Photoionization Cross Section of Neon*

KENNETH G. SEWELL

LTV Research Center, Dallas, Texas

(Received 23 November 1964)

The photoionization cross section of neon has been computed for the energy range from threshold to 11.5 Ry and compared with recent experimental results. Hartree-Fock radial functions were used to describe both the initial and final states of the transition.

INTRODUCTION

THE photoionization process of absorption of photons by gases has become of increasing interest in the last few years with the reasons behind this renewed interest coming from varied fields. The emphasis upon space flight and the desire to produce controlled thermonuclear reactions have resulted in a great growth of the field of plasma physics. For low-density plasmas, the predominant effects of the interaction between ions and electromagnetic radiation are photoionization and its inverse, radiative recombination between an electron and its ion. The photoionization process is also of importance in the study of ionized layers in the upper atmosphere and astrophysicists have long been interested in the photoionization cross sections of the light elements as tools for analyzing the compositions and temperatures of stars.

The rare gases hold a place of particular importance in the study of the photoionization process because they are monatomic gases at room temperature and molecular effects are absent. This simplifies tremendously the experimental problems involved in measuring the photoionization cross sections of the atoms; even so, it has been only recently that the experimental techniques have been refined to allow accurate measurements of these cross sections. Such techniques were used in the recent measurements of the photoionization cross

FIG. 1. Comparison of previous theoretical calculations with experiment. – – – – Bates; ———— Seaton, dipole length; —·—— Seaton dipole velocity; —— —— Cooper; — – – McGuire; · Ederer and Tomboulian; + Samson and Kelly.

* This paper is based upon a dissertation submitted to Texas Christian University in partial fulfillment of the Ph.D. degree.

sections of neon by Ederer and Tomboulian[1] and by Samson and Kelly.[2]

A comparison of the previous computations of the photoionization cross section of neon with the recent experimental data indicates a lack of agreement near threshold (see Fig. 1). A discussion of the methods and approximations used by the various authors is given below.

The earliest attempt to compute the photoionization cross section of neon was that of Bates.[3] He used the Hartree-type orbitals for neon as computed by Brown[4] for the initial state and the continuous radial function as computed by Bates et al.[5] for a free electron moving in the field of the oxygen ion O$^+$. Bates reasoned that the differences between the potential fields produced by neon and oxygen would cause only a slight change in the free-electron function. Probably the greatest deficiency in these calculations was the neglect of the effect of exchange upon the wave functions of both the initial and final states. The neglect of these effects caused the wave functions to be too diffuse and evidently increased the overlap of the bound and continuous functions.

The effects of exchange were later included by Seaton[6] at threshold. He made use of Hartree-Fock functions as computed by Garstang[7] for neutral neon and the doubly ionized ion Ne^{++} while the orbitals for Ne$^+$ were obtained by interpolating between those of Ne and Ne^{++}. The radial functions for the free electron with zero kinetic energy were computed in the field of Ne$^+$ including the effects of exchange. The cross section obtained from these functions was in good agreement with the previous work of Bates at threshold. In order to compute the cross section at higher photon energies, he employed an analytical approximation to the bound-state functions together with a Coulomb radial function for the free electron. He aslo employed two different formulations of the cross section, the dipole length and dipole velocity. If exact wave functions were used,
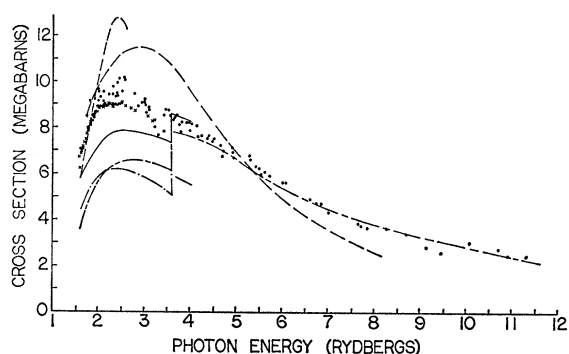
[1] D. L. Ederer and D. H. Tomboulian, Phys. Rev. **133**, A1525 (1964).

[2] J. A. R. Samson and F. L. Kelly, National Aeronautics and Space Agency Report NASA CR-68, 20, 1964 (unpublished).

[3] D. R. Bates, Monthly Notices Roy. Astrophys. Soc. **100**, 25 (1939).

[4] F. W. Brown, Phys. Rev. **44**, 214 (1933).

[5] D. R. Bates, R. A. Buckingham, H. S. W. Massey, and J. J. Unwin, Proc. Roy. Soc. (London) **A170**, 322 (1939).

[6] M. J. Seaton, Proc. Roy. Soc. (London) **A208**, 408 (1951).

[7] R. H. Garstang, Proc. Cambridge Phil. Soc. **47**, 243 (1951).

identical results would be obtained by both methods of computation; the large discrepancies between the two methods as obtained by Seaton are probably due to the approximate wave functions employed. Seaton[8] later extended these calculations to include ionization of the $2s$ electrons, but due to the unavailability of the orbitals of the configuration $Ne^+(1s)^2(2s)(2p)^6$, he used the orbitals of $Na^+(1s)^2(2s)^2(2p)^6$ to compute the potential field acting upon the free electron. The good agreement between his computations using the dipole-length formulation for energies greater than the L_1 edge must be considered fortuitous in view of the poorer agreement at the lower photon energies; the discrepancies between the results computed by the two methods also cast doubt upon any agreement which might be obtained by one method.

Cooper[9] has recently argued that a better approximation to the cross section would be obtained if the Hartree-Fock orbitals for the neutral atom were used to compute the potential and exchange functions in the free-electron equation rather than the orbitals of the positive ion. The cross section computed in this manner is somewhat greater in magnitude than that measured by Ederer and Tomboulian. Further discussion concerning the shape of the curve will be postponed until later.

McGuire[10] has recently computed the photoionization cross section of neon using the semiempirical quantum-defect method. This method allows one to determine the form of the radial functions at large distances from the nucleus, and its use assumes that the cross section is principally determined by the portions of the radial functions at large r. As observed from Fig. 1, the resulting cross section is in good agreement with the experimental data at the larger energies. However, this agreement may be fortuitous in view of the poorer agreement obtained at the lower energies.

In summary, the previous calculations have not resulted in satisfactory agreement with the experimental data. The need for employing wave functions that are as accurate as possible in the computation of the cross sections must be emphasized and the present approach to the problem is made with this need in mind. The cross section will be computed from both the dipole-length and dipole-velocity formulas.

PHOTOIONIZATION CROSS SECTION

An expression for the cross section which is consistent with the Hartree-Fock method of computing atomic radial functions has been derived by Bates,[11]

$$\sigma(\epsilon) = 0.855(I_g + \epsilon)\{C_{l-1}|M_{l-1}|^2 + C_{l+1}|M_{l+1}|^2\}|\zeta|^2,$$

$$(1)$$

where the various quantities are defined below. The cross section in megabarns is denoted by σ; I_g and ϵ are the ionization energy of the atom and kinetic energy of the free electron in rydbergs; and the coefficients $C_{l\pm1}$ result from averaging over all initial states and summing over the final states (values of $C_{l\pm1}$ for several transitions have been tabulated by Bates[12]). The radial matrix elements are denoted by $M_{l\pm1}$; these can be expressed in the two forms as:

(1) dipole-length form

$$M_{l\pm1} = \int_0^\infty P_{nl}(r)rP_{\epsilon,l\pm1}(r)dr,$$

$$(2)$$

(2) dipole-velocity form

$$M_{l\pm1} = \frac{2}{I_g + \epsilon} \int_0^\infty P_{nl}(r)\left[\frac{2l+1\pm1}{2r} \pm \frac{d}{dr}\right]P_{\epsilon,l\pm1}(r)dr. \quad (3)$$

In the above equations, $P_{nl}(r)$ denotes the radial function of the initial state, defined by the quantum numbers n and l, and $P_{\epsilon,l\pm1}(r)$ denotes the radial function of the final continuous state of the electron. If exact radial functions were available for the computation of the matrix elements it would be irrelevant to discuss which form of the matrix element should be used. However, in general, the two forms will not yield identical results if approximate functions are employed.[13] Differences arise because the dipole-length matrix form receives its maximum contribution from large values of r, while the dipole-velocity element receives its principal contribution from intermediate values of r. These considerations indicate that the dipole-velocity form should give the most reliable results when Hartree-Fock radial functions are used. However, the presence of the derivative in this form requires additional care in the numerical evaluation of the integral. In the present study, the cross section is computed from both forms of the matrix element in order to compare the accuracy of the computed radial functions.

In the derivation of Eq. (1) it has been assumed that only one electron makes a transition, where a transition is considered to involve a change in the quantum numbers n and l, but it is not assumed that the radial functions of the passive electrons remain unchanged. The factor ζ which can be termed a distortion factor accounts for the change in the radial functions of the passive electrons and is written as a product over all passive radial functions:

$$\zeta = \prod_{nl}\left[\int_0^\infty P^i(r)P^f(r)dr\right]_{nl}, \quad (4)$$

where the superscripts i and f refer to the initial and final state of the system.

[8] M. J. Seaton, Proc. Phys. Soc. (London) A67, 929 (1954).
[9] J. W. Cooper, Phys. Rev. 128, 681 (1962).
[10] E. J. McGuire, as reported in Ref. 1.
[11] D. R. Bates, Monthly Notices Roy. Astrophys. Soc. 106, 423 (1946).

[12] D. R. Bates, Monthly Notices Roy. Astrophys. Soc. 106, 432 (1946).
[13] S. Chandrasekhar, Astrophys. J. 102, 223 (1945).

RADIAL FUNCTIONS

The major approximations involved in computing the photoionization cross section are embodied in the method employed to obtain the radial functions. It is generally conceded that the Hartree-Fock method yields the best available functions for multielectron atoms; therefore it has been employed in this study as a means of computing both the initial- and final-state functions.

The final state of the transition is that of an electron of positive energy and a positive ion. Let the final state be written as a Slater determinant of the ten electrons where nine are in bound orbitals described in the usual manner

$$\psi_{nlms}(r,\theta,\rho)=r^{-1}P_{nl}(r)Y_l^m(\theta,l)\chi(s), \qquad (5)$$

and one electron has a positive energy and is assumed to be described by

$$\psi_\epsilon(r,\theta,\rho)=\sum_{t=0}^{\infty}\sum_{m=-t}^{t} r^{-1}P_{\epsilon t}(r)Y_t^m(\theta,\rho)\chi(s), \qquad (6)$$

where $Y_t^m(\theta,\rho)$ and $\chi(s)$ are the normalized spherical harmonic and spin functions, respectively. The radial functions are also normalized in the usual manner, i.e.,

$$\int_0^{\infty} P_{nl}^2(r)dr=1, \qquad (7)$$

and

$$P_{\epsilon t}(r) \xrightarrow[r\to\infty]{} \epsilon^{-1/4}\sin(\epsilon^{1/2}r). \qquad (8)$$

The Hartree-Fock (H-F) method for bound states has been amply documented[14,15] and is well known. The equations as given by Hartree et al.[16] were used in the present work to calculate the radial functions for the following states of neon: $Ne(1s)^2(2s)^2(2p)^6$, $Ne^+(1s)^2$-$(2s)^2(2p)^5$, and $Ne^+(1s)^2(2s)(2p)^6$. Recent computations[17] of the first excited state of neon indicate that the nine most tightly bound electrons move in orbitals that are quite nearly those of the ion; therefore, it will be assumed in the present work that the effect of the free electron upon the bound electrons is entirely negligible. The H-F equation for the free electron in the presence of the ion having a kinetic energy of ϵ and orbital quantum number of t can be written as

$$[d^2/dr^2+V_{\epsilon t}(r)-t(t+1)/r^2+\epsilon]P_{\epsilon t}(r)+F_{\epsilon t}(r)=0, \qquad (9)$$

where the potential field due to the nucleus and bound electrons is given by

$$V_{\epsilon t}(r)=2r^{-1}\{Z-\sum_{nl}q_{nl}Y_0(nl,nl,r)\} \qquad (10)$$

and the exchange term is defined as

$$F_{\epsilon t}(r)=r^{-1}\sum_{nl}q_{nl}\{f_{nl}[(2l+1)(2t+1)]^{-1/2}$$

$$\times\sum_{v=0}^{\infty} C^v(t0;l0)Y_v(nl,t\epsilon;r)-\delta_{t,l}\lambda_{nl,t}\}P_{nl}(r). \qquad (11)$$

In the above, q_{nl} denotes the number of electrons having the quantum numbers n and l, f_{nl} is the fraction of those electrons which have the same spin as the free electron, $\lambda_{nl,t}$ is an energy parameter which insures the correct orthogonality conditions, and the Y integrals are given by

$$Y_k(nl,n'l';r)=r^{-k}\int_0^r P_{nl}(u)P_{n'l'}(u)u^k du+r^{k+1}$$

$$\times\int_r^{\infty} P_{nl}(u)P_{n'l'}(u)u^{-k-1}du. \qquad (12)$$

Equation (9) was solved by using essentially the same computation scheme as described by Seaton[6] coupled with the normalization procedure of Bates and Seaton.[18] The coefficients $C^v(t0,l0)$ are tabulated by Slater.[19]

DISCUSSION OF RESULTS

The results of the computations of the cross sections using the set of equations described previously are presented in Fig. 2. The maximum difference between the cross sections as computed by the dipole-length and velocity formulations is about 13%, and occurs at threshold. The general agreement between these cross sections and the experimental data is apparent; however, it is profitable to discuss some of the specific areas of agreement and disagreement. The location and magnitude of the peak of the experimental data due to the photoionization from a $2p$ orbital with respect to photon energy is particularly well reproduced by the theoretical curves. This agreement provides information concerning the potential field acting upon the free electron. Cooper[9] has argued that near the nucleus the free electron probably moves in a central field that is more nearly that defined by the orbitals of the atom than the one specified by the orbitals of the ion. The cross section for the $Ne \rightarrow Ne^+(2p)^5+e^-$ transition was also computed in the present study by using the orbitals of the atom to compute the potential and exchange functions. The results were in good agreement with the results of Cooper for energies less than the L_1 edge. This cross section reaches a maximum at about 2.9 Ry, whereas the experimental data peak at about 2.5 Ry. The maximum in the cross-section curve should occur at the energy corresponding to maximum overlap between the bound orbital of the initial state and the free-electron functions of the final state. The

[14] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
[15] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960).
[16] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London A238, 229 (1939).
[17] K. G. Sewell (unpublished).

[18] D. R. Bates and M. J. Seaton, Monthly Notices Roy. Astrophys. Soc. 109, 698 (1949).
[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 281.

TABLE I. Oscillator sum rules.

| Energy range	$\frac{\mu_{-2}}{Ry^{-2}}$	$\frac{\mu_{-1}}{Ry^{-1}}$	μ_0
Discrete	0.147	0.205	0.28
1.55–3.51 Ry	0.388	0.893	2.16
3.51–11.5 Ry	0.133	0.713	4.05
11.5–63.7 Ry	0.002	0.091	1.56
63.7–∞ Ry		0.020	1.81
Sum	0.670	1.922	9.86
Piech and Levinger	0.67	1.96	10.32

FIG. 2. Comparison of present results with experimental data. —— dipole length; – – – dipole velocity; · Ederer and Tomboulian; + Samson and Kelly.

potential field acting upon the free electron affects this maximum overlap energy in the following manner: The radial position of the first maximum of the free electron function is governed primarily by the potential field assumed to be acting upon the free electron; if this field is weaker than the actual field, the position of the first maximum is displaced outward from the nucleus from its true position while if it is too strong the first maximum is displaced inward. As the kinetic energy of the free electron is increased, the position of this first maximum moves toward the nucleus; thus a potential field which is weaker than the actual field will result in a maximum overlap energy that is too large. The fact that the maximum overlap energy, as obtained when the ionic orbitals are used, is in agreement with the experimental data is a strong indication that the potential field acting upon the free electron is actually that of the ion. It also indicates that polarization of the ion by the free electron is small.

The somewhat poorer agreement between the theoretical calculations and the experimental data at the higher energies is probably due to cancellation effects. As the kinetic energy of the electron is increased, the first maximum of the free electron function moves toward the nucleus introducing negative contributions into the matrix elements of Eqs. (14) and (15). As the magnitudes of the positive and negative contributions become more nearly equal, the accuracy of the radial functions becomes of increasing importance. These cancellation effects are more important for ionization from the $2s$ shell than from the $2p$.

Following Piech and Levinger,[20] the sum rules

[20] K. R. Piech and J. S. Levinger, Phys. Rev. 135, A332 (1964).
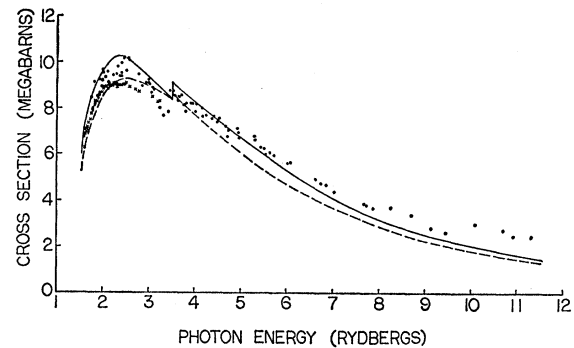
μ_{-2}, μ_{-1}, and μ_0 (where their notation is used) were evaluated and are displayed in Table I. For the energy range 1.55–11.5 Ry, the cross section was taken to be the average of the dipole-length and dipole-velocity cross sections; this curve was then extrapolated to the K edge at 63.7 Ry by the method of the previous authors. The values for the discrete transitions were obtained in the manner described by Piech and Levinger, and the values for energies greater than 63.7 Ry are precisely their values.

In conclusion, the use of H-F orbitals for bound electrons and the H-F equation for the free electron function produce photoionization cross sections which are in good agreement with experiment. The present results indicate that polarization effects should be negligible. The use of more accurate radial functions (i.e., those that account for correlation effects) might result in better agreement with the experimental data for the energy range where cancellation is important. However, the results obtained from the present method justify its application to other small atoms whose cross sections are more difficult to obtain experimentally.