

Theory of Photodetachment near Fine-Structure Thresholds*

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High-resolution measurements of S^- photodetachment near threshold are interpreted on the basis of an intermediate $[p^4(^3P) + e(l=0)]^2P$ complex which dissociates into jj -coupled constituents. The e - S interaction is represented by doublet and quartet scattering lengths a_d and a_q . Relative cross sections are calculated in terms of electron energies, and of a_d and a_q . Thereby we generalize to a multichannel process the scattering-length theory of cross sections near s -wave thresholds. Many features of the experimental data are accounted for. Predictions are made on the spin-polarization effects of circularly polarized light.

I. INTRODUCTION

The photodetachment cross section of S^- near threshold has been recently measured¹ with high resolution, clearly separating the various fine-structure components. Preliminary considerations might lead one to expect that the cross section should rise at each threshold, according to the Wigner law, with relative coefficients in the ratio of the statistical weights of the corresponding levels. The experiment does show such Wigner-law behavior at four of the six fine-structure thresholds that lie in the observed energy range. However, it also shows additional structure which not only masks the other two thresholds but leads to dips in an otherwise expected monotonic increase of the cross section. Further, the "step heights" at the observed thresholds are not in simple statistical ratios.

The experimental report sketched a way of explaining the observed step heights by considering the final state as a complex ($e+S$) in LS coupling and assuming that, upon dissociation of the complex, each of these LS states splits evenly into the alternative fine-structure levels of S . Stimulated by this suggestion and by a recent paper² on the analysis of the photoabsorption spectrum of H_2 by a method of "frame transformations," we have undertaken a similar analysis of the photodetachment problem working out in detail the dissociation of the complex into alternative channels. We derive analytical expressions for the intensities which reproduce the observed step heights and we present a preliminary numerical fit of these expressions to the experimental data which is reasonably good over the entire energy range. Some of the detailed structure of the data is not reproduced but only a preliminary numerical analysis has been attempted. This paper intends mainly to serve as a framework for further experimental and theoretical work. The possibility of observing additional interference structure in the cross section and of obtaining polarized electrons through the use of either circularly polarized light or magnetic selection of the S^- in

the initial state will be mentioned.

We will consider negative ions with the configuration $p^5(^6P_{1/2,3/2})$. Besides S^- , this class includes O^- , a system of great interest to astrophysics and which has been studied experimentally³ (though with lower resolution) and theoretically.⁴

The detached electron can be in either an s or a d wave. The Wigner threshold laws for these l values are, respectively, $\sigma \propto E^{1/2}$ and $E^{5/2}$, where E is the excess energy above threshold. For a narrow energy range above threshold, the d -wave contribution may therefore be expected to be negligible compared to the s wave. (Photodetachment into the d channel is suppressed by the centrifugal barrier seen by a low energy $l=2$ electron; the barrier also manifests itself in the near-zero quantum defect for d electrons in S . A modification of the threshold law for d electrons is considered in Sec. VI.) We will focus primarily on the range where only s channels are important. Further, we can restrict ourselves to the lowest term, 3P , of the residual S atom because the next term lies ≈ 1 eV higher. These restrictions are reasonable for the energy range ≈ 0.15 eV covered by the experiment.

In the absence of fine structure, the cross section for photodetachment into an s channel depends, near threshold, on the wave number k of the detached particle according to the simple formula $k/(1+k^2a^2)$.⁵ Here the factor k corresponds to the Wigner law $E^{1/2}$ and the parameter a in the denominator is the scattering length which characterizes the electron-atom interaction at zero energy. In essence, this paper extends the $k/(1+k^2a^2)$ law to a many-channel problem where the threshold is split by fine-structure interactions.

II. ANALYSIS OF PHOTODETACHMENT BY FRAME TRANSFORMATION

On the basis thus outlined we consider the process

$$p^5\ ^2P_{1/2,3/2} + h\nu - p^4\ (^6P_{2,1,0})S.$$

Figure 1 shows a level scheme of the various fine-

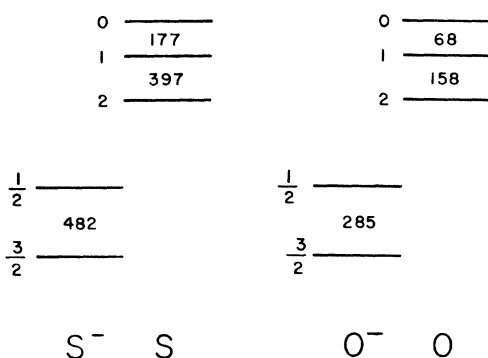


FIG. 1. Sketch of fine-structure levels of ($e+O$) and ($e+S$) systems. Numerical entries between levels are energy separations in cm^{-1} .

structure components for S^- and O^- . One expects to see six fine-structure thresholds, the lowest being ${}^2P_{1/2} \rightarrow {}^3P_2$. At any photon energy above 2.0175 eV, which corresponds to this particular transition in sulfur, one or more of the six transition channels are energetically allowed. Such allowed channels are called "open" whereas energetically forbidden channels are called "closed." Each of the six thresholds (arrows in Fig. 2) marks the opening of an additional channel, which was closed below

that energy.

We seek expressions for the relative intensities of the transitions in terms of two parameters, namely, the doublet and quartet scattering lengths for s -wave $e+({}^3P)$ scattering. This connection between photodetachment and electron scattering arises because one can picture both processes as passing through an intermediate state of a complex ($e+\text{atom}$). The final part of both processes is then identical, with the complex passing from a regime in which the electron is close to the atom to one in which it recedes to infinity. Hence photodetachment involves "half of a scattering" and depends on the same parameters that are relevant to scattering. These parameters may therefore be extracted either from the photodetachment data or from independent experimental or theoretical information on electron-atom scattering. In fact, there exists a program⁶ of close-coupling calculations designed to give these scattering lengths. Alternatively, the parameters may be extracted by extrapolation from discrete spectral data along the series isoelectronic to the negative ion.

In the language of "frame transformations," the detachment process can be pictured as follows. Consider either a ${}^2P_{1/2}$ or a ${}^2P_{3/2}$ state of S^- . When the photon is absorbed, it results in the formation of a complex ($e+S$). At this stage we can think of the electron as being close to the S and hence tightly coupled to it—a region where LS -coupling prevails as it does in the negative ion. We regard a_d and a_q , the doublet and quartet scattering lengths, as eigenparameters of the e - S interaction relevant for char-

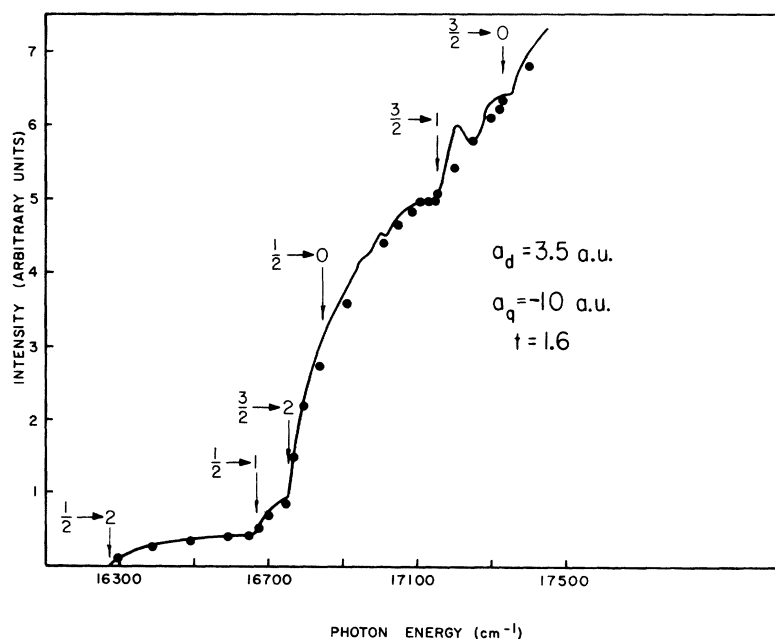


FIG. 2. Photodetachment spectrum of S^- . The continuous curve is experimental, the circles are values calculated in this paper with tentative parameters $a_d = 3.5$, $a_q = -10$ a.u., $t = 1.6$. The six fine-structure thresholds for transitions ${}^2P_{J'} \rightarrow {}^3P_j$ are marked by arrows and labeled $J' \rightarrow j$.

acterizing the complex in this region.⁷ While the electron remains close to the S atom we say that it is in "region A." The state of the $e+S$ system in region A is initially a doublet as the state of S^- from which it is formed. As the electron separates from S we say that the system passes into "region B" where it breaks up into alternative "dissociation channels" which correspond to the alternative fine-structure levels of S^- and are accordingly represented in jj coupling. A main element of a photodetachment process near threshold is the connection between different representations of the state of the complex, namely, the eigenchannels in LS coupling in region A and the dissociation channels in jj coupling in region B.

When all dissociation channels are open (i. e., all the fine-structure transitions are allowed), the doublet-state wave function of region A extends undisturbed into region B; here it is expanded into jj -coupled states to permit application of proper normalization and boundary conditions at infinity. These conditions determine the relative intensities of fine structure components. However, if some of the dissociation channels are closed, the electron cannot move to infinity along them and is reflected back into region A and rescattered into an open dissociation channel.

Based on the above picture, the derivation of intensity expressions breaks into two parts. The first part is the determination of the amplitudes of the LS multiplet components with different $J(\vec{J} = \vec{L} + \vec{S})$ of the complex formed on absorption of the photon. The second part involves the calculation of the amplitudes for transition to the different jj states starting from these LS amplitudes. Each part can be further resolved into separate steps. This analysis permits us to resolve the matrix element for each particular photodetachment transition into a number of factors.

The probability amplitude of the transitions of interest are proportional to the matrix elements of the electric dipole operator \vec{P} . We indicate the component of \vec{P} corresponding to a particular light polarization by $P^{[1]}_q$ (in tensorial notation) and its matrix element by

$$(p^4({}^3P)jm_j, ks_j e m_e | P^{[1]}_q | p^5({}^2P)J'M'). \quad (1)$$

Here j and m_j are quantum numbers of the residual S atom ($j=0, 1, 2$); $j_e = \frac{1}{2}$ and m_e pertain to the s electron escaping with wave number k , and J' and M' pertain to the initial S^- ion ($J' = \frac{1}{2}, \frac{3}{2}$). Capital letters are used for quantum numbers of S^- and of the $e+S$ complex. The wave function of the escaping electron is understood in (1) to be normalized per unit energy range. The form of the dipole operator \vec{P} need not be specified, as we shall see.

In the calculation of the matrix element (1), the

radial integration would extend only over the innermost part of the region A described above. Therefore the integration should be carried out appropriately with final-state wave functions adapted to the structure of the $(e+S)$ complex in region A, that is, with wave functions corresponding to the state symbol $(p^4({}^3P)\bar{s}({}^2P)JM|$. Here we have placed a bar over the channel symbol s to indicate adoption of an energy-independent normalization for the detached electron wave function in region A. If we normalize this wave function to a fixed value near the atomic nucleus, its values throughout region A will be practically independent of the escape energy over the narrow energy range (≈ 0.15 eV) of interest in this paper. [In essence the size of region A is defined by the very requirement that the radial wave function of the excited electron be energy independent throughout it.²] We need not spell out the normalization in this section. Accordingly, we represent the matrix element (1) by expanding it in terms of region A eigenchannel states, in the form

$$\sum_{JM} (p^4({}^3P)jm_j, ks_j e m_e | p^4({}^3P)\bar{s}({}^2P)JM) \times (p^4({}^3P)\bar{s}({}^2P)JM | P^{[1]}_q | p^5({}^2P)J'M'), \quad (2)$$

where J takes the values $\frac{1}{2}$ and $\frac{3}{2}$.

Calculation of the first factor of (2), which represents a transformation coefficient (overlap integral), is the main task of the frame transformation theory and will be carried out in Sec. III. The second factor of (2) is worked out by standard procedures of theoretical spectroscopy. First, application of the Wigner-Eckart theorem separates the dependence on magnetic quantum numbers

$$(p^4({}^3P)\bar{s}({}^2P)JM | P^{[1]}_q | p^5({}^2P)J'M') = (2J+1)^{-1/2} (p^4({}^3P)\bar{s}({}^2P)J || P^{[1]} || p^5({}^2P)J') \times (J'1JM | J'M'1q), \quad (3)$$

where the last factor is a Wigner coefficient and the preceding one a reduced matrix element. The dependence of this matrix element on J and J' can be further factored out by a recoupling transformation⁸ in the form

$$(p^4({}^3P)\bar{s}({}^2P)J || P^{[1]} || p^5({}^2P)J') = Q_{JJ'} D. \quad (4)$$

Here we have called $Q_{JJ'}$ a numerical factor which is expressed in terms of a $6j$ coefficient and is given by

$$Q_{JJ'} = (-1)^{J'+1/2} [(2J+1)(2J'+1)]^{1/2} \begin{Bmatrix} J & J' & 1 \\ 1 & 1 & \frac{1}{2} \end{Bmatrix}$$

$$= \begin{pmatrix} \frac{2}{3} & -\frac{1}{3}\sqrt{2} \\ \frac{1}{3}\sqrt{2} & \frac{1}{3}\sqrt{10} \end{pmatrix}, \quad (5)$$

where the columns (rows) on the right-hand side are labeled $J' = \frac{1}{2}, \frac{3}{2}$ ($J = \frac{1}{2}, \frac{3}{2}$). We have also indicated by

$$D = (p^4({}^3P)\bar{s}^2P || P^{[1]} || p^5({}^2P)) \quad (6)$$

an invariant matrix element which is common to all of our transition amplitudes and therefore need not be calculated in this paper.

III. TRANSFORMATION COEFFICIENT

The calculation of the first factor of (2) will proceed as follows. First, we identify the essential features of the wave functions of the states $|p^4({}^3P)\bar{s}({}^2P)JM\rangle$ and $|p^4({}^3P)jm_j, ks_j, m_s\rangle$ which pertain, respectively, to regions A and B. (The wave function dependence on the radial coordinate r of the s electron is one of the essential features.) Then we shall construct the superposition of states of region A which extrapolates for increasing r into a specific state of region B. Each of the desired transformation coefficients is the Hermitian conjugate of one coefficient of the superposition. The potential due to electric polarization of the sulfur atom by the detached electron is not treated explicitly here for the sake of simplicity; this is done in the belief that it does not affect the structure of the calculation even though its effect is not negligible.

For values of r lying *outside the sulfur atom but within the limits of region A*, the radial wave function of an s electron of near-zero energy is approximately linear. We represent this wave function by $r-a$, where a indicates the scattering length and is the only parameter that depends on the interaction between the electron and the atom inside the atomic radius. However, the value of a depends on the total spin S of all electrons of the $e+S$ complex ($S = \frac{1}{2}, \frac{3}{2}$), that is, on the symmetry characteristics of their combined wave function; thus we have two values of a which we call a_s , or, individually, a_d ("doublet") and a_q ("quartet"), respectively. Setting the coefficient of $(r-a_s)$ at unity fixes the energy-independent normalization of the states of $(e+S)$ which we have labeled \bar{s} . The range of linearity of this radial wave function is limited by the condition $k(r-a_s) \ll 1$, where k is the electron's wave number and is $\lesssim 0.1$ a.u. in our problem.

The radial wave function of the detached electron is to be combined with another factor which we indicate simply by X_{JM}^S . This factor represents the complete wave function of the sulfur atom in a 3P state, with its electron spins coupled to that of the detached electron to form a ${}^{2S+1}P$ state with total quantum numbers J and M . The structure of this

wave function need not be described because only its angular momentum coupling matters for our problem. We also omit explicit notation of the antisymmetrization of the coordinate r with the coordinates of the other electrons and we write the wave function of $|p^4({}^3P)\bar{s}({}^2P)JM\rangle$ as

$$X_{JM}^S(r-a_s). \quad (7)$$

For larger values of r , in region B, the radial wave function of the detached s electron depends on the wave number k . This wave function, normalized per unit energy range, has the form $(2/\pi k)^{1/2} \times [c \sin kr - d \cos kr]$, where the coefficients c and d can be adjusted to fit appropriate boundary conditions. The value of k (in a.u.) is fixed by the energy balance condition

$$\frac{1}{2}k^2 + E_j(p^4({}^3P)) = h\nu + E_{J'}(p^5({}^2P)), \quad (8)$$

where $h\nu$ is the incident photon energy and E_j and $E_{J'}$ are the S and S' fine-structure levels. Since photodetachment proceeds incoherently for the two values of J' , the calculations will be separate and we indicate a solution of (8) by k_j with the understanding that it is also a function of ν . With regard to the remaining factor of the wave function, we consider it first for a state of region B where the s electron and the sulfur atom are jj coupled with quantum numbers JM , $|p^4({}^3P)j, ks_j, JM\rangle$. We call this factor Φ_{JM}^j and write the wave function as

$$\Phi_{JM}^j(2/\pi k_j)^{1/2} [c_j \sin k_j r - d_j \cos k_j r]. \quad (9)$$

This wave function pertains to a single dissociation channel of the $(e+S)$ complex, but the various dissociation channels are coupled through the (e,S) interaction. Accordingly, any realistic state is represented in region B by a superposition of wave functions (9) with different values of j . The state which we call $|p^4({}^3P)j, ks_j, JM\rangle$ with $j = \bar{j}$ is represented by the superposition which fulfils the so-called "ingoing wave boundary condition" for the channel \bar{j} ; this condition requires the coefficients of all outgoing waves $e^{ik_j r}$ to vanish for $j \neq \bar{j}$. The wave function of this state must also be represented in region A by a superposition of wave functions (7),

$$\Psi^{(A)} = \sum_S X_{JM}^S(r-a_s) A_{S\bar{j}}^{(J)}. \quad (10)$$

The effects of (e,S) interaction are incorporated here in the scattering lengths a_s . The coefficients $A^{(J)}$ remain to be determined by application of the ingoing wave boundary condition after extrapolation into region B.

Extension of the wave function (10) into region B begins with the expansion

$$X_{JM}^S = \sum_j \Phi_{JM}^j U_{jS}^{(J)}, \quad (11)$$

whose coefficients $U_{jS}^{(J)}$ represent an orthogonal recoupling transformation, from jj to LS (Eq. 13.14

of Ref. 8) and are independent of M . The transformation matrices are

$$|U_{jS}^{(3/2)}| = \begin{matrix} j=1 & \left| \begin{array}{cc} \sqrt{\frac{5}{6}} & -\sqrt{\frac{1}{6}} \\ \sqrt{\frac{1}{6}} & \sqrt{\frac{5}{6}} \end{array} \right| \\ 2 & \end{matrix}, \quad (12)$$

$$|U_{jS}^{(1/2)}| = \begin{matrix} j=0 & \left| \begin{array}{cc} \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} \end{array} \right| \\ 1 & \end{matrix};$$

where the columns in the $| |$ are labeled $S = \frac{3}{2}, \frac{1}{2}$. The matrices coincide with those for coordinate rotations by $24^\circ 6'$ and $35^\circ 16'$, respectively, as illustrated in Fig. 3. (Note that the triangular conditions restrict j to two values for a given J .) Substitution of (11) changes (10) into

$$\Psi^{(A)} = \sum_j \Phi_{jM}^j [r \sum_S U_{jS}^{(j)} A_{S\bar{J}}^{(j)} - \sum_S U_{jS}^{(j)} a_S A_{S\bar{J}}^{(j)}]. \quad (13)$$

Comparison with the form of (9) for $k_j r \ll 1$ shows that (13) extrapolates into the superposition of region B wave functions

$$\Psi^{(B)} = \sum_j \Phi_{jM}^j k_j^{-1/2} [\sin k_j r \sum_S k_j^{-1/2} U_{jS}^{(j)} A_{S\bar{J}}^{(j)} - \cos k_j r \sum_S k_j^{1/2} U_{jS}^{(j)} a_S A_{S\bar{J}}^{(j)}]. \quad (14)$$

The coefficients c_j and d_j are now expressed in terms of the $A_{S\bar{J}}^{(j)}$.

The next problem is to determine the coefficients $A_{S\bar{J}}^{(j)}$ which fulfil the ingoing wave boundary conditions. To this end we rewrite (14) in terms of exponentials

$$\Psi^{(B)} = \sum_j \Phi_{jM}^j (2/\pi k_j)^{1/2} \frac{1}{2i} [e^{ik_j r} k_j^{-1/2} \sum_S B_{jS}^{(j)} A_{S\bar{J}}^{(j)} - e^{-ik_j r} k_j^{-1/2} \sum_S B_{jS}^{(j)*} A_{S\bar{J}}^{(j)}], \quad (15)$$

with

$$B_{jS}^{(j)} = U_{jS}^{(j)} (1 - ik_j a_S) (2/\pi)^{-1/2}. \quad (16)$$

When both channels are open, the boundary condition requires the coefficient of the outgoing wave $e^{ik_j r}$ in the brackets to be 1 for $j = \bar{j}$ and 0 for $j \neq \bar{j}$, i. e.,

$$\sum_S B_{jS}^{(j)} A_{S\bar{J}}^{(j)} = k_j^{1/2} \delta_{j\bar{J}}. \quad (17)$$

The solution of this system of equations is expressed in terms of the inverse of the matrix (16),

$$A_{S\bar{J}}^{(j)} = (B^{(j)-1})_{S\bar{J}} k_j^{1/2}. \quad (18)$$

When one of the channels is closed, its k value is imaginary according to (8) and will be indicated by $k_{j_c} = -ik_{j_c}$; the j value for this channel will be called j_{j_c} . With this notation the $e^{ik_j r}$ in (15) becomes divergent, $e^{k_{j_c} r}$. The requirement that the coefficient of this term vanishes is expressed by

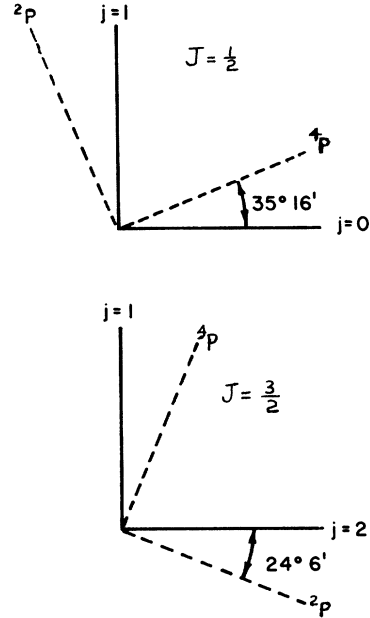


FIG. 3. Recoupling diagrams for transition from LS -coupled states (dashed lines) to jj -coupled states (full lines) of $(e+S)$ complex.

the boundary condition (17) with $j_c \neq \bar{j}$. In fact, the electron can only escape in the open channel, whose j value will be called j_o . Altogether the boundary conditions for the case of one closed channel are still represented by (17), with $\bar{j} = j_o$, $k_{\bar{j}} = k_{j_o}$ and $k_{j_c} = -ik_{j_c}$. This system has a single solution $A_{S_o}^{(j)}$, which is again given by (18), with analogous adaptation of symbols. Incidentally, in our case of a single open channel with ingoing wave normalization, the coefficient ratio of $\exp(-ik_{j_o} r)$ represents the reciprocal of the 1×1 scattering matrix, i. e., $(S^{-1})_{j_o j_o} = e^{-2i\Delta}$; thus we obtain the scattering phase shift Δ from

$$e^{-2i\Delta} = \sum_S (B_{j_o S}^{(j)})^* (B^{(j)-1})_{S j_o} = (B^{(j)*} B^{(j)-1})_{j_o j_o}. \quad (19)$$

Equation (19), which represents the unitary S^{-1} matrix for open channels as a product of a complex non-unitary matrix, B^* , and the inverse of its complex conjugate is familiar from the theory of Jost functions. For single-channel s -wave thresholds the phase shift is given in terms of the scattering length a , by $e^{-2i\Delta} = (1 + ika)(1 - ika)^{-1}$. Equations (16) and (19) generalize this expression to the case when the threshold is split by fine-structure interactions. The spirit of the method of "frame transformations," involving the definition of $\Psi^{(A)}$ with

suitable boundary conditions at $r=0$ and passage into $\Psi^{(B)}$ with correct asymptotic behavior, is very close to that of Jost's treatment of scattering theory and leads naturally to the formulation of the entire problem in terms of the Jost matrix, B . Close connections also exist with the "phase-amplitude method" (see Ref. 8a) and will be considered elsewhere.

One minor step remains to attain the objective of this section, namely, the calculation of the transformation coefficient ($p^4({}^2P)j m_j, k s j_e m_e | p^4({}^2P)\bar{s}({}^2P)JM$). We have calculated coefficients $A_{S\bar{J}}^{(J)}$ with the following property: When these coefficients are introduced in the region A wave function (10), this wave function extrapolates at large r into a wave function $\Psi^{(B)}$ normalized with ingoing wave conditions for the exit channel with $j=\bar{j}$. Accordingly, these coefficients are represented by a transformation matrix element

$$A_{S\bar{J}}^{(J)} \equiv (p^4({}^2P)\bar{j} s JM | p^4({}^2P)\bar{s}({}^{2S+1}P)JM). \quad (20)$$

The desired transformation matrix element is simply the product of the coefficient $A_{1/2\bar{J}}^{(J)}$ and of the Wigner coefficient that decouples the final-state angular momenta \bar{j} and $j_e=1/2$ of $(S+e)$,

$$(p^4({}^2P)\bar{j} m_j, k_T s j_e m_e | p^4({}^2P)\bar{s}({}^2P)JM) \\ = (\bar{j} m_{j\frac{1}{2}} m_e | \bar{j} \frac{1}{2} JM) A_{1/2\bar{J}}^{(J)}. \quad (21)$$

IV. CROSS SECTIONS

The cross section for a specific photodetachment transition is proportional to the squared matrix element (1). Substitution of (2), (3), (4), and (21) gives this squared quantity in the form

$$|\sum_{JM} (j m_{j\frac{1}{2}} m_e | j \frac{1}{2} JM) A_{1/2j}^{(J)} Q_{J,J'} D(2J+1)^{-1/2} \\ \times (J' 1 JM | J' M' 1 q)|^2. \quad (22)$$

(We omit any further distinction between \bar{j} and j .) In this section we consider only the cross section summed over the spin orientation states of the S atom and of the electron. This summation eliminates the first Wigner coefficient in (22) by orthogonality and draws the \sum_{JM} outside the square sign, thus eliminating any interference between the contributions of alternative values of J . In accordance with the experimental conditions of Ref. 1, we also set $q=0$ (linear polarization of incident light) and average over M' (random orientation of incident ions). These operations reduce (22) to

$$\frac{1}{3} (2J'+1)^{-1} D^2 \sum_J |A_{1/2j}^{(J)}|^2 Q_{J,J'}^2 \\ = \frac{D^2}{3(2J'+1)} k_j \frac{2}{\pi} \sum_J \frac{|1 - i k_{2J-j} a_q|^2}{|\mathfrak{D}_J|^2} \\ \times U_{2J-j,3/2}^2 Q_{J,J'}^2, \quad (23)$$

where \mathfrak{D}_J indicates the determinant of the matrix $B_{j\bar{S}}^{(J)}$.

Explicit formulas have been obtained for the energy dependence of the cross sections thus summed and averaged. Different expressions apply to spectral ranges in which different channels are open. All cross section formulas will be given in terms of a basic cross section $\bar{\sigma} = (8\pi^2/81)D^2(\nu/c)$, where ν/c is the photon wave number in cm^{-1} . [Centimeter units should also be used in the calculation of the dipole radial integral D , except for the radial wave function of the final state only. This wave function is understood to be dimensionless, i. e., in a. u., in D and is normalized to unit asymptotic slope as in (7). The factors k_j in the following cross-section formulas also remain in a. u.]

Range between 16273 and 16670 cm^{-1} . Here only the channel ${}^2P_{1/2} - {}^3P_2$ is open and only the intermediate state $J=\frac{3}{2}$ contributes to it. Thus we have $j=j_o=2$ and $j_c=1$. The cross section is

$$\sigma_2 = \bar{\sigma} \frac{5k_2(1 - \kappa_1 a_q)^2}{[1 - \kappa_1(a_d + 5a_q)/6]^2 + k_2^2[(5a_d + a_q)/6 - \kappa_1 a_d a_q]^2}. \quad (24)$$

The factor k_2 represents the dominant threshold behavior predicted by Wigner's law, but the remaining factors still depend on energy through k_2 and κ_1 . The dependence through κ_1 becomes singular at the approach to the next threshold ($j=1$) as one verifies by expanding (23) into powers of κ_1 . The expansion has the form

$$\sigma \sim f(k_2) + g(k_2)(a_d - a_q)\kappa_1 + \dots, \quad (25)$$

which leads to a divergence of $d\sigma/dE \sim -\kappa_1^{-1} d\sigma/d\kappa_1 + \dots$ at $\kappa_1=0$, provided $a_d \neq a_q$.

Note that above this threshold we expect $\sigma \propto k_1$ and $d\sigma/dE \propto k_1^{-1/2}$ very large. The cross section (24) joins to this infinite slope behavior smoothly for $a_d < a_q$, but with a downward "Wigner cusp" for $a_d > a_q$. There is a hint of dips corresponding to such threshold cusps in the data of Ref. 1; indeed a_d seems to exceed a_q according to both the numerical fit described in Sec. V and to the analogous $e+O$ data where $a_d=1.66$ and $a_q=1.31$ a. u.⁶

Region between 16670 and 16847 cm^{-1} . Two channels ${}^2P_{1/2} - {}^3P_2$ and ${}^2P_{1/2} - {}^3P_1$ are open while ${}^2P_{1/2} - {}^3P_0$ remains closed. The cross section σ_2 receives a contribution from $J=\frac{3}{2}$ only. We find that

$$\sigma_2 = \bar{\sigma} \frac{5k_2(1 + k_1^2 a_q^2)}{[1 - k_1 k_2 a_d a_q]^2 + [k_1(a_d + 5a_q)/6 + k_2(5a_d + a_q)/6]^2}. \quad (26)$$

On the other hand, the cross section σ_1 receives contributions from both $J=\frac{3}{2}$ and $J=\frac{1}{2}$. The former is a function of the open channel wave number k_2 , the latter of the closed channel κ_0 ,

$$\sigma_1 = \bar{\sigma} k_1 \left\{ \frac{1 + k_2^2 a_d^2}{[1 - k_1 k_2 a_d a_q]^2 + [k_1(a_d + 5a_q)/6 + k_2(5a_d + a_q)/6]^2} + \frac{8(1 - \kappa_0 a_q)^2}{[1 - \kappa_0(a_d + 2a_q)/3]^2 + k_1^2[(2a_d + a_q)/3 - \kappa_0 a_d a_q]^2} \right\}. \quad (27)$$

Region above 16847 cm⁻¹. Here all channels from ²P_{1/2} are open. The cross section σ_2 is still given by (26). The first term in the braces of (27) also remains unchanged, whereas the second one changes at the threshold for ³P₀. We have

$$\sigma_1 = \bar{\sigma} k_1 \left(\frac{1 + k_2^2 a_d^2}{[1 - k_1 k_2 a_d a_q]^2 + [k_1(a_d + 5a_q)/6 + k_2(5a_d + a_q)/6]^2} + \frac{8(1 + k_0^2 a_q^2)}{[1 - k_0 k_1 a_d a_q]^2 + [k_0(a_d + 2a_q)/3 + k_1(2a_d + a_q)/3]^2} \right) \quad (28)$$

and, in addition,

$$\sigma_0 = \bar{\sigma} k_0 \frac{4(1 + k_1^2 a_q^2)}{[1 - k_0 k_1 a_d a_q]^2 + [k_0(a_d + 2a_q)/3 + k_1(2a_d + a_q)/3]^2}. \quad (29)$$

Transitions from the ²P_{3/2} level of S⁻. Thus far we have given cross sections for transitions from the ²P_{1/2} level of S⁻. To these we must add incoherently the contributions of transitions from the lower level ²P_{3/2}. These contributions differ from those calculated above in the following respects:

(a) The wave numbers k_j (or κ_j) at each photon energy have different values for $J' = \frac{3}{2}$ and $\frac{1}{2}$, in accordance with (8).

(b) Differences of the factor $Q_{J,J'}$ of (23) cause the following changes. The cross sections σ_2 , Eqs. (24) and (26), are multiplied by 5; the cross section σ_0 , Eq. (29), is multiplied by $\frac{1}{2}$. In the expressions (27) and (28) for σ_1 , the first term in the braces is multiplied by 5 and the second one by $\frac{1}{2}$.

With these modifications, (24) applies between 16755 and 17152 cm⁻¹, (26) and (27) between 17152 and 17329 cm⁻¹, and (26), (28), and (29) apply above 17329 cm⁻¹.

V. ANALYSIS OF THE DATA

In Sec. IV, we have derived relative cross sections for all the transitions in terms of the two parameters a_d and a_q . In the case of the photodetachment of O⁻, we have accurate values of a_d and a_q from close-coupling calculations of $e + O$ scattering. For S no such calculation has been carried out but it is hoped that results will be available soon.⁹

The cross sections for photodetachment for ²P_{1/2} and ²P_{3/2} must be combined to construct a theoretical curve for the total of detached electrons. If the

S⁻ beam were in thermal equilibrium in the high temperature limit, the factor $(2J'+1)^{-1}$ in (23) would be simply cancelled by the statistical weight of the two levels of S⁻. Since this limit is probably not attained, we multiply all cross sections for the ²P_{3/2} level by an adjustable parameter t . This parameter would represent a Boltzmann factor if the S⁻ ions emerged from a source in thermal equilibrium at a finite temperature T . This factor depends on the energy difference of the ²P levels of S⁻ which amounts to 482 cm⁻¹ and is thus equivalent to $T_0 = (hc/k)482 \approx 700^\circ\text{K}$ on a temperature scale. On this basis t would be represented by $e^{T_0/T}$. The value $t \approx 1.6$, which gives good agreement with the data discussed below, implies $T \approx 1400^\circ\text{K}$; a value that is regarded as reasonable by the authors of Ref. 1.

Determination of a_d and a_q by fitting of the theoretical formulas to experimental data is conditioned by various features of the theory. First, consider the behavior of the cross sections (26), (28), and (29) at energies far above thresholds for which the differences among the k_j have become negligible. Here each cross section is approximately proportional to $k/(1 + k^2 a_d^2)$ and thus independent of a_q . This algebraic expression reaches a maximum at $k = a_d^{-1}$ after which it starts to fall. Earlier photodetachment data¹⁰ on S⁻, with poorer resolution than in Ref. 1 but carried out to larger energies above threshold, show that the cross section is still rising at an energy 0.5 eV above threshold. This information sets only an upper bound on a_d , $|a_d| < 5$ a.u. We can also estimate this parameter from experimental data on the bound states of elements isoelectronic to S⁻. In fact, a recent paper¹¹ has considered such a Z extrapolation along isoelectronic series to get parameters defining an effective model potential for each Z . Using these parameters, we estimate $a_d \approx 1$ a.u., a result which is probably only a crude estimate.

Consider now the spectral range near the thresholds, where all k_j or κ_j are $\ll 1$. Since a_d is not a large number (in a.u.) and assuming that a_q is not large either, all products ka or κa in the cross-section formulas are small. Each cross section σ_j is then essentially the product of $\bar{\sigma}$, of k_j and of a numerical coefficient, and it hardly depends on a_d and a_q . This simple structure of the approximate cross section yields quantitative predictions for the ratios among the crudely defined "step heights" which one observes at the various thresholds. These step heights are, in fact, just the numerical coefficients in the cross-section formulas. Their predicted ratios are given in Table I together with experimental values drawn from Ref. 1 and with contrasting predictions based on statistical factors. The prediction obtained in this paper appears satisfactory if one takes $t \approx 1.6$ as noted above.

The cross section slopes $d\sigma_2/dE$ and $d\sigma_1/dE$ be-

TABLE I. Step heights for various transitions.

S ⁻ S	² P _{1/2}			² P _{3/2}		
	³ P ₂	³ P ₁	³ P ₀	³ P ₂	³ P ₁	³ P ₀
Statistical ratios	1	0.6	0.2	2	1.2	0.4
Experimental results	1	2.3 ± 0.5	?	7.6 ± 1.5	4 ± 2	?
This paper	1	1.8	0.8	5 <i>t</i>	1.8 <i>t</i>	0.4 <i>t</i>

come singular at the thresholds for σ_1 and σ_0 , respectively, as noted in Sec. IV. The coefficients of these singularities do depend on a_d and a_q . Hence experimental study of the cross sections near the singularities should determine a_d and a_q in principle. In practice the total variation of the cross sections near these singularities is small and current experimental accuracy seems inadequate for the purpose.

Under these circumstances we have constructed a plot of the total cross section, shown in Fig. 2, which reproduces many of the experimentally observed features using the tentative parameter values: $a_d = 3.5$ a. u., $a_q = -10$ a. u., $t = 1.6$. In spite of its general agreement with experiments, the theory fails to reproduce some of the oscillations and other details displayed by the experimental data, particularly in the range of 17200–17400 cm⁻¹. The preceding discussion indicates it might be impossible to fit these additional features within the limited frame of the present calculation. Accordingly, the partial fit in Fig. 2 is presented mainly as a framework for possible extensions of theory and experiment.

VI. POLARIZATION AND INTERFERENCE STRUCTURE IN PHOTODETACHMENT

In this section we consider aspects of photodetachment which emerged from attempts to interpret the unexplained features discussed in Sec. V and which may be relevant to future experiments. It appears to us that, apart from known threshold effects, any structure of the cross-section spectrum should derive from interference between different contributions to photodetachment.

Long-range forces between e and S, disregarded in previous sections, can change the threshold law for photodetachment. In particular, the polarization potential leaves unaltered the s -wave threshold law but for all other partial waves it gives¹² a k^2 dependence for the cross section instead of the usual k^{2l+1} . Hence the amplitude of d -wave detachment from S⁻ may not be altogether negligible compared to the s -wave amplitude. The particularly important terms due to a non-negligible d wave are the cross terms with the s wave. These interference

terms can manifest themselves only in the angular distribution. The experiment of Ref. 1 employed a "4 π detector" and thus averaged over the interference terms. However, experiments that are becoming feasible may detect anisotropies of the photoelectron angular distribution and might thus show the effects of this interference.

Interference may occur between the contributions of $J = \frac{3}{2}$ and $J = \frac{1}{2}$ states of ($e + S$) to the cross section σ_1 . This interference is wiped out in the averaging over final spin orientations of e and S, as noted at the beginning of Sec. IV, but is preserved under appropriate conditions that select initial and/or final states with particular quantum numbers M' , q , m_e , and m . Notice that the relative signs of the Wigner coefficients with $J = \frac{1}{2}$ or $\frac{3}{2}$ in (22) depend on seemingly irrelevant permutations of the factors in the additions of angular momenta. Owing to this dependence, the interference between terms with $J = \frac{1}{2}$ and $J = \frac{3}{2}$ persists only when the initial state possesses some nonzero helicity parameter. This point is illustrated by the following examples of partial cross sections obtained from (22) rather than from the spin-averaged formula (23).

For this purpose we indicate the two terms in the braces of (27) by F and G . The first term F represents the contribution to σ_1 of transitions through the $J = \frac{3}{2}$ state of ($e + S$) while the second term G is due to $J = \frac{1}{2}$. We indicate by H an interference term which appears in partial cross sections and which differs from the geometric mean $(FG)^{1/2}$ owing to the complex character of the amplitudes $A_{1/2}^{(J)}$. The analytic form of H is not given here but can be derived from (18) and (22). Table II gives expressions of the partial cross sections ($mm_e | \sigma_1 | M'q$) for various combinations of quantum numbers, subject of course to $m + m_e = M' + q$.

Table II (a) pertains to linear polarization of the incident light, identified by $q = 0$ with respect to an axis of quantization parallel to the linear polarization. The cross section (27) is defined as the sum

TABLE II. Analytical structure of partial cross sections for $^2P_{1/2} \rightarrow ^3P_1$.

m_e	m	M'	q	$(m_e m \sigma_1 M' q) / \bar{\sigma} k_1$
(a)				
$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{2}{3}F + \frac{1}{3}G - H$
$-\frac{1}{2}$	1	$\frac{1}{2}$	0	$\frac{1}{3}F + \frac{2}{3}G + H$
$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	$\frac{1}{3}F + \frac{2}{3}G + H$
$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	$\frac{2}{3}F + \frac{1}{3}G - H$
(b)				
$\frac{1}{2}$	1	$\frac{1}{2}$	1	$\frac{3}{2}F$
$-\frac{1}{2}$	\times	$\frac{1}{2}$	1	0
$\frac{1}{2}$	0	$-\frac{1}{2}$	1	$\frac{1}{3}F + \frac{2}{3}G - H$
$-\frac{1}{2}$	1	$-\frac{1}{2}$	1	$\frac{1}{3}F + \frac{2}{3}G + H$

of the four partial cross sections listed, divided by the statistical weight $(2J'+1)=2$. The same result, with cancellation of the interference terms, is also obtained by summing over m_e at constant M' or by summing over M' at constant m_e . There is, however, a correlation between M' and m_e , showing that a spin polarization of the detached electron would result from the use of a spin-polarized S^- target. The degree of polarization thus achieved equals $[(\frac{1}{3})(F-G)-2H]/(F+G)$ times the degree of target polarization. Note the symmetry of Table II under sign reversal of all magnetic quantum numbers, which reflects invariance under time reversal.

Constrast Table II (a) with II (b) which pertains to circularly polarized light. This light is characterized by setting $q=1$ with respect to an axis parallel to the incident light beam [and thus different from the reference axis of Table II (a)]. Here again the sum of all four rows, divided by 2, reproduces the cross section (27). However a different result is obtained by summing over m_e at constant M' or by summing over M' at constant m_e . That is, the total cross section for photodetachment by circularly polarized light depends on the spin orientation of S^- ; alternatively, the detached electrons will be spin polarized irrespective of the spin orientation of S^- . The degree of spin polarization

amounts here to $[(\frac{1}{3})(5F-2G)-2H]/2(F+G)$. These results are analogous to those predicted and observed recently for the photoionization of alkali atoms by circularly polarized light¹³; the Cs effect is also associated with the interference of $J=\frac{1}{2}$ and $J=\frac{3}{2}$ channels.

Thus far we have discussed the ${}^2P_{1/2}-{}^3P_1$ transition because of its greater complexity. The other transitions will also yield electron spin polarization by incident circularly polarized light even though no interference occurs between different J channels. We give here the breakdown of the total cross section σ_2 [Eq. (24)] into partial cross sections $(mm_e|\sigma_2|M'q)$, because this cross section applies to a fairly large spectral range where all other cross sections vanish,

$$\begin{aligned} (1\frac{1}{2}|\sigma_2|\frac{1}{2}1) &= \frac{3}{10}\sigma_2, & (2-\frac{1}{2}|\sigma_2|\frac{1}{2}1) &= \frac{12}{10}\sigma_2, \\ (0\frac{1}{2}|\sigma_2|-\frac{1}{2}1) &= \frac{2}{10}\sigma_2, & (1-\frac{1}{2}|\sigma_2|-\frac{1}{2}1) &= \frac{3}{10}\sigma_2. \end{aligned} \quad (30)$$

The degree of polarization of the detached electrons equals -0.5 for unpolarized S^- .

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