CONTINUOUS ABSORPTION BY THE CARBON NEGATIVE ION

V. P. Myerscough and M. R. C. McDowell

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Summary

The bound-free absorption coefficients for $\text{C}^-$ are calculated, over a wide range of photon energies, in the dipole length and dipole velocity formulations, using Hartree–Fock bound state wave functions and central field continuum functions, taking into account orthogonalization and (a) polarization or (b) exchange. The final results obtained by method (b) show qualitative agreement with experimental results where available, except in the region very close to threshold.

1. Introduction.—The possible importance of continuous absorption by atomic and molecular negative ions, other than $\text{H}^-$, in stellar photospheres has been discussed by Branscomb & Pagel (1958). They point out that in stars of low hydrogen content, the atomic negative ions most likely to contribute are those of carbon and oxygen, $\text{C}^-$ and $\text{O}^-$. However, even for oxygen-rich stars, the concentration ratio $n(\text{O}^-)/n(\text{H}^-)$ is not large enough, in view of the small absolute magnitude of the photodetachment cross-section of $\text{O}^-$ compared with $\text{H}^-$ (Branscomb et al. 1958), to allow the detection of continuous absorption by $\text{O}^-$. For $\text{C}^-$, the case is otherwise. Branscomb & Pagel suggest that for G and K giants (in particular R Coronae Borealis), $\log [n(\text{C}^-)/n(\text{H}^-)]$ may be as large as 4. Thus, provided the photodetachment cross-section of $\text{C}^-$ is not abnormally small, one would expect a break in the infra-red spectrum of these stars at the absorption threshold for $\text{C}^-$ (approximately $1.0 \mu$).

Seman & Branscomb (1962) have determined the photodetachment cross-section of $\text{C}^-$ from the threshold of 1-25 eV (9893 Å) to 3 eV (4120 Å) by a cross-beam experiment. The threshold behaviour observed is in accordance with that expected from group theoretical arguments (Branscomb et al. 1958), and the absolute magnitude is approximately twice that of $\text{O}^-$. However, in order to examine in detail the continuous absorption by $\text{C}^-$ in a stellar atmosphere, one requires the bound-free absorption coefficients over a far wider range of photon energies, and also the contribution from the free–free absorption. In this paper we attempt to provide a theoretical estimate of the bound-free absorption coefficient at energies greater than 3 eV.

Less detailed theoretical studies have been carried out by Breene (1959) and Cooper & Martin (1962), while Myerscough & McDowell (1963) have given an account of their preliminary results at the Sixth International Conference on ionization phenomena in gases. Breene’s results are an order of magnitude lower than the observed cross-sections, while the results of Cooper & Martin (1962) and of Myerscough & McDowell (1963) although in reasonable internal accord and of the correct order of magnitude, display an incorrect energy variation near threshold, and are based on an inadequate atomic model. Each of these papers employs a separable electron central field approximation, exchange
being neglected, and the continuum wave functions are not required to be orthogonal to the bound state wave functions of the same orbital angular momentum. The present results are likewise obtained in a central field model, but exchange is included in both initial and final states, and proper account is taken of the requirements of orthogonality. The effect of including a polarization potential is also discussed.

2. *Theoretical formulation.*—The cross-section for photodetachment of an outer electron with kinetic energy $k^2$ rydbergs ($1$ rydberg = $13.6$ eV) from a negative ion of binding energy $E_b$(Ry) is given by (Bates 1946)

$$\sigma_\pi = 8.55 \times 10^{-19} (E_b + k^2) \mathcal{P} \left\{ C_{l+1} a_{l+1}^2 + C_{l-1} a_{l-1}^2 \right\}$$

in the separable electron central field approximation. Here $\mathcal{P}$ is a factor of order unity, $C_{l\pm 1}$ are angular momentum coefficients (Bates 1946), transitions to the $(l \pm 1)$th partial waves of the continuum only being allowed, and

$$\sigma_{l \pm 1}(\text{D.L.}) = \int_0^\infty \rho_{nl}(r) P_{kl, l \pm 1}(r) r \, dr$$

$$\sigma_{l \pm 1}(\text{D.V.}) = \frac{2}{(E_b + k^2)} \left\{ \int_0^\infty \rho_{nl}(r) P_{kl, l \pm 1}(r) r \, dr \pm \frac{(2l+1 \pm 1)}{2} \int_0^\infty \frac{1}{r} \rho_{nl}(r) P_{kl, l \pm 1}(r) r \, dr \right\}$$

in the dipole length (D.L.) and equivalent dipole velocity (D.V.) formulations (Bates & Seaton 1949). In these expressions $\rho_{nl}(r)$ and $P_{kl, l \pm 1}(r)$ are the $r$-multiplied radial parts of the initial ($nl$) and final ($k^2, l \pm 1$) orbitals, normalized according to

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

$$P_{kl, l}(r) \sim k^{-1/2} \sin (kr - \frac{1}{2} l \pi + \delta_r).$$

Analytic representations of the Hartree–Fock wave functions for the ground ($^4S$) state of C$^-$ and ground ($^3P$) state of C were calculated for us by Dr P. Kelly of Lockheed Missiles and Space Corporation, in the Roothaan formulation, (Roothaan et al. 1960). We write

$$\rho_{nl}(r) = r \sum c_{inl}(2n_l)!^{-1/2}(2\zeta_{ul})(n_{ul}+1)(n_{ul}-1) \exp (-\zeta_{ul} r)$$

and tabulate the coefficients $c_{inl}$, $n_{ul}$, $\zeta_{ul}$ for the 1s, 2s and 2p orbitals of ($^3P$)C and the 2p of ($^4S$)C$^-$, together with the total energies, in Table I. It may be seen that with these functions the calculated binding energy of C$^-$ is $0.04$ Ry compared with the experimental value of $0.092$ Ry (Seman & Branscomb 1962).

The Hartree–Fock equations for the $P_{kl, l}$ functions for an electron of energy $k^2$ Ry moving in the field of an undisturbed ($^3P$)C core are,

$$L_0^2 P_{kl, l}(r) = \left\{ \frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} + \frac{2}{r} V_{kl}(r) + V_p(r) \right\} P_{kl, l}(r)$$

$$= X[P_{kl, l}(r)] + \sum_{n=1}^3 \lambda_n P_{ns}(r) \delta_{n, l}$$

$$\left\{ \begin{array}{l}
\end{array} \right.$$
where
\[ V_{ks}(r) = \frac{Z - 2Y_0(1s, 1s) - 2Y_0(2s, 2s) - 2Y_0(2p, 2p)}{r} \]
and
\[ V_{kd}(r) = V_{ks}(r) + \frac{1}{2} Y_2(2p, 2p) \]  

\[ X[P_{ks}(r)] = -\frac{2}{r} Y_0(1s, k^2s) P_{1s}(r) - \frac{2}{r} Y_0(2s, k^2s) P_{2s}(r) \]
\[ - \frac{4}{3r} Y_1(2p, k^2s) P_{2p}(r) \]  
\[ X[P_{kd}(r)] = -\frac{2}{5r} Y_2(1s, k^2d) P_{1s}(r) - \frac{2}{5r} Y_2(2s, k^2d) P_{2s}(r) \]
\[ + \frac{4}{15r} Y_1(2p, k^2d) P_{2p}(r) - \frac{9}{35r} Y_3(2p, k^2d) P_{2p}(r), \]  
in the usual notation, and \( V_P(r) \) is a polarization potential discussed in Section 3. Here \( \lambda_n \) are orthogonalization parameters, chosen such that
\[ \int_0^\infty P_{ks}(r) P_{ns}(r) \, dr = 0 \quad (n = 1, 2). \]

### Table I

**Parameters for radial Hartree–Fock functions for \((^3P)^C and (^4S)^C^-\)**

<table>
<thead>
<tr>
<th>( i )</th>
<th>( n_{ks} )</th>
<th>( \zeta_{ks} )</th>
<th>( i )</th>
<th>( n_{kp} )</th>
<th>( \zeta_{kp} )</th>
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<td>2</td>
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<tr>
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<td>2</td>
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<tr>
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<td>5</td>
<td>3</td>
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</table>

Eigenvectors \( c_{i nl} \)

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<th>( 1s )</th>
<th>( 2s )</th>
<th>( 2p )</th>
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</tr>
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<tr>
<td>3</td>
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<td>0.06705</td>
<td>0.02031</td>
</tr>
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<tr>
<td>5</td>
<td>-0.00026</td>
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<td>0.4168</td>
</tr>
</tbody>
</table>

Total energy: \(-74.3770\) Ry

**C^-\((^3S)^C and (^4P)^C: 2p \) radial function**

<table>
<thead>
<tr>
<th>Eff. prin. qu. nos.</th>
<th>orb. expts.</th>
<th>eigenvectors</th>
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</thead>
<tbody>
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<td>( i )</td>
<td>( n_{kp} )</td>
<td>( \zeta_{kp} )</td>
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<tr>
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</tr>
<tr>
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</tr>
</tbody>
</table>

Total energy: \(-75.4168\) Ry
3. Effects of polarization.—If we neglect exchange equation (6) becomes

\[
\mathcal{L} P_{k',l}(r) = \left\{ \frac{d^2}{dr^2} + k^2 + \frac{2}{r} V_{kl}(r) - \frac{l(l+1)}{r^2} + V_P(r) \right\} P_{k',l}(r)
\]

\[
= \sum_{n=1}^{\infty} \lambda_{ns} P_{ns}(r) \delta_{0,l}
\]

(10)

where the polarization potential \( V_P(r) \) is required to behave as \( \alpha r^{-4} \) as \( r \to \infty \), where \( \alpha \) is the polarizability of C in atomic units, \( \alpha = 14.17 \) (Dalgarno & Parkinson 1959). We adopt the same choices of \( V_P(r) \) as in our previous work (Myerscough & McDowell 1963)

\[
Polarization \ 1: \quad V_P(r) = \frac{\alpha}{(r_P + 2)^2}
\]

\[
Polarization \ 2: \quad V_P(r) = \alpha(r)/r^4
\]

(11)

where the coefficients \( a_q \ (q = 1, \ldots, 5) \) are chosen so that \( \alpha(r) \to \beta r^5 \) as \( r \to 0 \), and \( \beta \) is determined by a first-order perturbation calculation of the binding energy of C (Myerscough & McDowell 1963). In our previous work we chose \( \lambda_{ns} = 0 \), \( n = 1, 2 \) but in the present case we take only \( \lambda_{1s} = 0 \) (Seaton 1951) and solve the homogeneous equation

\[
\mathcal{L} P_{k',l}(r)(0) = 0
\]

(12)

subject to the boundary conditions

\[
P_{k',l}(0) = 0; \quad P_{k',l}(r) \sim k^{-1/2} \sin (kr - \frac{1}{2} l \pi + \eta_l)
\]

\[
u(0) = 0; \quad u'(0) = 0; \quad u(r) \sim k^{-1/2} \sin (kr + \phi_0).
\]

(14)

The required orthonormal solution of equation (10) for \( l = 0 \) is then

\[
P_{k',0}(r) = \{ P_{k',0}(r)_0 + \lambda_{2s} u(r) \} / C_0
\]

(15)

where

\[
\lambda_{2s} = - \int_0^\infty P_{2s}(r) P_{k',0}(r)_0 \, dr / \int_0^\infty u(r) P_{2s}(r) \, dr
\]

(16)

and

\[
C_0 = \pm \{ 1 + \lambda_{2s}^2 + 2\lambda_{2s} \cos (\eta_0 - \phi_0) \}^{1/2}.
\]

(17)

(To a good approximation \( |C_0| \equiv 1 + \lambda_{2s} \) since \( \eta_0 \equiv \phi_0 \) for these potentials. The sign of \( C_0 \) is chosen to ensure continuity.)

The results (neglecting exchange) are shown in Figs. 1 and 2. Those corresponding to the choice of polarization 1 differ but little from our previously reported unorthonormalized results for this potential, which were in good accord in (D.L.) formulation with those of Cooper and Martin. However the effect of orthogonalization for polarization 2, which is theoretically preferable, is to bring the results in close agreement with those obtained using polarization 1, \( \sigma \) (D.L.) being somewhat larger and \( \sigma \) (D.V.) considerably smaller than for the
Fig. 1.—Continuous absorption coefficient of $C^-$ using H.F. bound state functions and central field continuum functions with orthogonalization and polarization 1. Curve 1: experiment (Seman & Branscomb 1962); curve 2: D.L.; curve 3: D.V.

Fig. 2.—Continuous absorption coefficient of $C^-$ using H.F. bound state functions and central field continuum functions with orthogonalization and polarization 2. Curve 1: experiment (Seman & Branscomb 1962); curve 2: D.L.; curve 3: D.V.
unorthogonalized results. Nevertheless the discrepancy between $\sigma$ (D.L.) and $\sigma$ (D.V.) remains uncomfortably large. (They should, of course, agree.) It is to be expected that the inclusion of correlation and exchange will tend to remove this discrepancy.

4. Calculations with exchange.—There is as yet no satisfactory way of including the effects of the long range polarization interaction in the central field approximation with exchange (see however Sloane & Massey 1964). We therefore neglect polarization in the central field exchange approximation.

We solved the equation (6) with $V_p(r) = 0$ for $l = 0, 2$ and $o < k^2 \leq 3$ Ry by a predictor–corrector technique normalizing by Strömgren's technique (Bates & Seaton 1949). Letting now

$$L_1 = \left\{ \frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} + \frac{2}{r} V_h(r) \right\}$$

then for $l = 2$ we solve at any stage (putting $P(r)$ for $P_{k^2,1}(r)$)

$$L_2 P_i(r) = X[aP_{i-1}(r) + bP_{i-2}(r)]$$

where $P_i(r)$ is the $i$th iterate of $P(r)$ and $a$, $b$, are mixing coefficients such that $a + b = 1$, except for $i = 1$ when we took $P_{i-1} = P_{i-2} = P_0$. Convergence of the solution usually occurred in less than six iterations with $a = b = \frac{1}{2}$. For $l = 0$, a similar procedure was followed, but at each iteration $P(r)$ was orthogonalized in the following manner:

We write $P^{(0)} = P_i + \lambda_i u$ where $\lambda_i$ is chosen so that $P^{(0)}(r)$ is orthogonal to $P_2(r)$, and $u(r)$ satisfies

$$L_0 u(r) = P_{2s}(r)$$

with boundary conditions as in Section 3. We must then solve at the $i$th iteration

$$L_2 P_i(r) = X[aP_{i-1}(r) + bP_{i-2}(r)]$$

which together with (20) is equivalent to (6). On convergence, which may require as many as 30 iterations if $k^2 \ll 1$, the orthonormal solution is $(P_i + \lambda_i u)/\lambda_i$, as before.

The results are shown in Figs. 3 and 4 for the energy ranges 0 to 3 eV and 0 to 40 eV. The calculated cross-sections are in rather better agreement with each other than were the best non-exchange results, but are in poor absolute agreement. The D.V. result is in good agreement with the experimental values except in the immediate neighbourhood of threshold, and since both $\sigma$ (D.L.) and $\sigma$ (D.V.) are in satisfactory agreement for $k^2 > 2$ Ry, we feel that the calculated values of $\sigma$ (D.V.) provide the best presently available results above 3 eV. The failure of the dipole length formulation is not unexpected in view of recent work on $H^-$ (Geltman 1962). In neither case is the calculated slope near threshold satisfactory. It appears that in order to account for the rapid rise of the cross-section within 0-2 eV of threshold detailed knowledge of rather sophisticated properties of the bound and free wave functions is required. Calculations on the effects of radially correlated continuum functions are in progress.

The experimental results of Seman & Branscomb (1962) suggest the existence of a bound excited state of the ground configuration of C−, possibly

$$(1s)^2(2s)^2(2p)^3 \#D.$$
Fig. 3.—Continuous absorption coefficient of $C^{-}$ using H.F. bound state functions and central field continuum functions with orthogonalization and exchange, 0 to 3 eV. Curve 1: experiment (Seman & Branscomb 1962); curve 2: D.L.; curve 3: D.V.

Fig. 4.—Continuous absorption coefficient of $C^{-}$ using H.F. bound state functions and central field continuum functions with orthogonalization and exchange, 0 to 40 eV. Curve 1: D.L.; curve 2: D.V.
Our results are compatible with this suggestion. Assuming the bound $2p^2D$ orbital of $C^-$ is not significantly different from that of the $(^4S)$ state, the resulting cross section for small $k^2$ is about one-tenth of that from $(^4S)C^-$. Thus provided not more than 50 per cent of the $C^-$ are in the $(^2D)$ state the contribution to the observed cross-section above the $(^4S)$ threshold should not exceed 3 per cent.

Acknowledgment

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Mathematics Department,
Royal Holloway College,
Englefield Green:
1964 January.

References