0.01
$Q(\mathrm{He}^+,4\rightarrow3)$ theoretical	3.7	3.8	3.5	3.2	3.0
$Q(\mathrm{He}^+,4\rightarrow3)$ experimental, Ref. 1	4.2	3.9	3.4	3.0	2.8

[a] Calculated by using $Z''=1.69$.
[b] Taken from Ref. 3.
[c] Obtained from the average of the calculated values using $Z''=1.53$ and $Z''=1.45$.

IV. EXCITATION OF THE $n=4\rightarrow n=3$ TRANSITIONS OF He^+

We are now in a position to calculate the excitation cross sections of the $n=4\rightarrow n=3$ transitions which we shall denote as $Q(\mathrm{He}^+,4\rightarrow3)$. Let us represent the transition probability from the jth state to the kth by $A(jk)$, the total probability of transition from the jth state to all the lower ones by $A(j)$, and introduce the branching ratio B in the usual manner[4]

$$B(jk)=A(j)/A(jk). \tag{11}$$

We can then express $Q(\mathrm{He}^+,4\rightarrow3)$ in terms of the excitations cross sections of the $n=4$ states of He^+ as

$$Q(\mathrm{He}^+,4\rightarrow3)=\frac{Q(\mathrm{He}^+,4S)}{B(4S,3P)}+\frac{Q(\mathrm{He}^+,4P)}{B(4P,3S)}+\frac{Q(\mathrm{He}^+,4P)}{B(4P,3D)}+\frac{Q(\mathrm{He}^+,4D)}{B(4D,3P)}+\frac{Q(\mathrm{He}^+,4F)}{B(4F,3D)}. \tag{12}$$

The values of these branching ratios are $B(4S,3P)=2.4$, $B(4P,3S)=27$, $B(4P,3D)=270$, $B(4D,3P)=3.9$, $B(4F,3D)=1.0$. Because $B(4P,3S)$ and $B(4P,3D)$ are much greater than $B(4S,3P)$, and because $Q(\mathrm{He}^+,4D)$ and $Q(\mathrm{He}^+,4F)$ are rather small, the major contribution to $Q(\mathrm{He}^+,4\rightarrow3)$ arises from the $Q(\mathrm{He}^+,4S)$ term. At 405 eV, for example, the magnitudes of the five terms in the right-hand side of Eq. (12) are 2.9, 0.10, 0.010, 0.16, and 0.01, respectively. The calculated cross sections $Q(\mathrm{He}^+,4\rightarrow3)$ are shown in Table I along with the experimental values. The theoretical values agree better with the experimental results of St. John and Lin[1] than with those of Hughes and Weaver.[2] The discrepancy between the two sets of experimental data has been pointed out in Ref. 1.

Before making a detailed comparison between the theoretical and experimental cross sections of the 4686-Å transitions, we must point out that the experimental values include the contribution from both the direct ionization-excitation processes and the cascading from the upper states. Since no other radiation associated with He^+ has been observed in the ionization-excitation experiment, we are not able to determine the cascade correction. However, from the results of the analysis[4] of the excitation cross section data of neutral He, the cascade correction is estimated to be about 10% which is within the experimental uncertainty of the data reported by St. John and Lin.[1]

Since the majority of the $n=4\rightarrow n=3$ radiation resulted from the ionization-excitation to the $He^+(4S)$ state, let us first consider the cross section of this process. In Sec. II we have shown that a variation of the effective charge in the Coulomb continuum wave function may produce as much as 25% change in the cross sections. Considering the uncertainty of the wave function of the ionized electron and the use of the Born approximation in the calculation, we see that the agreement between the theoretical and the experimental cross sections is quite satisfactory. It is interesting to compare (7) with the corresponding integral for ionization (excitation to the $1S$ state of He^+), viz.,

$$[\mathcal{B}(i,f)]_{\text{ionization}}=(4\sqrt{2}\pi/K^2)\times\int\exp(i\mathbf{K}\cdot\mathbf{r})\phi_{1s}(Z|\mathbf{r}_1)\varphi_\kappa^*(Z|\mathbf{r}_1)d\tau_1\times\int\phi_{1s}(Z|\mathbf{r}_2)\phi_{1s}(Z'|\mathbf{r}_2)d\tau_2,\quad(13)$$

which was used in the calculation of the ionization cross section.[6] Equations (7) and (13) differ only in the second integral (overlap integral) and in the relation between k_i and k_f due to the difference in the energy threshold of the inelastic collision processes. Since the overlap integrals in (7) and (13) involve only the bound-state wave functions and should be reasonably accurate, the cross sections $Q(He^+,4S)$ calculated in this work should have an accuracy comparable to that of the theoretical ionization cross sections of He given by Massey and Mohr.[6] The results of these authors agree with the experimental results to within 10% for incident electrons with energies greater than 150 eV.

For the calculation of the ionization-excitation to the $4P$, $4D$, and $4F$ states, one must recourse to Eq. (10). Here the overlap integral between $\phi_{1s}(Z|\mathbf{r})$ and the Coulomb continuum function vanishes at $Z''=Z$; hence the calculated cross sections depend very sensitively on the choice of Z'' in the neighborhood of 1.69. The values of Z'' shown in (8) are indeed rather close to 1.69. This places the cross sections in the "sensitive region" with respect to Z''. Thus Dalgarno and McDowell pointed out that their results are good to within a factor of 5. Calculations show that at 405 eV the value of $Q(He^+,4P)$ varies more or less steadily from 0 to 2.8×10^{-21} cm^2 in going from $Z''=1.69$ to $Z''=1.45$. Fortunately, the contribution to the intensity of the 4686-Å radiation from the $Q(He^+,4P)$, $Q(He^+,4D)$, and $Q(He^+,4F)$ terms in Eq. (12) totals to about only 10%. In spite of the large uncertainty of these cross sections, the values of $Q(He^+, 4\rightarrow3)$ should remain fairly accurate.

In conclusion, we have shown that the observed intensity of the 4686-Å line in helium discharge experiment can be accounted for quantitatively by the direct process,

$$He(1S)^2\rightarrow_e He^+(4L)+e\,,$$
$$He^+(4L)\rightarrow He(3L')+h\nu(4686\text{ Å})\,.$$

The agreement between the calculated and observed cross sections for this process is comparable to that of the case of single ionization of helium.[6] Since the great majority of the 4686-Å radiation originates from the $4S\rightarrow3P$ transition, our analysis shows that, unlike the case of the excitation of the triplet series of neutral He,[4] the population of the $4S$ state of He^+ is produced primarily by direct ionization-excitation rather than indirect mechanisms.