Polarization in Low-Energy Electron Scattering: Carbon and Nitrogen*

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(Received 11 March 1968)

The polarized-orbital method has been applied to low-energy scattering of electrons from atomic carbon and nitrogen. Cross sections for the elastic scattering of electrons by C and N are given for energies up to 5.5 and 10 eV, respectively. The shape of the cross sections for nitrogen is in good agreement with the shape obtained by experiment. The photodetachment cross sections for C^- and N^- are given for ejected electron energies <7 eV, and those for C^- are found to be in good agreement with experiment when polarization terms are included and the dipole velocity approximation is used. For N^-, photodetachment cross sections are given for electron affinity values of 0.05 and 0.15 eV.

I. INTRODUCTION

In this paper we will present calculations of photodetachment cross sections for C^- and N^-, and elastic scattering cross sections for electrons incident on carbon and nitrogen atoms. In the photospheres of carbon-rich stars, photodetachment of C^- may contribute to their continuous opacity,[1] especially in *G* and *K* giants where, due to the high temperatures, molecular bands will not dominate the spectrum. During atmospheric re-entry of space vehicles, a major portion of the radiant energy arises from the continuous spectrum due to the free-free and free-bound transitions of electrons in fields of ions and atoms. Photodetachment of N^- may contribute significantly to this continuous spectrum.[2]

For photo-ionization of atoms and positive ions, the Coulomb term dominates the long-range interaction, but for photodetachment of negative ions this term vanishes. In this case the long-range interaction is due primarily to polarization effects, which are induced by the reaction of the external electron on an atomic system. Thus, this interaction must be included in order to obtain reliable cross sections for photodetachment or low-energy electron scattering from atoms.

Various theoretical attempts have been made to include the polarization effects induced on carbon or nitrogen atoms by incident electrons.[3-7] In these calculations, a polarization potential was included through the use of semiempirical parameters. Temkin[8] developed a method in which polarization terms arise naturally in the formalism. This method was extended by Henry[9] to include all direct contributions from the polarized orbitals and the exchange contribution from the most important type of polarized orbital. The essential points in his treatment are given in Sec. II, where we also give the expressions used in our calculation of photodetachment cross sections. We will use the formalism of Sec. II to obtain elastic scattering cross sections for carbon and nitrogen, and these are presented in Sec. III, where we also give photodetachment cross sections for C^- and N^-. The main conclusions of the paper are given in Sec. IV.

II. THEORY

We will consider a system consisting of an *N*-electron atom and an incident electron. In the exchange approximation, the total wave function for this system may be written in the form

$$\Psi(1,\cdots,N+1) = A\Phi(1,\cdots,N)F(N+1), \qquad (1)$$

where A is the antisymmetrization operator, Φ is an eigenfunction of the atomic system, and F is the wave function for the incident electron. In this approximation, the reaction of the scattered electron on the atomic system is neglected. This reaction is important for low-energy electron scattering so Temkin[8] suggested the alternative expansion

$$\begin{aligned}\Psi(1,\cdots,N+1) &= A[\Phi(1,\cdots,N) \\ &\quad + \Phi_p(1,\cdots,N;N+1)]F(N+1), \qquad (2)\end{aligned}$$

where the function Φ_p represents the dipole distortion of the atom by the incident electron. If the perturbation due to this electron is adiabatic and if the predominant polarization effects occur exterior to the space occupied by the atomic electrons, the perturbation V on the atom may be written as

$$\begin{aligned} V &= r_{N+1}^{-2} \sum_{k=1}^{N} r_k \cos\theta_{k,N+1} \qquad (r_{N+1} > r_k), \\ &= 0 \qquad (r_{N+1} < r_k), \end{aligned}$$

where $\theta_{k,N+1}$ is the angle between $\vec{r}_k$ and $\vec{r}_{N+1}$, the radial vectors for the atomic and incident electrons, respectively. The perturbed wave functions may then be obtained by Sternheimer's method.[10]

The scattering equation for the function F is obtained by requiring that

$$\int \Phi(1,\cdots,N)(H-E)\Psi(1,\cdots,N;N+1)d\tau = 0,$$

where H and E are the Hamiltonian and energy of the total system, respectively. We thus obtain a scattering equation of the form

$$[\nabla^2 + k^2 - 2(V + V_p)]F(r) + W(r,F) + W_p(r,F) = 0, \qquad (3)$$

where V and W are the direct and exchange potentials, and V_p and W_p are the direct and exchange polarization potentials. The direct and exchange potentials have been given by Smith, Henry, and Burke.[11]

In calculating the direct polarization potential, we assume that there is no contribution from the closed $1s^2$ shell. Then V_p is given by

$$V_p(r) = -r^{-4}[\alpha_{2s\to p}(r) + \alpha_{2p\to s}(r) + \alpha_{2p\to d}(r)], \tag{4}$$

where

$$\alpha_{2l\to l'}(r) = A_{ll'}\int_0^r P_{2p}(r_1) r_1 u_{2l\to l'}(r_1)dr_1 + B_{ll'}\int_0^r P_{2l}(r_1) r_1 P_{2l'}(r_1)dr_1 \times \int_0^r P_{2l'}(r_1) u_{2l\to l'}(r_1)dr_1, \tag{5}$$

and $A_{ll'}$ and $B_{ll'}$ are atomic parameters. The radial functions $P_{nl}(r)$ and $u_{nl\to l'}(r)$ represent unperturbed and perturbed orbitals, respectively. The differential equation for $u_{nl\to l'}(r)$ was first obtained by Sternheimer.[10] It is

$$\left[\frac{d^2}{dr^2} - \frac{1}{P_{nl}}\left(\frac{d^2P_{nl}}{dr^2}\right) + \frac{l(l+1)-l'(l'+1)}{r^2}\right] \times u_{nl\to l'}(r) = -rP_{nl}(r). \tag{6}$$

In calculating W_p, we have only considered the most important type of polarized orbital, $2p\to d$. The exchange polarization potential contains integrals of the form

$$\int_r^\infty P_{2p}(r_1)F(r_1)r_1^{-\lambda-3}dr_1,$$

plus terms in dF/dr which arise from the operation of the Laplacian operator on the step function $\epsilon(r_{N+1}, r_k)$, where

$$\epsilon(r_{N+1}, r_k) = 1 \quad (r_{N+1} > r_k)$$
$$= 0 \quad (r_{N+1} < r_k).$$

This step function ensures that the scattered electron is always outside the atomic electrons, and although it produces an unphysical discontinuity in the total wave function, Sloan[12] has shown that no special effects arise from this discontinuity.

Complete expressions for the direct and exchange polarization potentials have been given by Henry.[9]

Photodetachment cross sections may be calculated using the expressions given by Henry and Lipsky.[13] For single-channel photodetachment, the cross section in the dipole-velocity formalism may be written as

$$\sigma_V = 3.42\times10^{-18}C_p^2(I+k^2)^{-1}(C_0M_0^2 + C_2M_2^2)\ \text{cm}^2,$$

where I, the electron affinity of the atom, and k^2, the energy above threshold, are in rydbergs. In the dipole-length formalism, the cross section may be written

$$\sigma_L = 8.56\times10^{-19}C_p^2(I+k^2)(C_0M_0^2 + C_2M_2^2)\ \text{cm}^2.$$

The overlap integral is given by

$$C_p = (1s|1\bar{s})^2(2s|2\bar{s})^2(2p|2\bar{p})^q,$$

where terms of the form $(a|b)$ represent overlaps of the radial wave functions $1s$, $2s$, and $2p$ of the negative ion and $1\bar{s}$, $2\bar{s}$, and $2\bar{p}$ of the atom. The constants C_0 and C_2 depend on the initial and final states of the system and have been calculated by Bates.[14] The matrix element M is given by

$$M_l = (2p|\Theta|F) - \delta_{l0}(2s|F)(2s|2\bar{s})^{-1}(2p|\Theta|2s),$$

where the operator, in the dipole-velocity approximation, is

$$\Theta = \frac{d}{dr} - \frac{1+(1-l)(2l+1)}{2r}$$

and, in the dipole-length approximation, is

$$\Theta = r.$$

III. RESULTS AND DISCUSSION

We used the self-consistent-field functions given by Clementi[15] to describe the unperturbed ground state of carbon. Those given by Clementi and McLean[16] were used for C^-, and those given by Roothaan and Kelly[17] were used for N and N^-.

We computed the perturbed functions $u_{nl\to l'}(r)$ by solving Eq. (6). These solutions were then used in a calculation of the direct polarization potential from Eqs. (4) and (5). The parameters for Eq. (5) are given in Table I. We thus obtain

$$2V_p(r) \underset{r\to\infty}{\simeq} -14.5r^{-4}$$

for carbon. This value is in agreement with the calculation of Dalgarno and Parkinson,[18] who also used the Sternheimer procedure. For nitrogen, our computed value for the polarizability is $8.1a_0^3$, which compares favorably with the value $7.6a_0^3$ measured by Alpher and White.[19]

TABLE I. Parameters $A_{ll'}$ and $B_{ll'}$ for Eq. (5); $B_{01} = -A_{01}$; $B_{10} = -A_{10}$; $B_{12} = 0$.

l	l'	$A_{ll'}$ carbon	$A_{ll'}$ nitrogen
0	1	$\frac{4}{3}$	$\frac{4}{3}$
1	0	$\frac{4}{9}$	$\frac{2}{9}$
1	2	$\frac{8}{9}$	$\frac{4}{9}$

A. Elastic Scattering Cross Sections

In Fig. 1 we present elastic scattering cross sections for electrons incident on the ground ^3P state of carbon. All the potential terms in Eq. (3) were retained in the calculation of the s-, p-, and d-wave contributions to the total cross section. The contribution from higher-order waves was estimated in the Born approximation.[20]

Smith, Henry, and Burke[21] have solved the set of coupled integrodifferential equations, which arises when all terms of the ground-state configuration are included in the expansion of the wave function for the total system. They did not include any polarization effects, since these terms all belong to the same configuration, and thus obtained elastic scattering cross sections which decrease from 2.4×10^{-15} cm² at 1.0 eV to 1.8×10^{-15} cm² at 5.5 eV.

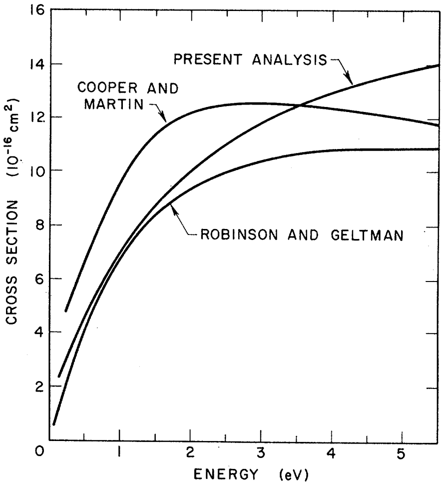

FIG. 1. Elastic cross sections for electrons incident on carbon atoms, compared with theoretical calculations of Cooper and Martin (Ref. 4) and Robinson and Geltman (Ref. 7).

As can be seen from Fig. 1, we obtain cross sections much less than these values, and furthermore they increase with energy. Thus, the effect of inclusion of polarization terms on total elastic cross sections is significant for low-energy electron impact on carbon.

The results of Cooper and Martin[4] and Robinson and Geltman[7] are shown in Fig. 1. In these calculations, a potential, which has asymptotic form $-\alpha r^{-4}$, was included through the use of semiempirical parameters. Cooper and Martin[4] used a modified Klein-Brueckner model.[3] They determined the polarizability by requiring that α is the eigenvalue in the solution of the bound state equation for the radial functions for C^-. In this equation, they assumed that the electron affinity is known, and used the value given by the experimental determination of Seman and Branscomb.[22] Robinson and Geltman[7] modified the Hartree-Fock-Slater (HFS) model by including two terms which have adjustable parameters. One term removes the Coulomb tail in the HFS potential, and the other term introduces the effects of polarization.

No experimental measurements have been reported for elastic scattering of electrons by carbon. The theoretical calculations of Cooper and Martin[4] and Robinson and Geltman[7] are in good agreement with the results of the present analysis.

Elastic cross sections for electrons incident on the ground ^4S state of atomic nitrogen are given in Fig. 2. The present results were obtained in a similar manner to those reported for carbon. The calculations of Smith *et al*.[21] did not include any polarization effects, and the shape of their cross-section-versus-energy curve is completely different to that obtained in the present analysis. The results of the theoretical calculation by Bauer and Browne[5] are also given in Fig. 2. They modified the HFS model by introducing adjustable parameters to account for exchange and polarization effects.

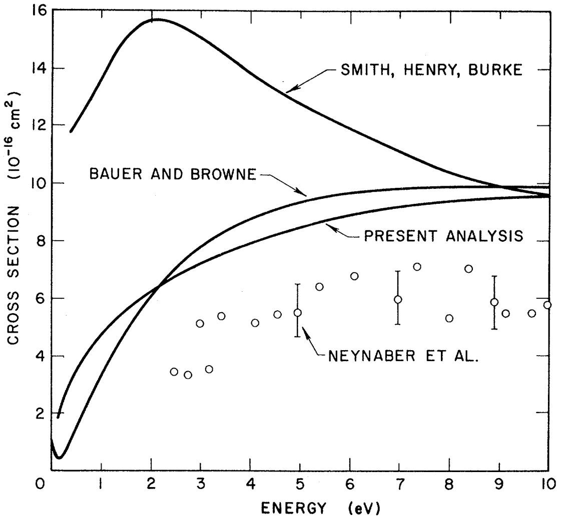

FIG. 2. Elastic cross sections for electrons incident on nitrogen atoms, compared with theoretical calculations of Bauer and Browne (Ref. 5) and Smith *et al*. (Ref. 21), and with experimental results: O. Neynaber *et al*. (Ref. 23).

The circles in Fig. 2 represent the experimental results of Neynaber *et al*.,[23] who measured total cross sections for the scattering of electrons by atomic nitrogen for the energy range 1.6-10 eV. They compared the number of electrons scattered from a region, defined by the intersection of an electron beam and a modulated molecular nitrogen beam, with the number scattered when the nitrogen beam was partially dissociated. They then obtained the atomic cross sections by multiplying the ratios of atomic to molecular scattering cross sections by the molecular nitrogen cross sections measured by Normand.[24] The shape of the cross sections calculated in the present analysis is in good agreement with the shape obtained by experiment.

B. Photodetachment Cross Sections

In Fig. 3, we present photodetachment cross sections for the ejection of an outer-shell electron from C^-, corresponding to the transition

$$C^-(1s^22s^22p^3)^4S + h\nu \rightarrow C(1s^22s^22p^2)^3P + e^- .$$

The solid and dashed curves represent cross sections calculated in the dipole-velocity and -length formalisms, respectively. Curves A and C are the cross sections we obtain when we use continuum wave functions, which are solutions of Eq. (3). Curves B and D represent the results of Henry,[25] who did not include any polarization terms in the calculation of continuum wave functions.

The experimental results of Seman and Branscomb[22] are given as circles in Fig. 3. We note that curve A agrees well with experiment, especially at energies near threshold, i.e., the inclusion of polarization enhances the agreement between theory and experiment. The dipole-velocity-for-

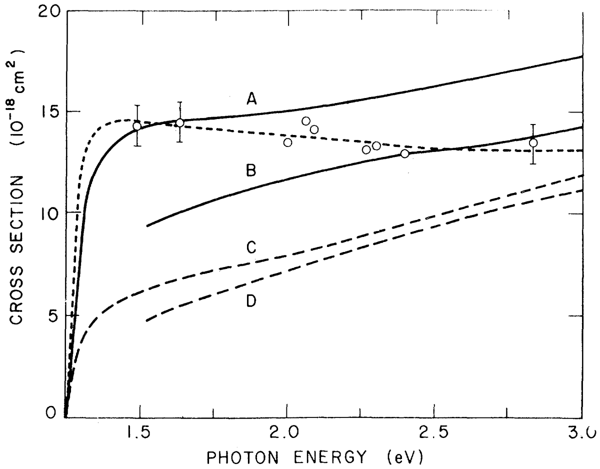

FIG. 3. Photodetachment cross sections for C^-. Solid curves were calculated using the dipole-velocity approximation, and dashed curves using the dipole-length approximation. Curves *A* and *C* were obtained on retaining all polarization terms in Eq. (3), and curves *B* and *D* on neglecting all polarization terms [Henry (Ref. 25)]. The circles represent experimental results of Seman and Branscomb (Ref. 22).

malism cross sections are also in better agreement with experiment than those calculated in dipole-length approximation. This may be due to the poor representation provided for C^- by the Hartree-Fock orbitals, since these functions do not have the correct asymptotic form.

In Fig. 4 we compare the results of the present analysis (Fig. 3, curve A) with theoretical calculations of Cooper and Martin,[4] Robinson and Geltman,[7] and Henry.[25] The circles represent the experimental results of Seman and Branscomb.[22] The present results provide good agreement with experiment near threshold, but none of the theoretical calculations has produced the shape of the experimental results for photon energies in the range 1-3 eV.

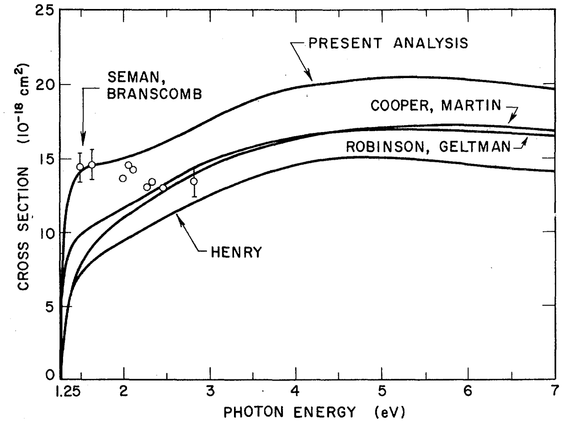

FIG. 4. Photodetachment cross sections for C^-, compared with theoretical calculations of Cooper and Martin (Ref. 4), Robinson and Geltman (Ref. 7), and Henry (Ref. 25). The circles represent experimental results of Seman and Branscomb (Ref. 22).

The stability of the nitrogen negative ion is questionable, although experimental evidence of Boldt,[26] and Fogel *et al.*[27] indicates the existence of this ion. The ion is difficult to detect due to its low electron affinity. Bates and Moiseiwitsch[28] used an extrapolation procedure, based on excitation potentials of the atom and singly and doubly charged ions of the isoelectronic sequence, to obtain the detachment potential of negative ions. For N^- they obtained 0.15 eV, but it is evident that, where experimental results are available, they slightly overestimated the electron affinity. Edlén,[29] also using an extrapolation procedure, obtained good results for all negative ions except those with small atomic charges, and for N^- calculated 0.05 eV. Thus the range 0.05-0.15 eV should be representative of the electron affinity for N^-.

Photodetachment cross sections for N^- are presented in Fig. 5 for the transition

$$N^-(1s^2 2s^2 2p^4)^3P + h\nu \rightarrow N(1s^2 2s^2 2p^3)^4S + e^- .$$

Curves A and B were calculated in the dipole-velocity approximation for electron affinities 0.05 and 0.15 eV, respectively. The shape of the cross sections is markedly different near threshold. Moskvin[30] has used analytical expressions for the bound and free wave functions and obtained cross sections which are about a factor of 5 smaller than those reported here. Morris *et al.*,[2] who studied arc-heated plasmas, state that Moskvin's results are low compared with their data. Thus the present calculations are at least qualitatively consistent with experiment. However, we cannot discriminate between the values chosen for the electron affinity.

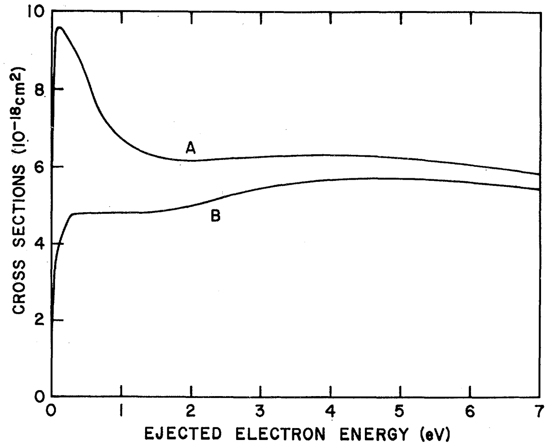

FIG. 5. Photodetachment cross section for N^- calculated using the dipole-velocity approximation. Curves *A* and *B* were calculated for electron affinities 0.05 and 0.15 eV, respectively.

IV. CONCLUSIONS

The magnitude and shape of elastic scattering cross sections are radically changed when polarization terms are included in the potentials. The extension of the polarized-orbital method to atomic nitrogen provides elastic scattering cross sections which are in good agreement with the experimental shape, but the magnitude is about 50% higher than experiment.

The photodetachment cross sections for C^- are in good accord with experiment near threshold, but fail to reproduce the spectral shape in the photon energy range 1-3 eV. For N^-, the cross sections are in qualitative agreement with the experimental magnitude for values 0.05-0.15 eV for the electron affinity, but more experimental work is necessary in order to determine accurately both the electron affinity and photodetachment cross sections.

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*Contribution No. 336 from the Kitt Peak National Observatory.

†Operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation.

[1] L. M. Branscomb and B. E. J. Pagel, Monthly Notices Roy. Astron. Soc. 118, 258 (1958).

[2] J. C. Morris, G. R. Bach, R. U. Krey, R. W. Liebermann, and J. M. Yos, AIAA J. 4, 1223 (1966).

[3] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 115 (1958).

[4] J. W. Cooper and J. B. Martin, Phys. Rev. 126, 1482 (1962).

[5] E. G. Bauer and H. N. Browne, as discussed in Ref. 23.

[6] V. P. Myerscough and M. R. C. McDowell, Monthly Notices Roy. Astron. Soc. 128, 287 (1964).

[7] E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967).

[8] A. Temkin, Phys. Rev. 107, 1004 (1957).

[9] R. J. W. Henry, Phys. Rev. 162, 56 (1967).

[10] R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

[11] K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. 147, 21 (1966).

[12] I. H. Sloan, Proc. Roy. Soc. (London) A281, 151 (1964).

[13] R. J. W. Henry and L. Lipsky, Phys. Rev. 153, 51 (1967).

[14] D. R. Bates, Monthly Notices Roy. Astron. Soc. 109, 432 (1946).

[15] E. Clementi, IBM J. Res. Develop. 9, 2 (1965).

[16] E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964).

[17] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. 131, 1177 (1963).

[18] A. Dalgarno and D. Parkinson, Proc. Roy. Soc. (London) A250, 422 (1959).

[19] R. A. Alpher and D. R. White, Phys. Fluids 2, 153 (1959).

[20] D. G. Thompson, Proc. Roy. Soc. (London) A294, 160 (1966).

[21] K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. 157, 51 (1967).

[22] M. L. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962).

[23] R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. 129, 2069 (1963).

[24] C. E. Normand, Phys. Rev. 35, 1217 (1930).

[25] R. J. W. Henry, J. Chem. Phys. 44, 4357 (1966).

[26] G. Boldt, Z. Physik 154, 330 (1959).

[27] Ya. M. Fogel, V. F. Kozlov, and A. A. Kalmykov, Zh. Eksperim. i Teor. Fiz. 36, 1354 (1959), [English Transl.: Soviet Phys.—JETP 9, 963 (1960).]

[28] D. R. Bates and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) A68, 540 (1955).

[29] B. Edlén, J. Chem. Phys. 33, 918 (1960).

[30] Yu. V. Moskvin, Opt. i Spektroskopiya 17, 499 (1964), [English Transl.: Opt. Spectry. (USSR) 17, 270 (1964).]