

## Electron Photodetachment from Ions and Elastic Collision Cross Sections for O, C, Cl, and F

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Photodetachment cross sections for  $O^-$ ,  $C^-$ ,  $Cl^-$ , and  $F^-$  have been computed in the energy range from threshold to 50 eV by the Klein-Brueckner method. Elastic cross sections for electron scattering from O, C, Cl, and F in the energy range 0–15 eV have also been computed. The method of calculation is described and the results compared with earlier theoretical and experimental work.

### I. INTRODUCTION

OUR understanding of the related processes of low-energy ( $\sim 15$  eV) elastic scattering from atoms and photodetachment from negative ions is at present fragmentary.<sup>1</sup> Even though much progress has been made recently both theoretically<sup>2</sup> and experimentally<sup>3–5</sup> for the important case of atomic hydrogen, little has been done for heavier atomic systems. Only recently have experimental techniques been developed which make possible the measurement of low-energy electron scattering cross sections from atoms other than the rare gases.<sup>6</sup> The same is true of photodetachment measurements.<sup>7</sup> On the theoretical side even less has been done, probably because it is felt that the many-body aspects of such problems can best be studied by considering the case of atomic hydrogen.

The theoretical work on low-energy elastic scattering for non-closed-shell atoms centers on oxygen and nitrogen.<sup>8–13</sup> Photodetachment studies have been made

for oxygen<sup>12,14,15</sup> and carbon<sup>16</sup> ions. In all of the work described in references 8–16 (with the possible exception of reference 13), the effects of electron exchange, of core polarization, and of higher multipole interactions are neither disregarded, or at best represented by semiempirical terms with adjustable coefficients. Complete neglect of these effects can lead to misleading results. For example, Breene<sup>16</sup> predicts a cross section for photodetachment from carbon ions an order of magnitude greater than that observed experimentally,<sup>17</sup> whereas Yamanouchi<sup>14</sup> predicts for oxygen ions a cross section about an order of magnitude smaller than experiment.<sup>18</sup>

Of the above-mentioned methods, only that of Klein and Brueckner<sup>12,19</sup> yields photodetachment cross sections that are in fair agreement (10–20%) with experiment. Since computer codes were available<sup>20</sup> which could be easily adopted to the KB method, calculations of this type have been carried out for the photodetachment from  $O^-$ ,  $C^-$ ,  $F^-$ , and  $Cl^-$ . Cross sections for electron scattering from O, C, F, and Cl atoms were obtained as a by-product. This work was motivated primarily by a desire to compare results obtained by the KB method with recent experiments on  $C^-$  photodetachment.<sup>17</sup> The remaining calculations were intended to provide additional data for detailed comparison with existing or future experiments.

The original KB calculation for  $O^-$  covered only the range where experimental evidence was available. Since the method can easily be extended to higher energies, photodetachment cross sections have been computed for electron energies as high as 50 eV. Elastic scattering cross sections for the atoms C, O, Cl, and F have been computed in the range 0–15 eV.

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<sup>1</sup> See (a) the review by H. W. S. Massey, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXV, pp. 232–306, for information on low-energy electron scattering from atoms, and (b) the review by L. M. Branscomb in *Advances in Electronic and Electron Physics* (Academic Press Inc., New York, 1957), Vol. IX, pp. 43–94, for information on photodetachment from negative ions.

<sup>2</sup> The list of recent papers on these two processes for atomic hydrogen would comprise a complete bibliography. We list a few of the more important: (a) A. Temkin and J. Lamkin, *Phys. Rev.* **121**, 788 (1961); (b) B. H. Bransden *et al.*, *Proc. Phys. Soc. (London)* **A71**, 877 (1958); (c) L. Rosenberg, L. Spruch, and T. O'Malley, *Phys. Rev.* **119**, 164 (1960); (d) S. Geltman, *ibid.* **119**, 1283 (1960); (e) T. L. John, *Proc. Phys. Soc. (London)* **A76**, 532 (1960); (f) S. Chandrasekhar, *Astrophys. J.* **128**, 114 (1958).

<sup>3</sup> S. Smith and D. Burch, *Phys. Rev.* **116**, 1125 (1959).

<sup>4</sup> R. Brackman, W. Fite, and R. H. Neynaber, *Phys. Rev.* **112**, 1157 (1958).

<sup>5</sup> R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, *Phys. Rev.* **123**, 148 (1961).

<sup>6</sup> W. Fite and R. Brackman, *Phys. Rev.* **112**, 1141 (1958).

<sup>7</sup> S. Smith and L. Branscomb, *Rev. Sci. Instr.* **31**, 733 (1960).

<sup>8</sup> D. R. Bates and H. S. W. Massey, *Proc. Roy. Soc. (London)* **A192**, 1 (1947).

<sup>9</sup> T. Yamanouchi, *Prog. Theoret. Phys. (Kyoto)* **2**, 23 (1947).

<sup>10</sup> L. Robinson, *Phys. Rev.* **105**, 922 (1957).

<sup>11</sup> P. Hammerling, W. Shine, and B. Kivel, *J. Appl. Phys.* **28**, 760 (1957).

<sup>12</sup> M. Klein and K. Brueckner, *Phys. Rev.* **111**, 1115 (1958).

<sup>13</sup> A. Temkin, *Phys. Rev.* **107**, 1004 (1957).

<sup>14</sup> T. Yamanouchi, *Proc. Phys. Math. Soc. Japan* **22**, 569 (1940).

<sup>15</sup> D. R. Bates and H. S. W. Massey, *Phil. Trans. Roy. Soc. London* **A239**, 269 (1941).

<sup>16</sup> R. G. Breene, *Planetary and Space Science* **2**, 10 (1959).

<sup>17</sup> M. Seman and L. Branscomb, *Phys. Rev.* **125**, 1602 (1962).

<sup>18</sup> L. Branscomb, S. Smith, D. Burch, and S. Geltman, *Phys. Rev.* **111**, 504 (1958).

<sup>19</sup> Since this method forms the basis of the present work we shall henceforth refer to reference 12 and this method as KB.

<sup>20</sup> J. Cooper, in *Proceedings of the Second International Conference on the Physics of Electronic and Atomic Collisions, Boulder, Colorado, June, 1961* (W. A. Benjamin Inc., New York, 1961), pp. 7–10.

## II. METHOD OF CALCULATION

The cross section for photodetachment of an electron in the subshell  $nl$  of a negative ion may be derived under the assumption that the wave functions for the system both before and after detachment may be expressed as sums of products of one-electron central field orbitals. The cross section is<sup>21</sup>

$$\sigma = \frac{4}{3} \pi \alpha_f a_0^2 P(E_b + k^2) (C_{l-1} M_{l-1}^2 + C_{l+1} M_{l+1}^2) \text{ cm}^2, \quad (1)$$

where

$$M_{l\pm 1} = \int_0^\infty P_{nl}(r) r P_{k,l\pm 1}(r) dr. \quad (2)$$

The fine structure constant  $\alpha_f$  and Bohr radius  $a_0$  have been introduced here so that  $\sigma$  is expressed in  $\text{cm}^2$  although  $r$  is in atomic units,  $E_b$  is the binding energy and  $k^2$  the energy of the outgoing electron (both in rydbergs),  $P_{nl}(r)$  and  $P_{k,l\pm 1}(r)$  are radial wave functions for the bound  $nl$ , and free electrons of angular momentum quantum number  $l\pm 1$  normalized so that

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

and

$$P_{k,l\pm 1}(r) \xrightarrow{r \rightarrow \infty} k^{-\frac{1}{2}} \sin(kr + \delta).$$

$P$  is the overlap integral of the electrons which are in the same state both before and after detachment, and will be assumed to be unity. The constants  $C_{l\pm 1}$  depend on the initial and final states of the system.

The  $C_l$ 's are obtained by evaluating the angular part of the dipole matrix element for each transition. In the present work  $l=1$  always, and the appropriate value of  $C_0$  and  $C_2$  as tabulated by Bates<sup>21</sup> are listed in Table I for each transition of interest. It should be noted that for  $O^-$  three transitions are possible since the O atom may be left in the  $^3P$ ,  $^1D$ , or  $^1S$  states of the ground configuration after detachment. The relative probability of these transitions is taken as equal to the weighting factors 1, 5/9, 1/9 as indicated in Table I. Note that these ratios depend upon our assumption of an independent particle model and may be modified by correlation effects.

In this formulation the main problem is the determination of the radial functions  $P_{nl}(r)$  and  $P_{kl}(r)$ . Following KB we assume both of these to be eigenfunctions of the same central potential; i.e., to satisfy the radial Schrödinger equation:

$$\left[ \frac{d^2}{dr^2} - 2V(r) + \frac{\alpha}{(r^2 + r_p^2)^2} - \frac{l(l+1)}{r^2} - E_b \right] P_{nl}(r) = 0. \quad (3)$$

Here  $V(r)$  is a central potential derived from the charge distribution of the neutral atom to which an  $nl$

TABLE I. Values of  $C_0$  and  $C_2$  used in Eq. (1) for each transition.

Transition	$C_0$	$C_2$
$O^-(^3P) \rightarrow O(^3P) + e$	1	2
$O^-(^3P) \rightarrow O(^1D) + e$	5/9	10/9
$O^-(^3P) \rightarrow O(^1S) + e$	1/9	2/9
$C^-(^4S) \rightarrow C(^3P) + e$	1	2
$F^-(^1S) \rightarrow F(^2P) + e$	2	4
$Cl^-(^1S) \rightarrow Cl(^2P) + e$	2	4

electron is bound by energy  $E_b$ . The correction factor  $\alpha/(r^2 + r_p^2)^2$  is allowed to absorb the effects of polarization and exchange as they affect the binding energy.  $r_p$  is taken, somewhat arbitrarily, to be the average distance from the nucleus of the outer  $nl$  electrons of the neutral atom.  $\alpha$  is a polarizability parameter which serves as an eigenvalue once the binding energy  $E_b$  is specified. For free electrons  $P_{nl}(r)$  is replaced by  $P_{kl}$  in (3) and  $-E_b$  by  $k^2$ .  $V(r)$  has been obtained for each atom from the relation

$$V(r) = -\frac{Z}{r} + \int \frac{d\mathbf{r}' \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

where  $\rho(\mathbf{r}')$  is the charge distribution of electrons derivable from Hartree or Hartree-Fock wave functions for an atom of atomic number  $Z$ .<sup>22</sup> Binding energies have been obtained from the recent work of Edlén<sup>23</sup> which agree well with available experimental evidence.<sup>24</sup>

The steps in the evaluation of (1) are as follows:

(1)  $V(r)$  is computed using (4) from the available wave functions.<sup>25</sup>

(2) The bound state equation (3) is solved treating  $\alpha$  as an eigenvalue. This yields a value of  $\alpha$  and a radial bound-state wave function  $P_{nl}(r)$ .

(3) The free wave functions  $P_{kl}(r)$  are evaluated for various energies  $k^2$  using the value of  $\alpha$  found in step (2).

(4) The integrals  $M_{l\pm 1}$  are evaluated for each energy and from them the cross sections computed using (1).

The cross sections for elastic scattering of electrons from atoms are obtained as a by-product of the calculation, since  $P_{kl}(r)$  may be interpreted as the  $l$ th partial wave of an electron moving in the field of a polarized atom.<sup>26</sup> Asymptotically,

$$P_{kl}(r) \xrightarrow{r \rightarrow \infty} k^{-\frac{1}{2}} \sin(kr + \delta_l - \frac{1}{2}\pi l),$$

<sup>22</sup> We have used the Hartree-Fock wave functions of D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **A238**, 229 (1939); of A. Jucys, Proc. Roy. Soc. (London) **A173**, 59 (1939) for O and C; and the Hartree wave functions of D. R. Hartree, R. de L. Kronig, and H. Peterson, Physica **1**, 895 (1934) and of F. W. Brown, Phys. Rev. **44**, 214 (1933) for Cl and F.

<sup>23</sup> B. Edlén, J. Chem. Phys. **33**, 918 (1960).

<sup>24</sup> See Branscomb, reference 1b, p. 52.

<sup>25</sup> We computed  $V(r)$  using (4) only for C and O. For Cl and F we used the function  $Z_p(r)/r$  tabulated by Brown and by Hartree *et al.*, respectively.  $Z_p(r)/r$  contains some effects of electron exchange, but differs little from  $V(r)$  as calculated by (4).

<sup>26</sup> See reference 1a, pp. 236-7.

<sup>21</sup> D. R. Bates, Monthly Notices, Roy. Astron. Soc. **109**, 432 (1946).

and the scattering cross section is

$$\sigma_s = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \delta_l. \quad (5)$$

Since at the low energies considered, only  $s$ ,  $p$ , and  $d$  wave contribute, and since the free wave equations must be solved (for  $p$  orbitals) for  $s$  and  $d$  waves to obtain the photodetachment, we have only to solve in addition the equations for  $l=1$  to obtain estimates of the elastic scattering cross sections.

The rationale for the above procedure is given by KB in reference 12. Its chief advantages are:

(1) The method yields bound radial orbitals with the correct binding energy. The low-energy photodetachment cross section is strongly affected by the "tail" of the radial wave function which is of the form  $(1+E_b^{-1/2}/r) \exp(-E_b^{1/2}r)$ . Thus a bound state of this form should yield improved photodetachment cross sections over the methods of references 14 and 15, where Hartree-Fock bound state orbitals for  $O^-$  are used, and the "tail" region is of the form  $\exp(-E_b^{1/2}r)$  with  $E_b=3.5$  ev. ( $E_b=1.46$  ev experimentally.)

(2) To the extent that an atom can be considered spherically symmetric, the asymptotic form of the central potential is correctly  $\alpha/r^4$ .

This method has the following disadvantages:

(1) The use of a one-electron model cannot be expected to treat adequately the effects of electron correlation. These effects are expected to be important in photodetachment from negative ions, particularly in the case of  $O^-$ , since the neutral atom may be left in excited states of the ground configuration after detachment.

(2) The semiempirical parameters  $\alpha$  and  $r_p$  do not arise naturally from the formalism as they do in more sophisticated treatments.<sup>13,27</sup> Thus the only criteria we have for the accuracy of the method is its agreement with experimental results.

In addition to the assumptions made above, KB made the following additional approximations in carrying out the numerical calculations for  $O^-$  photodetachment:

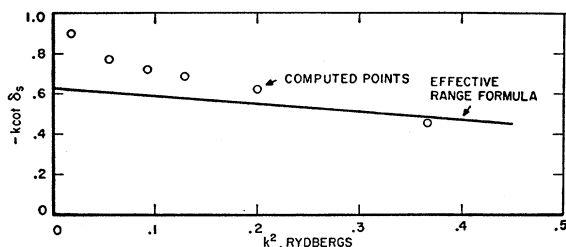


FIG. 1. The deviations of our computed phase shifts from the effective range fit of KB for oxygen.

<sup>27</sup> B. A. Lippmann, M. H. Mittleman, and K. M. Watson, Phys. Rev. **116**, 920 (1959).

(a) In determining the bound-state  $2p$  radial function, Eq. (3) was integrated out to  $r=3a_0$  and the function there adjusted to fit the asymptotic form  $P_{2p}(r)=N(1+E_b^{-1/2}/r) \exp(-E_b^{1/2}r)$ .  $\alpha$  was varied until a fit is obtained.

(b) The  $d$ -wave matrix element  $M_d$  was obtained by assuming the asymptotic form for the bound-state wave function and a spherical wave  $J_{5/2}(kr)$  for the free electron.

(c) Calculations of continuum  $s$ -wave functions were carried out only for a few energies. The phase shifts  $\delta_s$  for additional energies were obtained from the effective-range formula,

$$k \cot \delta_s = -1/a + \frac{1}{2} r_0 k^2, \quad (6)$$

where  $a$  and  $r_0$  were fitted to the computed values of  $\delta_s$ .

$M_s$  was then evaluated by entering  $\delta_s$  in an analytic approximation formula which ignores the integrations over the range  $r < R_0$  (KB take  $R_0=3.0a_0$ ) and uses the asymptotic forms for both bound and free electrons.

Since a high-speed computer was available for our work we have computed matrix elements by direct numerical integration without making approximations  $b$  and  $c$ . Our method of computing  $\alpha$  is somewhat different from KB, since we integrated the bound-state wave function out to large ( $\sim 20a_0$ ) distances and adjusted  $\alpha$  until the wave function approached zero asymptotically. The value we obtain for  $O^-$  is  $\alpha=5.499$ , for  $r_p=1.2$ . The slight variation of this from KB's value of  $\alpha=5.587$  has practically no effect on subsequent calculations.

The approximation (b) made for  $M_d$  was checked and found to be valid (to 1 or 2% accuracy) up to electron energies of  $\sim 10$  ev. However, the approximation (c) requires closer examination.

Spruch *et al.*<sup>28</sup> have pointed out that for a central potential with asymptotic form  $\alpha/r^4$  the correct effective-range formula is not (6) but

$$k \cot \delta_s = -1/a + \pi \alpha k / 3a^2 + (4\alpha/3a) k^2 \ln(\alpha^{1/2} k / 4) + O(k^2). \quad (7)$$

In Fig. 1 we have plotted our numerical results<sup>29</sup> for  $k \cot \delta_s$  vs  $k^2$  and also KB's fit to (6) using  $a=1.613$ ,  $r_0=0.860$ . The figure shows that (6) is not a good fit to the numerical results.

We have tried to fit (7) to our data, but obtained poor results for two reasons. First, and most important, the energies at which calculations were carried out are too high for (7) to be a good approximation. For example, if we assume  $a=1$ , then the successive terms in (7) for  $k=0.1356$  (the lowest energy at which our

<sup>28</sup> L. Spruch, L. Rosenberg, and T. F. O'Malley, Phys. Rev. Letters **5**, 375 (1960).

<sup>29</sup> The phase shifts in all cases were obtained by comparing the zeros of the integrated wave function with the zeros of the spherical Bessel function  $J_{l+1/2}(kr)$ . For machine computations this seems to the authors to be the best, if not the most elegant, procedure provided  $k$  is not too small.

computations were made) are:

$$k \cot \delta_s \cong -1 + 0.780 - 0.341 + O(k^2),$$

and it appears that higher-order terms must be included to give meaningful results. Since (7) is not valid in our energy range we cannot obtain  $a$  by fitting to our numerical results. Second, our method of computing phase shifts leads to inaccuracies at low energies. At  $k=0.1356$  the phase shift is computed at  $r=24a_0$  and one would expect an additional phase shift due to the polarization potential for  $r>24a_0$ . Temkin<sup>30</sup> has evaluated the effect of the polarization for distances  $r>20a_0$  for the case of scattering from hydrogen at low energies, and from his results we would expect our calculated phase shifts at  $k=0.1356$  to be in error by less than 10%.

### III. PHOTODETACHMENT-DISCUSSION OF RESULTS

The results of all of the photodetachment cross sections computed are presented in Table II. The numerical accuracy of the results is about 1-2%, which is certainly smaller than the errors introduced by other approximations.

In Table III we list the values of  $\alpha$ ,  $r_p$ , and  $E_b$  used in each calculation.  $E_b$  was taken from reference 23 (except for  $O^-$  where we use the old experimental value 1.45 ev) and  $r_p$  was evaluated from the wave functions listed in footnote 22. The values of  $\alpha$  shown are eigenvalues of Eq. (3) in each case. Also shown in the table are the polarizabilities calculated by Dalgarno and Parkinson<sup>31</sup> for O, C, and F which agree reasonably well with our values.

#### A. $O^-$ Photodetachment, Threshold to 10 ev

Our  $O^-$  cross section is compared with the earlier work of KB<sup>12</sup> and with two experimental determina-

TABLE II. Summary of photodetachment results. All cross sections are in units of  $10^{-18} \text{ cm}^2$ .

Electron energy (ev)	$O^-$ <sup>a</sup>	$C^-$	$F^-$	$Cl^-$
0.25	5.1	7.8	4.0	...
0.75	6.6	11.0	5.6	...
1.25	7.2	12.9	6.2	...
1.75	7.7	14.5	6.8	16.0
4.75	9.5	17.2	9.8	37.7
6.75	9.2	16.5	11.1	49.9
8.75	8.9	14.8	11.9	49.9
13.61	7.9	11.6	12.2	16.4
27.21	5.3	4.2	10.5	0.6
54.42	2.4	1.1	6.1	1.0

<sup>a</sup>  $^2P \rightarrow ^3P$  only.

<sup>30</sup> A. Temkin, Phys. Rev. Letters **6**, 354 (1961).

<sup>31</sup> A. Dalgarno and D. Parkinson, Proc. Roy. Soc. (London) **A250**, 422 (1959).

TABLE III. Polarization distances ( $r_p$ ), binding energies ( $E_b$ ) and polarizabilities ( $\alpha$ ) for C, F, Cl, and O.

Element	$r_p$ ( $a_0$ )	$E_b$ (ev)	$\alpha$ (this paper) ( $a_0^3$ )	$\alpha$ (reference 31) ( $a_0^3$ )
C	1.71	1.25	16.149	14.17
F	1.16	3.50	4.077	4.048
Cl	2.046	3.70	23.26	...
O	1.2	1.45	5.499	6.005

tions<sup>18,32</sup> in Fig. 2. The difference between our curve and that of KB is due entirely to their use of the incorrect effective-range formula [Eq. (6)].

The two experimental cross sections show a disagreement in slope for electron energies greater than 2 ev. The reason for the disagreement<sup>33</sup> is that the apparatus in the earlier work was slightly wavelength sensitive. Since the primary purpose of the first experiment was an accurate determination of the binding energy this sensitivity escaped detection until a new apparatus was built.<sup>34</sup>

The agreement of our results with experiment for energies up to 2 ev is remarkably good. However, the difference in slope for larger energies shows the need for more theoretical work.

The results shown in Fig. 2 refer only to transitions which leave the oxygen atom in its  $^3P$  ground state. For higher excitation energies the atom may be left in a  $^1D$  or  $^1S$  state, the threshold for these processes being 3.43 ev and 5.66 ev, respectively. Since one would expect the free-electron radial wave functions to be the same for these processes, an estimate of the total cross section up to 10 ev can be obtained by using the same radial matrix elements for each transition in Eq. (1), but using the values of  $E_b$  which correspond to each threshold and the appropriate values of  $C_0$  and

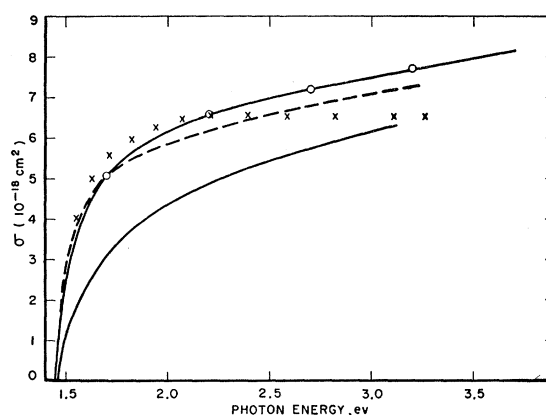


FIG. 2. Photodetachment from  $O^-$ , 1.45-3.5 ev.  $\circ$ , this paper; dashed line, reference 18 (exp.);  $\times$ , reference 32 (exp.); solid line, reference 12 (KB).

<sup>32</sup> S. J. Smith, *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases Uppsala* (North-Holland Publishing Company, Amsterdam, 1960), p. 219.

<sup>33</sup> L. M. Branscomb (private communication).

<sup>34</sup> See reference 7 for a description of the experimental setup.

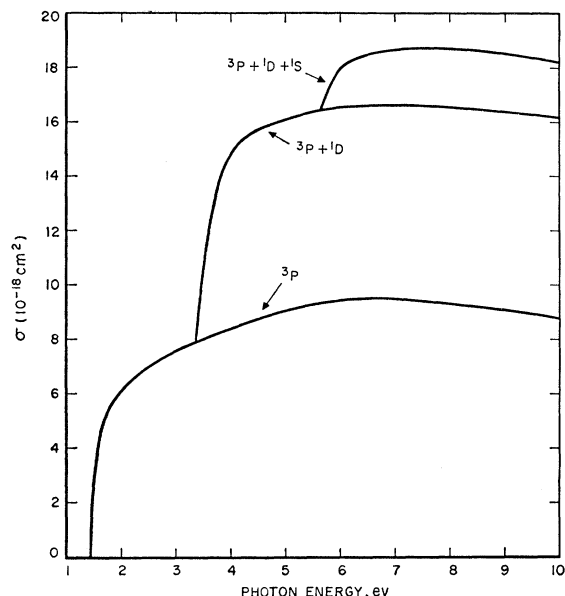


FIG. 3. Photodetachment from  $O^-$ , 1.45–10.0 ev.

$C_2$  from Table I. The results when this is done are shown in Fig. 3. Similar plots have been given by Yamanouchi<sup>14</sup> and by Smith.<sup>32</sup>

Figure 3 points up the need for further experimental and theoretical work on photodetachment cross sections. Although the experimental results in the region 1.45–2.0 ev are in good agreement with the results of this paper, the fact that the best experimental curve remains flat in the region 2.0–3.0 ev while the theoretical curve rises will lead to discrepancies of about 60–70% in the extrapolated results for energies between 5 and 10 ev.

### B. $C^-$ Photodetachment, 1.25–3.0 ev

The detailed photodetachment results for carbon are given in Table II. In Fig. 4 we show a comparison of

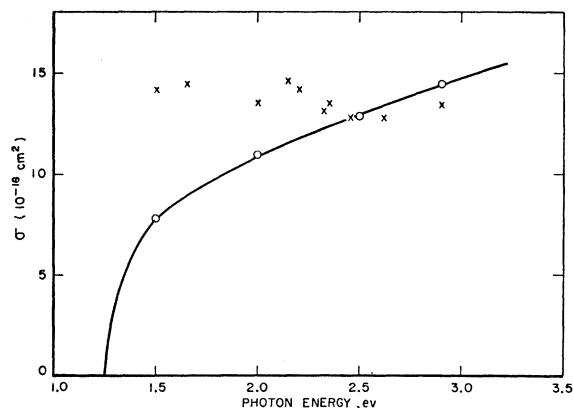


FIG. 4. Photodetachment from  $C^-$ , 1.25–3.0 ev. O, this paper; X, reference 17 (exp.).

the low-energy results with the experimental determination of reference 17. The discrepancy in slope between theory and experiment is much worse in this case than for oxygen. While in oxygen theory predicts roughly the same shape of the cross section as experiment in the region up to about 1 ev above threshold, the carbon cross section as measured is practically flat in this region. On the other hand, the calculations agree with experiment at higher energies and the discrepancy in slope is not as important in this case, as in the case of oxygen, in estimating cross sections in the region 3–10 ev since the ground state of  $C^-$  is  $^4S$  and there is only one transition possible  $C^-(^4S) \rightarrow C(^3P) + \text{electron}$ .

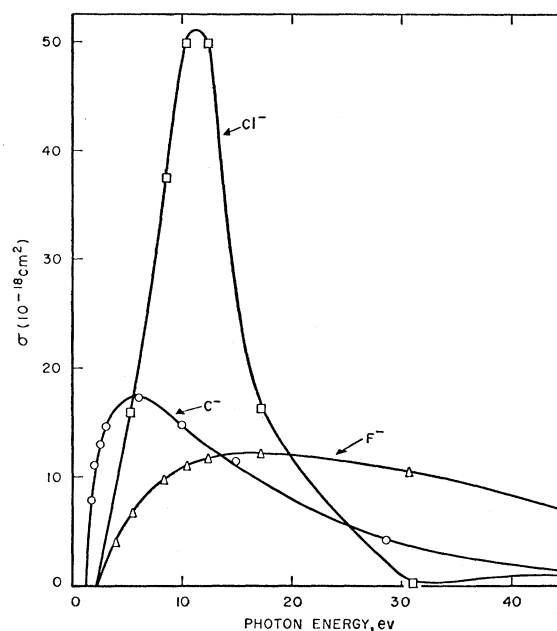


FIG. 5. Photodetachment from  $C^-$ ,  $F^-$ , and  $Cl^-$ , threshold to 45 ev. Points at which computations were made are shown. Circles represent  $C^-$ , squares  $Cl^-$ , and triangles  $F^-$ .

### C. $C^-$ , $Cl^-$ , and $F^-$ Photodetachment, Threshold to 50 ev

Since the negative ions  $Cl^-$  and  $F^-$  are  $^1S_0$  states, the only allowed state of the atom after detachment is  $^2P$ . Thus, under the assumption that the neutral atom is left in its ground configuration after detachment, the cross sections for  $C^-$ ,  $Cl^-$ , and  $F^-$  may be calculated directly from Eq. (1). Curves based on the results in Table II are shown in Fig. 5.

Certain conclusions can be drawn about the general behavior of photodetachment cross sections from the results shown in Fig. 5. First, it should be mentioned that to the extent that no bound excited states of the ion exist outside the ground configuration,<sup>35</sup> the photo-

<sup>35</sup> Although experimental evidence exists for an excited state in  $C^-$  (reference 17) it is almost certainly either  $(2p^3)^2D$  or  $(2p^3)^2P$ . Our effective potential for  $C^-$  was found to be too weak

detachment cross sections calculated on a central field model rigorously satisfy a sum rule of the form<sup>36</sup>:

$$\frac{1}{4\pi\alpha_f} \int_{E_b}^{\infty} \sigma(E) dE = Z' + \epsilon. \quad (8)$$

Here  $\sigma(E)$  is the cross section of Eq. (1) in atomic units,  $Z'$  is the number of electrons in the outer ( $2p$  or  $3p$  for our calculations) shell, and  $\epsilon$  makes allowance for transitions to the states  $1s$ ,  $2s$  (and  $3s$  for  $\text{Cl}^-$ ) which are excluded by the Pauli principle. Since most of the photodetachment cross section is due to  $np$ - $ed$  transitions,  $\epsilon$  will be small compared to  $Z'$ . Thus, the area under the  $\text{Cl}^-$  and  $\text{F}^-$  ( $Z'=6$ ) curves in Fig. 5 should roughly be equal and twice that of the area under the  $\text{C}^-$  curve ( $Z'=3$ ). The maxima in the cross sections can be interpreted as due to a resonance effect which occurs when the  $d$  wave for the free electron is "in phase" with the largest peak of the ground-state radial wave function. The difference in shape between the cross

TABLE IV. Phase shifts (modulo  $\pi$ ) and contributions to the elastic scattering cross sections for  $s$ ,  $p$ , and  $d$  waves for oxygen. The contributions are  $\sigma_l = [4\pi(2l+1)/k^2] \sin^2\delta_l$ .

Electron energy (ev)	$\delta_s$	$\sigma_s$ ( $a_0^2$ )	$\delta_p$	$\sigma_p$ ( $a_0^2$ )	$\delta_d$	$\sigma_d^a$ ( $a_0^2$ )	$\sigma_s + \sigma_p$ ( $a_0^2$ )
0.25	-0.151	4.92	-0.009	0.05	...	...	4.97
0.75	-0.295	6.13	-0.052	0.59	...	...	6.72
1.25	-0.401	6.63	-0.096	1.20	...	...	7.83
1.75	-0.487	6.81	-0.136	1.72	...	...	8.53
2.72	-0.622	6.79	-0.202	2.41	...	...	9.20
5.0	-0.855	6.20	-0.315	3.13	-0.054	0.140	9.33
10.0	-1.186	4.68	-0.473	3.39	...	...	8.07
13.61	-1.356	3.82	-0.554	3.32	-0.169	0.71	7.14

<sup>a</sup> Since  $\delta_d$  was computed only at 5 and 13.61 ev, the  $d$ -wave contribution is neglected in the totals.

section of  $\text{Cl}^-(3p)^6$  and  $\text{F}^-(2p)^6$  is analogous to the difference in shape of the photoionization cross sections for Ar and Ne.<sup>37</sup>

It should be mentioned that the above discussion refers only to the photodetachment from the outer ( $2p$  or  $3p$ ) subshell. The total photodetachment from the ion will, of course, rigorously satisfy the Thomas-Kuhn sum rule:

$$\frac{1}{4\pi\alpha_f} \int_{E_b}^{\infty} \sigma(E) dE = Z.$$

Equation (8) is merely a special case of the more general Thomas-Kuhn rule. However, the approxi-

to support a bound ( $2p^23s$ ) state. The existence of excited states in  $\text{F}^-$  and  $\text{Cl}^-$  is highly unlikely since the ground states of these ions are  $^1S_0$  (closed shells).

<sup>36</sup> H. A. Bethe and E. Salpeter, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. XXXV, Sec. 61.

<sup>37</sup> U. Fano, *Proceedings of the Second International Conference on the Physics of Electronic and Atomic Collisions*, Boulder, Colorado, June, 1961 (W. A. Benjamin Inc., New York, 1961), pp. 10-11.

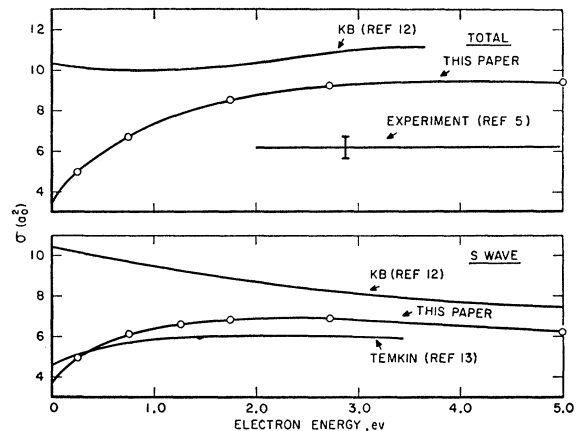


FIG. 6. Total and  $s$ -wave scattering cross sections for oxygen.

mation that the contributions to the photodetachment from each subshell can be considered separately is a good one. Detachment from the inner subshells will occur only at higher energies. For example, detachment of a  $2s$  electron will have a threshold at about 22 ev in  $\text{O}^-$  and  $\text{F}^-$ , while  $3s$  photodetachment in Cl will occur at about 20 ev.

#### IV. ELASTIC SCATTERING CROSS SECTIONS

Our results for elastic scattering of electrons from O, C, F, and Cl are presented in Figs. 6-9.

In Fig. 6 we show our results for oxygen along with the results of KB<sup>12</sup> and Temkin.<sup>13</sup> Also shown in a recent experimental result.<sup>5</sup> The figure shows the effect of the incorrect effective range expansion on the cross section. Our results for  $s$  waves are seen to be in good agreement

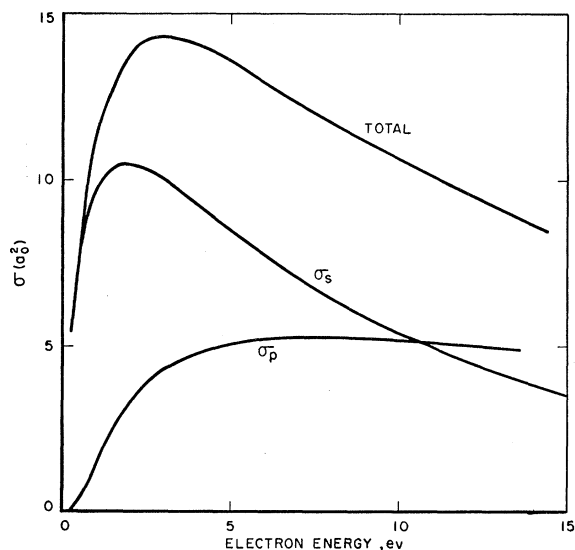


FIG. 7.  $s$ -wave,  $p$ -wave, and total ( $s+p$ ) scattering cross sections for C.

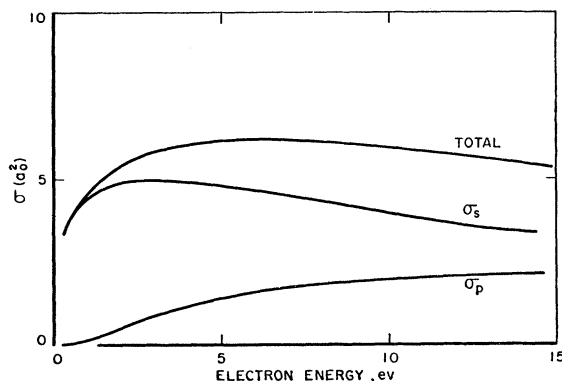


FIG. 8. *s*-wave, *p*-wave, and total (*s*+*p*) scattering cross sections for F.

with those of Temkin.<sup>38</sup> The results of the calculations for oxygen are also listed in Table IV.

In Figs. 7 and 8 we show the cross sections for C and F. Individual contributions of *d* waves was found to be negligible for energies below 10 ev.

Our results for chlorine are similar to those for argon computed by Holtmark.<sup>39</sup> We noticed in preliminary work that the Cl phase shifts for *s* and *p* waves vanish (modulo  $\pi$ ) at small energies below 1 ev. In order to explore this "Ramsauer minimum" we have computed *s*- and *p*-wave phase shifts at a number of points below 1 ev. These calculations were carried out to large

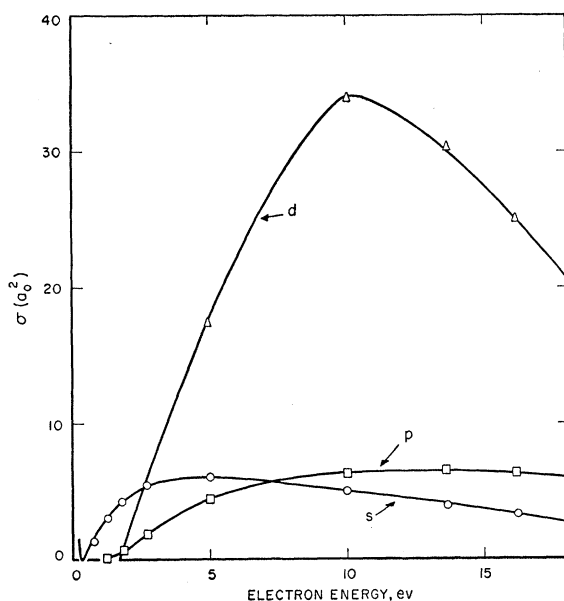


FIG. 9. *s*-wave, *p*-wave, and *d*-wave scattering cross sections for Cl.

<sup>38</sup> Even better agreement would be obtained if the phase shifts were evaluated more accurately for electron energies less than 1 ev as mentioned in Sec. II.

<sup>39</sup> J. Holtmark, Z. Physik 55, 437 (1929).

distances ( $r=50-60a_0$ ) so that the neglect of the polarization "tail" does not introduce large errors. The results are shown in Table V.

We have attempted to fit the *s*-wave data of Table V to the effective range formula (7). For  $\delta_s \sim n\pi$  and  $k$  small (7) may be written as:

$$\delta_s \sim -ak - \frac{1}{3}\pi\alpha k^2 - \frac{4}{3}\alpha^2 k^3 \ln(\alpha^2 k/4) + \dots \quad (9)$$

An examination of the size of the terms in (7) shows, however, that (9) is not a good approximation even for energies as low as 0.1 ev. The only information we can obtain from (9) is that  $\alpha$  must certainly be negative for  $\delta_s$  to vanish. Additional calculations at lower energies would be desirable, but have not been attempted.

In Fig. 9 we show the *s*-, *p*-, and *d*-wave contributions to the Cl cross section. As in argon, the *d*-wave contribution dominates the cross in the region 5-15 ev.

## V. FINAL REMARKS

The extension of the KB model to other atomic systems provides photodetachment cross sections which agree in magnitude but not in spectral shape with

TABLE V. *s* and *p* phase shifts for Cl at low energies.

Energy (ev)	$\delta_s - 3\pi$	$\delta_p - \pi$
0.1	0.080	0.022
0.2	0.051	0.033
0.3	0.012	0.034
0.4	-0.025	0.032
0.5	-0.057	0.031
0.6	-0.090	0.025
0.7	-0.152	0.009
0.8	-0.180	0.001
0.9	-0.206	-0.007
1.0	-0.230	-0.015

experiment. The agreement of theory and experiment for  $O^-$  at low energies is fortuitous. Our prediction of the  $F^-$  and  $Cl^-$  cross sections are probably good to within a factor of 2 although correlation effects will "smear out" the spectral dependence which we obtain and flatten the curves.

Our elastic scattering results are more uncertain since experimental evidence is scant. However, the good agreement of our results for oxygen with the more elaborate treatment of Temkin<sup>13</sup> is encouraging.

The prediction of a Ramsauer effect for Cl scattering at low energies on this model should be noted. An experimental verification of this would be desirable.

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