We must now consider the question of whether these relationships are useful in the interpretation of collision cross-section data. From the angular distribution function of collision cross sections we may derive the curve of generalized oscillator strengths, f_n, *versus* the square of the change of momentum on impact, K^2. The slope of this curve at any value of K^2 is given, from Eq. (3), as

$$\frac{df_n}{d(K^2)}=\sum_{p>1}(2p-2)a_{np}K^{2p-3}.$$

If we now sum the slopes for the f_n *vs* K^2 curves for all transitions, we obtain

$$\sum_n\frac{df_n}{d(K^2)}=\sum_n\sum_{p>1}(2p-2)a_{np}K^{2p-3}=\sum_{p>1}(2p-2)K^{2p-3}(\sum_n a_{np})=0. \quad (7)$$

Hence we have the result that the summation over all transitions of the slopes of the f_n *vs* K^2 curves is equal to zero. The method used here may be generalized to show that the sum of the *n*th derivatives, for all transitions, is equal to zero. These results, when taken in conjunction with the generalized oscillator strength sum rule, should be useful as a criterion for judging the accuracy of experimental and theoretical cross sections.

Generalized oscillator strength *vs* K^2 curves are now available for several gases.[5] An examination of these curves shows that, in general, the slopes of the f_n *vs* K^2 curves for discrete transitions and for points in the continuum not too far above the ionization potential are always negative over the angular range studied. For points further out in the continuum the slopes are positive at low K^2 and negative at high K^2. The value of K^2 at which the slope is zero increases as one goes further out in the continuum. The behavior outlined here is general for all gases that have been studied thus far. It is clear that this type of behavior is exactly what is to be expected on the basis of the theorem presented in this paper, and thus constitutes at least qualitative experimental proof of its validity.

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[5] See, for example, reference 2, and other reports in that series.

PHYSICAL REVIEW VOLUME 111, NUMBER 4 AUGUST 15, 1958

Interaction of Slow Electrons with Atomic Oxygen and Atomic Nitrogen†

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(Received April 16, 1958)

The polarization potential for an electron in the field of an oxygen atom has been determined by utilizing recent experimental results on the binding energy of O^-. The corresponding polarization potential for atomic nitrogen has been obtained from the results for oxygen by an extrapolation based on the theory of polarization. From these results the photodetachment cross section for O^- and the scattering cross sections for oxygen and nitrogen have been calculated. The photodetachment cross section is in good agreement with experimental results. The scattering cross sections are compared with other recent calculations.

It is also shown on the basis of the general theory of the photodetachment cross section that the energy dependence of the cross section determines the scattering length for electron scattering. The agreement of the computed photodetachment cross section with experiment therefore is a direct check on the scattering prediction.

I. INTRODUCTION

THE properties of air at temperatures sufficiently high to dissociate the air molecules and ionize the resulting atoms depend upon the scattering processes between slow electrons and the atoms of oxygen and nitrogen. Because of the difficulties involved in the experimental determination of low-energy scattering cross sections, good theoretical calculations are essential. In this paper we shall utilize recent experimental results of Branscomb, Burch, Smith, and Geltman[1] on the photodetachment cross section to obtain improved predictions of the scattering cross sections.

Calculations of the elastic scattering cross section in oxygen and nitrogen have recently been made by Robinson[2] and Hammerling, Shine, and Kivel.[3] We

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† Work performed under the auspices of the U. S. Air Force Ballistic Missiles Division.

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[1] Branscomb, Burch, Smith, and Geltman (private communication). The authors are indebted to Dr. S. Geltman for information on these results in advance of publication.

[2] L. B. Robinson, Phys. Rev. **105**, 922 (1957). This paper also includes a discussion of earlier work.

[3] Hammerling, Shine, and Kivel, J. Appl. Phys. **28**, 760 (1957).

shall defer discussion of this work and comparison with our results until Sec. VI.

The scattering of slow electrons by an atom may be determined if the potential acting on the electron is known. A first approximation to this potential is obtainable from the wave functions calculated by the Hartree-Fock method for the neutral atom. Such an approximation is inadequate in that exchange effects between the free electron and the bound electrons of the atom are neglected, and more important, the distortion of the wave functions of the bound electrons (polarization) by the incident electron is ignored. The latter effect may be represented by a polarization potential as discussed by Bates and Massey.[4] Such a procedure is probably adequate for most purposes but not sufficiently accurate when the incident electron and the atom form bound or virtual states of O^- near zero energy. The scattering cross section becomes very large for such states near zero energy and is very sensitive to the exact position of the resonance levels. Recognizing this uncertainty, Bates and Massey introduced an adjustable parameter into their polarization potential which could be adjusted to give a bound $3s$ state at any desired level for the additional electron. For a given value of the polarization parameter the photodetachment cross section for O^- could then be calculated. At the time of their work, insufficient experimental data was available to fix this parameter. The recent experimental work[1] on the photodissociation cross section for O^- enables us to fix the polarization parameter and thus obtain the scattering cross section, at least to an improved approximation.

Even in the absence of information concerning the polarization potential, useful information may be obtained from the experimental photodetachment cross section. As will be shown later, the photodetachment cross section depends principally upon the continuum s wave scattering length and the normalization constant for the bound $2p$ electron wave functions. Observation of the photodetachment cross section as a function of energy thereby enables us to determine both these quantities. The s wave phase shifts are then obtained from the scattering length as a function of energy by an effective range formula.[5]

As noted here, the calculation of the scattering cross section for oxygen depends upon the determination of the polarization potential from the photodetachment cross section for the negative ion O^-. Such a procedure is not possible for nitrogen since it does not form a stable negative ion. The polarization potential for nitrogen has therefore been obtained from the results for oxygen by use of some theoretical work on polarizibility by Buckingham.[6]

In Sec. II we review briefly the theory of the photodetachment process, while in Sec. III we discuss the procedures for fixing the polarization potential and determining the photodetachment cross section. In Sec. IV the results are compared with the experimental photodetachment cross section. In Sec. V we show how the polarization potential for nitrogen is determined from that for oxygen and give the scattering cross sections for both atoms. In Sec. VI the results are discussed and compared with those obtained in other recent investigations of this problem.

II. THEORY OF THE PHOTODETACHMENT CROSS SECTION

The cross section for the process

$$O^- + h\nu \rightarrow O + e^-$$

as given by Bates and Massey is

$$\sigma = \frac{8\pi}{3}\frac{mke^2\omega}{\hbar^2 c}(M_s^2 + 2M_d^2), \tag{1}$$

where

$$M_s = \int_0^\infty u_s(r)u_{2p}(r)r^3 dr, \tag{2}$$

$$M_d = \int_0^\infty u_d(r)u_{2p}(r)r^3 dr. \tag{3}$$

The radial function $u_{2p}(r)$ is the ground-state wave function for the bound electron and has the normalization

$$\int_0^\infty r^2 u_{2p}^2(r)dr = 1. \tag{4}$$

The continuum functions $u_s(r)$ and $u_d(r)$ for the s and d states are normalized to the asymptotic forms

$$u_s(r) \rightarrow \frac{1}{kr}\sin(kr+\delta_s), \tag{5}$$

$$u_d(r) \rightarrow \frac{1}{kr}\sin(kr+\delta_d-\pi), \tag{6}$$

where δ_s and δ_d are the scattering phase shifts for the s and d waves.

We now consider some simplifying approximations that may be made in Eq. (1). Since the d phase shifts are small at low energy, it is an excellent approximation to use for $u_d(r)$ the Born approximation value $j_2(kr)$. In evaluating M_d it is also sufficient to use only the form for the bound-state wave function valid outside of the range of interaction R. This is

$$u_{2p}(r) = \frac{Ne^{-\lambda r}}{r}\left(1+\frac{1}{\lambda r}\right), \tag{7}$$

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[4] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) **A239**, 269 (1943).

[5] R. G. Sachs, *Nuclear Theory* (Addison-Wesley Press, Cambridge, 1953), Chap. 4.

[6] R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 (1937).

where N is a normalization constant, $\lambda^2 = 2mE_B/\hbar^2$, and E_B is the binding energy. The accuracy of this approximation follows from the small contribution to the integral from the range of $r < R$ where $j_2(kr)$ is of order r^2. The integral for M_s can also be simplified. As in the case of M_d, the contribution to the integral for $r < R$ is small. This follows from the fact that the expectation value of the dipole operator depends largely on the outside form of the wave function, this effect being enhanced by the very slow fall off of the wave function for the weakly bound electron. In addition, the wave function of the s electron penetrates only weakly into the potential as shown in Fig. 2, the wave function having 3 nodes for r less than R. For these reasons it is an excellent approximation to use only the outside form of u_s and u_{2p} and neglect the contribution from the interval $r < R$ in evaluating Eq. (1). This approximation has been checked numerically by using the actual wave functions determined in the next section.

Using these simplifying approximations Eqs. (2) and (3) for M_s and M_d become

$$M_s = \frac{Ne^{-\lambda R}}{(\lambda^2+k^2)^2}\left\{[2\lambda^2 + R\lambda(\lambda^2+k^2)]\frac{\sin(kR+\delta_s)}{k} + \left[3\lambda + \frac{k^2}{\lambda} + R(\lambda^2+k^2)\right]\cos(kR+\delta_s)\right\}, \quad (8)$$

$$M_d = \frac{N2k^2}{\lambda(\lambda^2+k^2)^2}. \quad (9)$$

We express these results in a simpler form by writing

$$k^2 = \frac{2m}{\hbar}(\omega - \omega_0) = 2m\omega_0(x-1),$$

$$\lambda^2 = 2m\omega_0/\hbar.$$

Equation (1) for the cross section σ then becomes

$$\sigma = \frac{4\pi}{3}N^2\frac{e^2}{\hbar c}\left(\frac{2m\omega_0}{\hbar}\right)^{-\frac{3}{2}}\frac{(x-1)^{\frac{1}{2}}}{x^3}[f^2 + 8(x-1)^2], \quad (10)$$

where

$$f = e^{-\lambda R}\left\{\frac{2+\lambda Rx}{(x-1)^{\frac{1}{2}}}\sin(kR+\delta_s) + [2 + x(1+\lambda R)]\cos(kR+\delta_s)\right\}. \quad (11)$$

The simplified form of the cross section given in Eqs. (10) and (11) shows clearly the dependence of the cross section on the $2p$-state normalization constant N and on the s-state scattering phase shift δ_s. There is also a very weak dependence on the interaction range R; this, however, can be approximately determined by only a rough solution of the problem and hence does not enter the theoretical formula as a sensitive parameter.

The normalization constant affects only the magnitude of the cross section; the scattering phase shift is important, however, in determining both the magnitude and the energy dependence of the cross section. These features of the simplified equation for the cross section make it possible to determine the s-state scattering directly from the photo cross section. We shall use the effective-range expansion for the s phase shift δ_s,

$$k\cot\delta_s = -\frac{1}{a} + \frac{r_0}{2}k^2, \quad (12)$$

where a is the scattering length and r_0 is the effective range. The results of the following sections show that r_0 is about 0.860 atomic unit; this value is relatively insensitive to approximations made in determining the s-wave scattering. Therefore, the photodetachment cross section really depends only on the p-state normalization N and the s-wave scattering length. Observation of the photodetachment cross section as a function of energy thus enables us to determine both these quantities. We shall return to this result in more detail in the following sections.

III. DETERMINATION OF THE BOUND 2*p* ELECTRON WAVE FUNCTION

The $2p$ electron wave function for O^- may be obtained from the complete Hartree-Fock solution for all 9 electrons, the configuration being $(1s)^2(2s)^2(2p)^5$. This method, however, cannot be expected to give the binding energy with sufficient precision since the bound state of O^- lies so close to zero energy. We therefore shall adopt an alternative procedure in which we take as a starting point the Hartree-Fock solutions for neutral oxygen and add the effects of polarization and exchange by the inclusion of a polarization potential with strength to be determined to predict correctly the observed binding energy.

We use the Hartree-Fock wave functions ψ_{1s}, ψ_{2s}, and ψ_{2p} for neutral oxygen as given by Hartree and Swirles.[7] The interaction energy of an additional electron, neglecting polarization of these states and exchange is

$$V_c = -\frac{8e^2}{r} + \int[2\psi_{1s}{}^2(\mathbf{r}') + 2\psi_{2s}(\mathbf{r}') + \sum_m \psi_{2p}{}^2(\mathbf{r}')] \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \quad (13)$$

where, in the last term, the sum over m runs over the magnetic quantum numbers of the occupied p states. This interaction will not, in general, be spherically symmetric; we shall, however, drop the nonspherical terms by averaging $V(r)$ over r. In this case, all p

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[7] Hartree, Hartree, and Swirles, Trans. Roy. Soc. **A238**, 229 (1939).

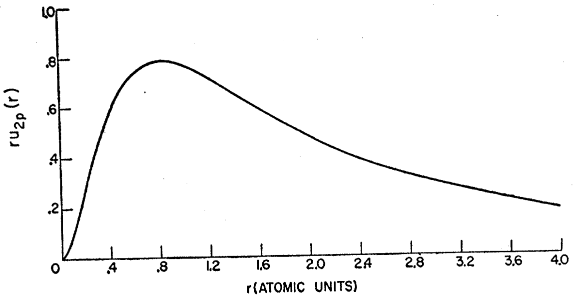

FIG. 1. Bound electron wave function $ru_{2p}(r)$ for O⁻. The wave function is normalized as in Eq. (4).

electrons give the same contribution and we obtain

$$V_c=-8\frac{e^2}{r}+8\pi\int_0^r(u_{1s}^2+u_{2s}^2+2u_{2p}^2)\frac{r'^2}{r}dr'$$
$$+8\pi\int_r^\infty(u_{1s}^2+u_{2s}^2+2u_{2p}^2)r'dr'. \quad (14)$$

This interaction potential is incorrect in that the effects of polarization and exchange have not been included. We shall account for these effects approximately by adding a polarization potential $V_p(r)$,

$$V_p(r)=-\tfrac{1}{2}\frac{p}{(r_p^2+r^2)^2}, \quad (15)$$

where p is the polarization parameter and r_p the screening distance. The form for V_p is the one usually chosen for a polarization potential. The exchange correction, however, adds to the polarization term an additional interaction of considerably shorter range than the polarization potential. Therefore its inclusion is approximately equivalent to a slight alteration of the strength and range of the polarization. Because the exchange effect is, in general, small compared to the polarization effect, and because of the theoretical uncertainty in the strength and range of the polarization potential, we have felt it sufficient to treat both effects together.

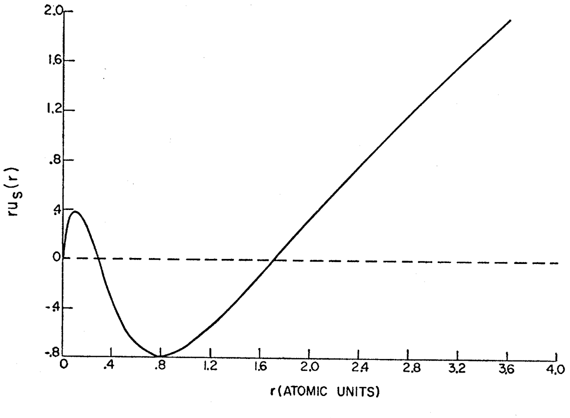

FIG. 2. Electron wave function $ru_s(r)$ for scattering by neutral oxygen. The wave function is normalized as in Eq. (5).

The screening distance r_p, as determined by polarization theory, is approximately equal to the mean radius of the states polarized, which are almost entirely $2p$ electrons. The value determined from the Hartree-Fock wave functions for neutral oxygen was $r_p=1.2$ atomic units. The correct value of the polarization parameter (which in our approximation also includes the exchange correction) was obtained by adjusting it to give a binding energy of 1.45 electron volts for the negative ion O⁻. The result obtained was $p=5.589$ atomic units, which is close to the theoretical value of 5.4 obtained by Buckingham, although the close agreement is probably somewhat fortuitous. The normalized wave function is given in Fig. 1; the normalization constant of Eq. (7) is found to be $N=0.374$.

With the polarization potential determined, the photodetachment cross section may now be calculated.

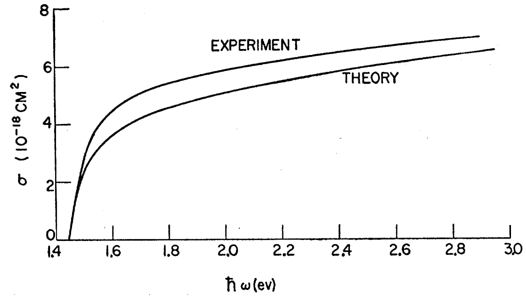

FIG. 3. Comparison of calculated photodetachment cross section with the experimental results of Branscomb *et al.*

The s wave continuum function required for the M_s integral has been obtained by numerical integration at several energies, using the same combined exchange and polarization potential as for bound $2p$ electron. The theory of the potential indicates that this is the correct procedure for the polarization potential above, since this is simply the polarization energy of a test charge in the atomic field and does not depend on the quantum number l. This does not quite hold for the exchange terms which we have combined with the polarization potential; consequently we should expect a weak l dependence in the combined exchange and polarization. This effect vanishes, however, in the Slater approximation to the exchange term[8] and in general is expected to be only a small perturbation on the already relatively small exchange term. We therefore have assumed the same polarization parameters for the continuum state and the bound $2p$ state. The normalized s wave continuum function at zero energy is shown in Fig. 2. The results for the s wave at several energies also determine

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[8] J. C. Slater, Phys. Rev. **81**, 385 (1951).

the effective-range and scattering-length constants of Eq. (12) which are

$$r_0 = 0.860 \text{ atomic unit}, \quad a = 1.613 \text{ atomic units}.$$

IV. PHOTODETACHMENT CROSS SECTIONS; COMPARISON WITH EXPERIMENT

The results of the last section enable us to determine the photodetachment cross section. The approximations discussed in Sec. II can also be checked, using the computed wave functions, and have been found to give negligible error. The computed photodetachment cross section is shown in Fig. 3, together with the cross section deduced by Branscomb *et al.*, from their experimental data. The theoretical curve is seen to agree quite well with the experimental curve in shape, but the predicted cross section is about 15% too small. The good agreement with regard to the form of the curves indicates that out prediction of the scattering length is nearly correct. This is shown in Fig. 4 where we have plotted the photodetachment cross section for a range of values of the scattering length. The figure shows that the photodetachment cross section is very sensitive to the scattering length and that values of a outside the range $a = 1$ to 2 may be safely ruled out.

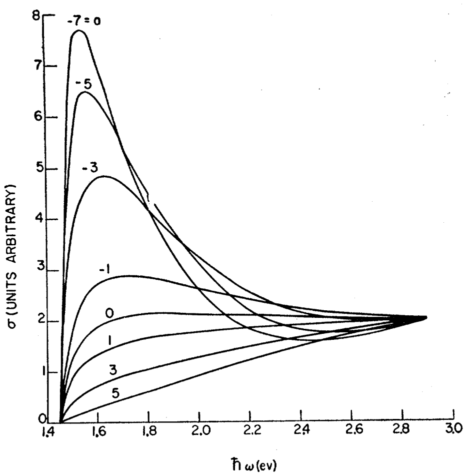

FIG. 4. Photodetachment cross section in Born approximation for several scattering lengths. The curves have been normalized to the same value at 2.90 ev.

The somewhat too small predicted cross section is very probably due to an incorrect normalization of the bound $2p$ wave function outside the range of interaction. This may be attributed to a too short range in the polarization potential since an increase in range would lead to a slower rise of the wave function toward its asymptotic form and hence to an increase in the normalization of the $2p$ wave function. We have not investigated this feature of the results in further detail.

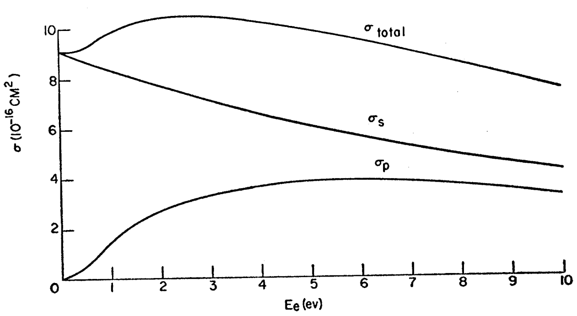

FIG. 5. Total scattering cross section and s and p wave contributions for atomic oxygen.

V. SCATTERING CROSS SECTIONS FOR OXYGEN AND NITROGEN

As mentioned previously, the polarization potential for nitrogen may not be calculated in the same way as for oxygen since nitrogen does not form a stable negative ion. We have therefore made use of some work on polarization by Buckingham which relates the polarization to the atomic number Z and the screening distance r_p. The relation may be expressed as

$$p = \text{const} Z r_p^4. \tag{16}$$

Evaluation of the screening distance r_p by use of the Hartree-Fock wave functions for nitrogen[9] yielded

$$r_p = 1.32 \text{ atomic units}.$$

Since the atomic number for nitrogen is very close to that for oxygen, the polarization potentials for the two atoms should not differ greatly. The polarization constant p for nitrogen was therefore calculated by extrapolating the corresponding results for oxygen by means of Eq. (16) to give

$$p = 7.084 \text{ atomic units}.$$

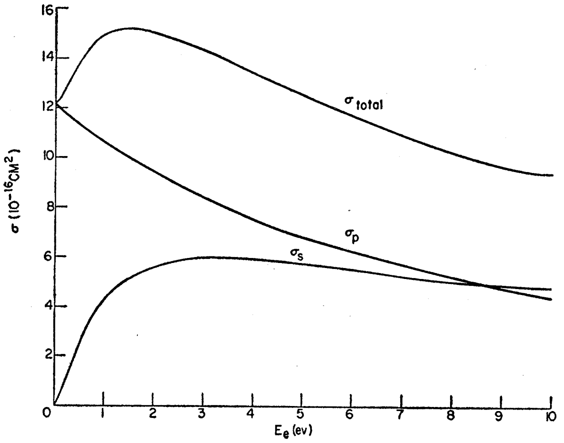

FIG. 6. Total scattering cross section and s and p wave contributions for atomic nitrogen.

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[9] D. R. Hartree and W. H. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

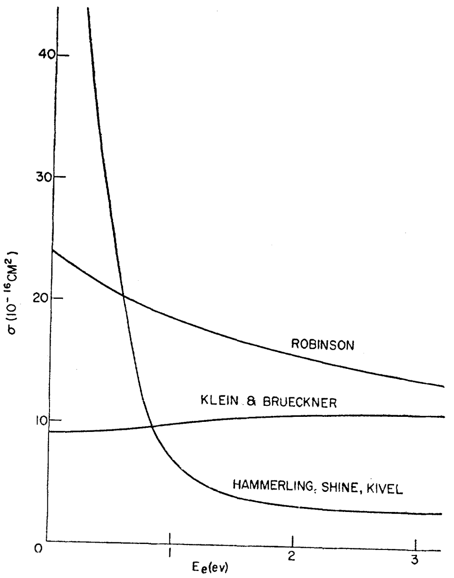

FIG. 7. Comparison of several calculations of total scattering cross section for atomic oxygen.

The continuum s and p wave functions for nitrogen were then calculated in the same way as for oxygen. The effective range and scattering length constants of Eq. (12) for nitrogen were

$$r_0 = 0.845 \text{ atomic unit}, \quad a = 1.857 \text{ atomic units.}$$

The s- and p-wave scattering amplitudes σ_s and σ_p were calculated by numerical integration for both oxygen and nitrogen in the low-energy range 0 to 10 ev. The d wave contribution was found to be quite negligible in the energy range considered. The s and p wave contributions together with the total cross section for oxygen and nitrogen are given in Figs. 5 and 6, respectively.

VI. COMPARISON WITH OTHER THEORETICAL RESULTS

In this section we shall comment briefly on the results of Robinson and of Hammerling, Shine, and Kivel. Their predicted scattering cross sections for oxygen are given in Fig. 7. From these it is possible to deduce the scattering lengths which have the values

$$a = 2.61 \text{ atomic units (Robinson),}$$

$$a = -5.86 \text{ atomic units (Hammerling } et\ al.\text{).}$$

We have used these values of the scattering parameters to determine the photodetachment cross sections which are given in Fig. 8.§ The predicted curves have been arbitrarily normalized at an energy of 2.9 electron volts.

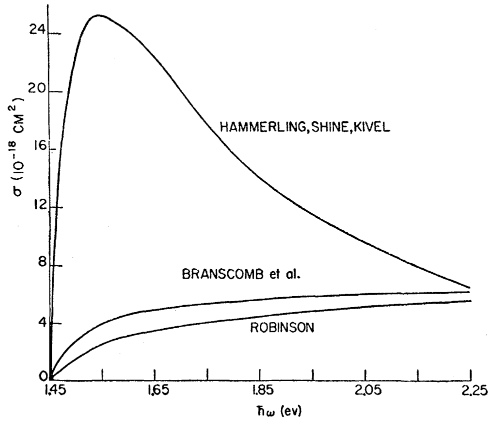

FIG. 8. Comparison of the experimental photodetachment cross section with the theoretical results obtained from the scattering predictions of Robinson and Hammerling *et al.*

The results of Robinson were obtained neglecting exchange and polarization effects which decrease the potential strength seen by the scattered electron. The effect is to increase the scattering length from our value of 1.61 atomic units to 2.61 atomic units. The reason for this increase can be seen in Fig. 2, which shows that a decrease in the potential strength causes an increase in the slope of the wave function outside the range of the interaction with a resulting increase in the scattering length. Robinson's value for the scattering length leads to a larger cross section and also, as is shown in Fig. 8, to a change in the shape of the photodetachment cross section. The latter result does not agree with the experimental result of Branscomb *et al.*

The calculation of Hammerling, Shine, and Kivel included an estimate of the polarization potential and also an estimate of the exchange correction. The inclusion of these terms considerably increases the effective potential strength with the result that the scattering length passes through zero and changes sign, now reaching the negative value of −5.86. This potential strength is very close to that required to bind the 3s electron at zero energy, which would correspond to a negatively infinite scattering length. Their large value for the scattering length also results in the large cross section which they predict at low energy and also to the sharp rise in the photodetachment cross section at low energy shown in Fig. 8. This prediction is again in disagreement with Branscomb's observations.

VII. CONCLUSIONS

Our results show that it is possible to determine the parameters of the polarization and exchange potential seen by an electron added to neutral oxygen, making use of the experimental results on the binding energy of O⁻. It is then possible to determine the scattering cross section as well as the photodetachment cross section if the same polarization potential is assumed to act on a scattered electron. The internal consistency of this procedure is supported by the quantitative agreement of the predicted photodetachment cross section with the experimental results of Branscomb.

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§ *Note added in proof.*—We would like to emphasize that the curves labelled Robinson and Hammerling, Shine, and Kivel in Fig. 8 were obtained with our bound 2p wave function for O⁻.