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Angular distributions of photoelectrons from atomic oxygen*

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Using close-coupling theory, multichannel expressions are derived for the angular distributions of photoelectrons from atomic oxygen. These expressions are used to calculate angular distributions for photoelectron ejection from either the outer $2p$ subshell or the inner $2s$ subshell. Comparison with other theoretical work is made.

I. INTRODUCTION

In Earth's ionosphere, atomic oxygen is the dominant neutral species above about 150 km for average solar conditions. At low to mid latitudes and at altitudes above about 200 km, the major source of photoelectrons is the photoionization of atomic oxygen by sunlight. In the upper part of Earth's ionosphere, energetic photoelectrons can travel a considerable distance along geomagnetic field lines before losing their energy. It is therefore important to know the angular distributions of photoelectrons from atomic oxygen, so that properties of the photoelectron flux in the upper ionosphere can be studied (Takayanagi and Ikikawa,[1] Whitten and Poppoff,[2] and J. R. Jasperse[3]).

At present there are no experimental measurements of photoelectron angular distributions for atomic oxygen. However, there has been a recent theoretical effort by Dill, Kennedy, Manson, and Starace,[4,5] who calculated the angular distributions of photoelectrons that make a transition from the $\mathrm{O}(2p^4;\,{}^3P,{}^1D,{}^1S)$ states into the continuum relative to the $\mathrm{O}^+(2p^3;\,{}^4S^0,{}^2D^0,{}^2P^0)$ states. Within the framework of Bates[6] and Cooper and Zare,[7] they assumed that the coupling between the channels of the final-state wave function was negligible and that the core relaxation, which results from ionization, could be taken into account by a multiplicative factor. They also assumed that Hartree-Fock wave functions were adequate to represent both the bound and continuum orbitals, within the LS coupling scheme.

In the present work, a similar formalism is presented, except that it does not neglect the coupling between the final-state channels. From a consideration of the multichannel work of Henry,[8,9] we note that the final-state coupling should not be neglected when calculating the total photoionization cross section for atomic oxygen. Therefore, the purpose of the present work is to investigate this coupling effect on the photoelectron angular distributions for atomic oxygen.

A brief discussion is given in Sec. II of the present multichannel formalism, which is used to obtain the photoelectron angular distributions presented in Sec. III over the spectral range from their respective thresholds to 30 Å. The angular distributions considered here are for photoelectrons which make transitions from the $\mathrm{O}(2p^4;\,{}^3P)$ state into the continuum relative to the $\mathrm{O}^+(2p^3;\,{}^4S^0,{}^2D^0,{}^2P^0)$ and $\mathrm{O}^+(2s\,2p^4;\,{}^2P,{}^4P)$ states. Concluding remarks are given in Sec. IV.

II. THEORY

A. General comments

In obtaining the present photoelectron angular distributions for atomic oxygen within the framework of nonrelativistic quantum mechanics and semiclassical radiation theory, certain approximations are made. First, the basic quantum-mechanical formula for the angular distribution of photoelectrons that make a transition from an initial bound state into a final continuum state is discussed by Heitler.[10] The quantum-mechanical formula is then approximated using the familiar electric-dipole and long-wavelength approximations (Bethe and Salpeter,[11] and Shore and Menzel[12]). The resulting formula is given in Sec. II B. Second, the bound and continuum states are obtained straightforwardly, where we neglect spin-dependent interactions (such as spin-orbit coupling) in the total Hamiltonian and assume that LS coupling is valid. The O and O^+ bound states used here are obtained from the Roothaan-Hartree-Fock states given by Clementi.[13] A specification of the necessary bound states is given later in Sec. III A.

The final continuum state is represented by a close-coupling expansion (Henry and Lipsky,[14] Smith and Morgan,[15] Burke and Seaton,[16] and Smith[17]), which consists of expanding the total wave function (the O^+ ion plus ejected electron) in terms of a limited number of discrete O^+ states, performing a partial-wave expansion for the ejected electron, and applying the Kohn variational principle. The resulting coupled integro-differential equations with associated boundary conditions can then be solved numerically to obtain the continuum functions. These solutions describe the radial motion of the ejected electron relative to the residual ion. The solutions are obtained using an integral-equation method as discussed by Smith and Henry.[18,19] We also choose a representation for the total wave function so that the total Hamiltonian H is diagonal in the partial-wave quantum numbers $LSM_LM_S\pi$. Note that L (S) is the quantum number for the total orbital (spin) angular momentum and M_L (M_S) is its z component. Also, the parity is

$$\pi=(-1)^{\sum_i l_i},$$

where $\sum_i l_i$ is the sum over all the orbital quantum numbers l_i of the ejected electron and the O^+ electrons. In obtaining the present photoelectron angular distributions, we shall see in Sec. III that only a few partial waves need be considered. Last, we also constrain the continuum functions to be orthogonal to all the O^+-state orbitals included in the close-coupling expansion in order to reduce the total number of exchange terms. As a result the expansion for the total wave function consists of an explicit O correlation expansion, as well as the familiar O^+-state expansion. In the present calculations only correlation terms are included which arise as a direct consequence of the orthogonality constraints.

B. Photoelectron angular distributions

In a slightly different notation than that of Henry and Lipsky,[14] and Smith,[17] let us consider the following photoionization process. An unpolarized beam of photons of energy $h\nu \ll mc^2$ moves in the z direction through a gas containing atomic oxygen, which has nuclear charge $Z=8$ and $N+1=8$ electrons. The initial states of the atom are described by the wave functions $\Phi(\mathcal{L}\zeta M_{\mathcal{L}} M_\zeta \pi_0; \vec{x}_1, \ldots, \vec{x}_{N+1})$, which depends upon the $N+1$ electron coordinates $\vec{x}_i$ and the usual quantum numbers $\mathcal{L}\zeta M_{\mathcal{L}} M_\zeta \pi_0$. Note that $\mathcal{L}$ (ζ) is the quantum number for the total orbital (spin) angular momentum. After ionization takes place, the final continuum states can be described by the wave functions

$$\Psi(\gamma M_{L_1} M_{S_1} m_{1/2}; \vec{k}; \vec{x}_1, \ldots, \vec{x}_{N+1}) = \sum_{l m_l} i^l e^{-i\eta_l} Y^*_{l m_l}(\hat{k}) \sum_{L S M_L M_S \pi} C(L_1 l M_{L_1} m_l | L M_L) C(S_1 \tfrac{1}{2} M_{S_1} m_{1/2} | S M_S) \psi(\Gamma; \vec{x}_1, \ldots, \vec{x}_{N+1}), \quad (1)$$

where the collective index Γ is defined by $\Gamma = \gamma k l L S M_L M_S \pi$, the quantum numbers of the residual O^+ ion are denoted by the collective index $\gamma = \alpha_1 L_1 S_1$, the unit vector $\hat{k}$ denotes the direction of the ejected electron, k^2 and l are, respectively, the energy and the angular momentum quantum number associated with the ejected electron, and the C's are Clebsch-Gordon coefficients (Rose[20]). Employing the familiar ingoing-wave modification for the final-state wave function (Briet and Bethe[21]), we obtain

$$\psi(\Gamma; \vec{x}_1, \ldots, \vec{x}_{N+1}) = (N+1)^{-1/2} \sum_{p=1}^{N+1} (-1)^{N+1-p} \sum_{\Gamma'} \phi_1(\Gamma'; \vec{x}, \hat{x}_p) f(\Gamma'; \Gamma; r_p) \quad (2)$$

and

$$\phi_1(\Gamma; \vec{x}, \hat{x}_p) = \sum_{\alpha\beta\bar{\alpha}\bar{\beta}} C(L_1 l \alpha\beta | L M_L) C(S_1 \tfrac{1}{2} \bar{\alpha}\bar{\beta} | S M_S)\, \phi_2(\gamma; \vec{x}_1, \ldots, \vec{x}_{p-1}, \vec{x}_{p+1}, \ldots, \vec{x}_{N+1}) Y_{l\beta}(\hat{r}_p) \chi_{\bar{\beta}}(p), \quad (3)$$

where $\phi_2(\gamma)$ is the antisymmetric O^+ eigenstate in channel Γ, and $f(\Gamma', \Gamma; r_p)$ are continuum functions describing the radial motion of the ejected electron.

As discussed in Sec. II A, recall that the continuum solutions associated with the partial-wave quantum numbers ($LSM_LM_S\pi$) can be obtained separately, since the total Hamiltonian used here is diagonal in this set of quantum numbers. Therefore, it is convenient to introduce another collective index μ defined by $\mu = \gamma_\mu k_\mu l_\mu$, where $\Gamma = \mu L S M_L M_S \pi$. The notation for the continuum functions in Eq. (2) then reduces to

$$f(\Gamma', \Gamma; r) = f(\mu', \mu; r) \delta_{LL'} \delta_{SS'} \delta_{M_L M_{L'}} \delta_{M_S M_{S'}} \delta_{\pi\pi'}. \quad (4)$$

Moreover, its asymptotic behavior is

$$f_{\mu'\mu}(r) \underset{r\to\infty}{\sim} (\delta_{\mu'\mu} e^{i\theta_{\mu'}} - S^\dagger_{\mu'\mu} e^{-i\theta_{\mu'}})/2ir(\pi k_{\mu'})^{1/2}, \quad (5)$$

where

$$\begin{aligned} &\theta_\mu = k_\mu r - l_\mu \pi/2 + \alpha_\mu \ln 2k_\mu r + \eta_\mu, \\ &\alpha_\mu = (Z-N)/k_\mu, \quad \eta_\mu = \arg\Gamma(l_\mu + 1 - i\alpha_\mu), \end{aligned} \quad (6)$$

and the matrix $S^\dagger_{\mu'\mu}$ is the adjoint of the partial-wave scattering matrix. At this point, note that Ψ of Eq. (1) is normalized per unit energy range as discussed by Bethe and Salpeter.[11] Also, the normalized wave function given by Henry and Lipsky[14] is in error by a multiplicative factor. However, the resulting formula for the photoionization cross section used by Henry[8] is correct.

Let us rotate the wave function $\psi(\Gamma)$ given in Eq. (2) to obtain an alternative wave function which is expressed in terms of real continuum functions $g_{\mu'\mu}(r)$ that satisfy the boundary conditions

$$g_{\mu'\mu}(r) \underset{r\to\infty}{\sim} k_{\mu'}^{-1/2}[\delta_{\mu'\mu}\sin\theta_{\mu'} + R_{\mu'\mu}\cos\theta_{\mu'}]r^{-1} . \quad (7)$$

As a result, we can substitute

$$f_{\mu'\mu}(r) = [\underline{g}(r)(\underline{1} + i\underline{R})^{-1}]_{\mu'\mu}/\pi^{1/2} \quad (8)$$

for $\underline{f}(r)$ in Eq. (2). Note that the matrix $\underline{R}$ is the open-channel reactance matrix. The continuum functions $\underline{g}(r)$ are then obtained in the usual fashion (Burke and Seaton[16]).

The quantum-mechanical formula used here for the photoelectron angular distribution is (in Rydberg units: $\hbar = 1$, $m = \frac{1}{2}$, $e^2 = 2$)

$$\frac{d\sigma}{d\Omega}(\alpha L_1 S_1; k^2) = \frac{16\pi}{c\nu\omega} \sum_{\substack{M_{\mathcal{L}} M_\zeta m_1, M_{L_1} M_{S_1} m_{1/2} \\ m_1 \neq 0}} |D|^2 , \quad (9)$$

where

$$D = \int \Psi^*(\gamma M_{L_1} M_{S_1} m_{1/2}; \vec{\mathrm{k}}; \vec{\tau}) \times \left[\sum_{i=1}^{N+1} \hat{\theta}_i^{(m_1)}\right] \Phi(\mathcal{L}\zeta M_{\mathcal{L}} M_\zeta \pi_0; \vec{\tau})\, d\vec{\tau} , \quad (10)$$

$$\hat{\theta}_j^{(m_1)} = \begin{cases} \nabla_j^{(\pm 1)} = \dfrac{1}{\sqrt{2}}\left(\mp \dfrac{\partial}{\partial x_j} - i \dfrac{\partial}{\partial y_j}\right), & \text{velocity form} \\ (\pi\nu) r_j (\tfrac{4}{3}\pi)^{1/2} Y_{1 m_1}(\hat{r}_j) , & \text{length form} . \end{cases} \quad (11)$$

The statistical weight ω is $2(2\mathcal{L}+1)(2\zeta+1)$. Next, using Eqs. (2) and (10) and the useful relation

$$Y_{l m_l}(\hat{k}) Y^*_{l' m_{l'}}(\hat{k}) = (-1)^{m_{l'}} \sum_{PQ} Y_{PQ}(\hat{k}) \left(\frac{(2l+1)(2l'+1)}{4\pi(2P+1)}\right)^{1/2} C(ll' m_l - m_{l'}|PQ) C(ll'00|P0) , \quad (12)$$

we obtain

$$\begin{aligned} |D|^2 = DD^* = &\sum_{l m_l, l' m_{l'}} (-1)^l i^{l+l'} e^{i(\eta_l - \eta_{l'})} (-1)^{m_{l'}} \\ &\times \sum_{PQ} Y_{PQ}(\hat{k}) \left(\frac{(2l+1)(2l'+1)}{4\pi(2P+1)}\right)^{1/2} C(ll' m_l - m_{l'}|PQ)\, C(ll'00|P0) \\ &\times \sum_{\substack{L S M_L M_S \pi \\ L' S' M_{L'} M_{S'} \pi'}} C(L_1 l M_{L_1} m_l|L M_L) C(L_1 l' M_{L_1} m_{l'}|L' M_{L'}) C(S_1 \tfrac{1}{2} M_{S_1} m_{1/2}|S M_S) \\ &\times C(S_1 \tfrac{1}{2} M_{S_1} m_{1/2}|S' M_{S'}) \langle\Gamma|\beta\rangle \langle\Gamma'|\beta\rangle^* , \end{aligned} \quad (13)$$

with

$$\langle\Gamma|\beta\rangle = \langle\mu L S M_L M_S \pi| \sum_{i=1}^{N+1} \hat{O}_i^{(m_1)} |\mathcal{L}\zeta M_{\mathcal{L}} M_\zeta \pi_0\rangle . \quad (14)$$

Application of the Wigner-Eckhart theorem yields

$$\langle\Gamma|\beta\rangle = (2L+1)^{-1/2} C(\mathcal{L} 1 M_{\mathcal{L}} m_1|L M_L)(\alpha_1 L_1 S_1 k l L S \pi||\hat{O}||\mathcal{L}\zeta\pi_0)\delta_{S\zeta}\delta_{M_S M_\zeta} . \quad (15)$$

The reduced matrix element will be specified later in Eq. (25). Using Eqs. (10), (13), (15), and the two magnetic-sum equations

$$\begin{aligned} &\sum_{m_l} (-1)^{-m_l} C(L_1 l M_L - m_l, m_l|L M_L) C(L_1 l' M_L - m_l, m_l|L' M_L) C(ll' m_l - m_l|P0) \\ &\quad = (-1)^{P-l-l'-L_1-M_L} [(2L'+1)(2L+1)]^{1/2} W[L'Ll'l; P L_1] C(L'LM_L - M_L; P0) \end{aligned} \quad (16)$$

and

$$\begin{aligned} &\sum_{M_L} (-1)^{M_L} C(L'LM_L - M_L|P0) C(\mathcal{L} 1 M_L - m_1, m_1|L M_L) C(\mathcal{L} 1 M_L - m_1, m_1|L' M_L) \\ &\quad = (-1)^{-P-\mathcal{L}+m_1} [(2L+1)(2L'+1)]^{1/2} W[11LL'; P\mathcal{L}] C(11 m_1 - m_1; P0) , \end{aligned} \quad (17)$$

we obtain the angular distribution formula

$$\frac{d\sigma}{d\Omega}(\alpha_1 L_1 S_1; k^2) = \frac{A(\alpha L_1 S_1; k^2)}{2(2\mathcal{L}11)} \sum_{ll'P} Y_{P0}(\hat{k})\left[(-1)^l i^{l+l'} e^{i(\eta_l - \eta_{l'})}\right]\left(\frac{(2l+1)(2l'+1)}{4\pi(2P+1)}\right)^{1/2} C(ll'00|P0)$$
$$\times \sum_{LS\pi,L'S'\pi'} (\alpha_1 L_1 S_1 lkLS\pi||\hat{O}||\mathcal{L}\zeta\pi_0)(\alpha_1 L_1 S_1 l'kL'S'\pi'||\hat{O}||\mathcal{L}\zeta\pi_0)^* \delta_{S\zeta}\delta_{S'\zeta}$$
$$\times[(2L'+1)(2L+1)]^{1/2}(-1)^{l+l'+L_1+\mathcal{L}}\, W[L'Ll'l; PL_1]W[11LL'; P\mathcal{L}]I(P), \tag{18}$$

with

$$I(P) = -(2/\sqrt{3})\delta_{P0} - C(1100|20)\delta_{P2}, \tag{19}$$

$$A(\alpha_1 L_1 S_1; k^2) = \begin{cases} 3.228(-17)/[I+k^2], & \text{velocity form} \\ 8.067(-18)/[I+k^2], & \text{length form}. \end{cases} \tag{20}$$

The W coefficients are the Racah coefficients (Rose[20]), and $I = h\nu - k^2$ is an ionization potential of the atom.

The angular distribution is usually written as

$$\frac{d\sigma}{d\Omega}(\alpha_1 L_1 S_1; k^2) = \frac{\sigma(\alpha_1 L_1 S_1; k^2)}{4\pi}\left[1 - \tfrac{1}{2}\beta(\alpha_1 L_1 S_1; k^2)P_2(\cos\theta)\right], \tag{21}$$

where

$$\sigma(\alpha_1 L_1 S_1; k^2) = \int d\Omega \frac{d\sigma}{d\Omega}(\alpha_1 L_1 S_1; k^2), \tag{22}$$

θ is the angle between the incident photon beam and the photoelectron direction, the Legendre polynomial is $P_2(x) = \frac{1}{2}(3x^2 - 1)$, and the $\beta(\alpha_1 L_1 S_1; k^2)$ term is the asymmetry parameter. Note that σ governs the "magnitude" of the distribution, and β governs the "shape" of the distribution. Furthermore, the photoionization cross section σ can be obtained using Eqs. (18)–(22), namely,

$$\sigma(\alpha_1 L_1 S_1; k^2) = \frac{A(\alpha_1 L_1 S_1; k^2)}{3(2\mathcal{L}+1)} \sum_{lLS\pi} |(\alpha_1 L_1 S_1 klLS\pi||\hat{O}||\mathcal{L}\zeta\pi_0)|^2 \delta_{S\zeta}. \tag{23}$$

The total photoionization cross section is simply

$$\sigma_T(k^2) = \sum_{\alpha_1 L_1 S_1} \sigma(\alpha_1 L_1 S_1; k^2). \tag{24}$$

Let us now specify the reduced matrix elements that were alluded to in Eq. (15). Using a five-state close-coupling expansion and an analysis similar to that of Smith,[17] we obtain using Eq. (8)

$$(\mu LS\pi||\hat{O}||\mathcal{L}\zeta\pi_0) = \frac{1}{\sqrt{\pi}} \sum_{\mu_1} (\underline{1} - i\underline{R})^{-1}_{\mu\mu_1} \langle \mu_1 LS\pi||\hat{O}||\mathcal{L}\zeta\pi_0\rangle, \tag{25}$$

with $\mu = \alpha_1^\mu L_1^\mu S_1^\mu k_\mu l_\mu$ and

$$\langle \mu_1 LS\pi||\hat{O}||\mathcal{L}\zeta\pi_0\rangle = (2L+1)^{1/2}\Big(\sum_{\mu} (1\bar{s}|1s)^2(2\bar{s}|2s)^2(2\bar{p}|2p)^3(12)^{1/2}(2\mathcal{L}+1)^{1/2}(4\mathcal{L}\zeta] L_1^\mu S_1^\mu)(g_{\mu\mu_1}|O_{l_\mu 1}|2p)$$
$$\times(1100|l_\mu 0)W[LL_1^\mu 11; l_\mu\mathcal{L}]\Big) + (2L+1)^{1/2}(1\bar{s}|1s)^2(2\bar{s}|2s)(2\bar{p}|2p)^4$$
$$\times\Big(\sum_{\mu} (2)^{1/2}(g_{\mu\mu_1}|O_{10}|2s)(0100|l_\mu 0)\,(2S_1^\mu+1)^{1/2}$$
$$\times W[S_1^\mu S\tfrac{1}{2}0; \tfrac{1}{2}S]\delta_{1\zeta}(2\mathcal{L}+1)W[\mathcal{L}0\mathcal{L}1; \mathcal{L}1]W[\mathcal{L}0\mathcal{L}0; \mathcal{L}0]\delta_{1\mathcal{L}} + C^{(\mu_1)}(2\bar{p}|O|2s)(\tfrac{2}{3})^{1/2}\delta_{L1}\delta_{S1}\delta_{\pi,-1}\Big). \tag{26}$$

Note that

$$(2\bar{p}|O|2s) = \begin{cases} -0.562\,215, & \text{velocity form} \\ 1.098\,08, & \text{length form}, \end{cases} \tag{27}$$

$$(1\bar{s}|1s) = 1.0000, \quad (2\bar{s}|2s) = 0.998\,44, \quad (2\bar{p}|2p) = 0.991\,32, \tag{28}$$

$$O_{l_1 l_2} = \begin{cases} \dfrac{1}{r}\dfrac{d}{dr}r + \dfrac{l_2(l_2+1) - l_1(l_1+1)}{2r}, & \text{velocity form} \\ r, & \text{length form}. \end{cases} \tag{29}$$

Also the $(4\mathcal{L}\zeta\rbrace L_1^{\mu}S_1^{\mu})$ terms are fractional parentage coefficients, the overlap integrals are obtained using the nl orbitals of the atom and the $n\bar{l}$ orbitals of the ion, and the $C^{(\mu_1)}$ factor is a correlation constant for the $O(2s\,2p^5;\,{}^3P^0)$ correlation term that is included to compensate for the $2p$-orthogonality constraint. The term in the first large parentheses in Eq. (26) is obtained with the $O^+(2p^3)$ states. It agrees with the formula given by Henry,[8] except the present formula neglects the s-wave core-relaxation terms. The error incurred by neglecting the core-relaxation terms is small, as demonstrated by Henry.[8] The second bracket is obtained with the $O^+(2s\,2p^4;\,{}^4P,\,{}^2P)$ states, where the p-wave core-relaxation terms are neglected. The error incurred by this approximation is assumed to be small.

III. PHOTOIONIZATION OF $O(2p^4;{}^3P)$

A. Angular distributions

Recall that we are considering the photoelectron transitions

$$O(2p^4;\,{}^3P)+h\nu\rightarrow O(LS\pi)^*\rightarrow O^+(2p^3;\,{}^4S^0,\,{}^2D^0,\,{}^2P^0)+e^-,\qquad(30)$$

$$O(2p^4;\,{}^3P)+h\nu\rightarrow O(LS\pi)^*\rightarrow O^+(2s\,2p^4;\,{}^4P,\,{}^2P)+e^-,\qquad(31)$$

where the quantum numbers of the intermediate states are $S=1$, $\pi=-1$, and $L=0,1,2$. The photoionization model, as discussed in Sec. II, does not change the initial spin of the system ($\zeta=1$), but changes the parity ($\pi_0=+1$) and the orbital angular momentum ($\mathcal{L}=1$), since the photon has p-wave characteristics. For example, consider the ${}^3D^0$ partial wave, where the resulting channels used here are

$$O({}^3D^0)^*\rightarrow\left\{\begin{array}{l}1.\ O^+({}^4S^0)+k^2d\\ 2.\ O^+({}^2D^0)+k^2s\\ 3.\ O^+({}^2D^0)+k^2d\\ 4.\ O^+({}^2P^0)+k^2d\\ 5.\ O^+({}^4P)+k^2p\\ 6.\ O^+({}^4P)+k^2p\\ 7.\ O^+({}^2P)+k^2p\\ 8.\ O^+({}^2P)+k^2p\,.\end{array}\right.\qquad(32)$$

Note that any channel which has $l_i>3$ was not included, as the effect on the photoelectron angular distributions was found to be negligible. Furthermore, at a given photon energy of $h\nu$, only the channels which are open to photoionization (i.e., $k_\mu^2>0$) are included in the close-coupling expansion. As a result, no autoionization effects are included since the closed channels (i.e., $k_\mu^2<0$) introduce Feshbach resonances (Henry[9]). However, in Sec. III B, the first resonance below the $O^+\ ({}^2D^0)$ threshold is examined for the $(d\sigma/d\Omega)({}^4S^0;\,k^2)$ angular distribution.

TABLE I. $(d\sigma/d\Omega)({}^4S^0)$ angular distribution. The photoelectron makes a transition from the $O(2p^4;\,{}^3P)$ state into the continuum relative to the $O^+\,(2p^3;\,{}^4S^0)$ state. See text for a description of the columns.

M	λ	σ^L	σ^V	β^L	β^V
1	902	2.38	2.77	−0.351	−0.212
	900	2.39	2.78	−0.350	−0.210
	890	2.43	2.82	−0.329	−0.189
	880	2.48	2.86	−0.296	−0.157
	860	2.56	2.93	−0.218	−0.0835
	850	2.60	2.97	−0.176	−0.0443
	830	2.67	3.03	−0.0911	0.0350
	820	2.71	3.06	−0.0487	0.0743
	800	2.78	3.12	0.0349	0.151
	770	2.88	3.18	0.156	0.262
	750	2.94	3.22	0.233	0.332
	730	3.00	3.25	0.308	0.400
2	725.99	2.80	2.89	0.266	0.389
	720	2.81	2.89	0.287	0.407
	710	2.83	2.89	0.321	0.437
	700	2.85	2.90	0.355	0.466
	690	2.87	2.90	0.388	0.494
	680	2.89	2.90	0.420	0.522
	670	2.91	2.90	0.452	0.550
3	660	2.72	2.60	0.441	0.534
	650	2.73	2.58	0.471	0.560
	630	2.75	2.57	0.529	0.611
	600	2.78	2.54	0.613	0.683
	570	2.81	2.49	0.692	0.751
	550	2.82	2.46	0.743	0.795
	530	2.82	2.42	0.792	0.837
	500	2.83	2.35	0.864	0.897
	450	2.80	2.21	0.976	0.992
4	433.34	2.52	1.96	0.955	0.976
	425	2.51	1.94	0.974	0.992
	400	2.49	1.86	1.03	1.04
	360	2.41	1.72	1.11	1.11
	340	2.36	1.64	1.15	1.15
	320	2.29	1.56	1.19	1.19
5	309.09	2.19	1.48	1.22	1.20
	300	2.16	1.44	1.24	1.22
	280	2.08	1.35	1.28	1.26
	250	1.91	1.20	1.33	1.31
	220	1.69	1.03	1.38	1.36
	200	1.51	0.898	1.41	1.40
	150	0.953	0.548	1.47	1.48
	100	0.383	0.217	1.48	1.53
	80	0.206	0.118	1.46	1.52
	50	0.0453	0.0275	1.38	1.45
	30	0.006 49	0.004 72	1.23	1.27

TABLE II. $(d\sigma/d\Omega)(^4S^0)$ angular distribution for various M. The photoelectron makes a transition from the O$(2p^4;{}^3P)$ state into the continuum relative to the O$^+(2p^3;{}^4S^0)$ state. See text for a description of the columns.

λ	M	σ^L	σ^V	β^L	β^V
700	1	3.07	3.28	0.414	0.495
	2	2.85	2.90	0.355	0.466
600	1	3.23	3.25	0.726	0.772
	2	2.99	2.85	0.657	0.725
	3	2.78	2.54	0.613	0.683
500	1	3.22	3.01	0.986	0.998
	2	2.99	2.63	0.910	0.936
	3	2.83	2.35	0.864	0.897
400	1	2.94	2.54	1.21	1.19
	2	2.81	2.25	1.12	1.11
	3	2.73	2.04	1.08	1.08
	4	2.49	1.86	1.03	1.04
300	1	2.33	1.84	1.39	1.35
	2	2.35	1.69	1.30	1.27
	3	2.39	1.59	1.26	1.24
	4	2.20	1.46	1.22	1.22
	5	2.16	1.44	1.24	1.22
200	1	1.33	0.970	1.52	1.48
	2	1.47	0.959	1.43	1.40
	3	1.60	0.958	1.40	1.38
	4	1.47	0.880	1.40	1.40
	5	1.51	0.898	1.41	1.40
100	1	0.293	0.209	1.52	1.51
	2	0.362	0.224	1.43	1.45
	3	0.418	0.236	1.42	1.45
	4	0.364	0.209	1.47	1.54
	5	0.383	0.217	1.48	1.53

TABLE III. $(d\sigma/d\Omega)(^2D^0)$ angular distribution. The photoelectron makes a transition from the O$(2p^4;{}^3P)$ state into the continuum relative to the O$^+(2p^3;{}^2D^0)$ state. See text for a description of the columns.

M	λ	σ^L	σ^V	β^L	β^V
2	725.99	3.74	2.88	−0.270	−0.138
	720	3.80	2.93	−0.276	−0.144
	710	3.89	3.00	−0.253	−0.122
	700	3.97	3.07	−0.213	−0.0845
	690	4.05	3.14	−0.166	−0.0404
	680	4.13	3.21	−0.115	0.006 77
	670	4.20	3.26	−0.0619	0.0551
3	660	4.44	3.40	0.167	0.289
	650	4.50	3.44	0.218	0.335
	630	4.59	3.52	0.318	0.423
	600	4.71	3.60	0.458	0.545
	570	4.77	3.65	0.586	0.656
	550	4.80	3.66	0.665	0.724
	530	4.80	3.65	0.739	0.788
	500	4.77	3.60	0.842	0.876
	450	4.62	3.44	0.994	1.01
4	433.34	3.56	2.68	1.07	1.08
	425	3.53	2.65	1.09	1.10
	400	3.42	2.56	1.16	1.15
	360	3.20	2.37	1.25	1.23
	340	3.06	2.25	1.30	1.27
	320	2.91	2.13	1.34	1.30
5	309.09	2.59	1.88	1.36	1.35
	300	2.52	1.82	1.38	1.37
	280	2.34	1.69	1.42	1.40
	250	2.05	1.48	1.46	1.45
	220	1.72	1.24	1.51	1.49
	200	1.48	1.08	1.53	1.52
	150	0.853	0.636	1.56	1.58
	100	0.321	0.246	1.54	1.60
	80	0.172	0.134	1.50	1.58
	50	0.0398	0.0319	1.39	1.47
	30	0.006 21	0.005 68	1.22	1.26

The O(^3P) and O$^+(^4S^0)$ states are represented by the Roothaan-Hartree-Fock wave functions given by Clementi.[13] The same nl orbitals are used in the single-configuration wave functions of all the O$^+$ states. Experimental energy splittings between the O$^+$ states are used as well as experimental values for the ionization thresholds.[22] The error incurred by these approximations is assumed to be small. Note that the O$^+$ threshold energies are $E(^2D^0)=0.244\,30$ Ry, $E(^2P^0)=0.368\,76$ Ry, $E(^4P)=1.092\,04$ Ry, and $E(^2P)=1.937\,29$ Ry, relative to the O$^+(^4S^0)$ ground state. The first ionization threshold is located at 1.000 91 Ry.

In Table I, the $(d\sigma/d\Omega)(^4S^0)$ angular distribution parameters σ and β are presented in both the length and velocity forms from threshold (910.44 Å) to 30 Å. (In all the tables, the cross sections are given in units of 10^{-18} cm^2 and the wavelengths are given in units of Å.) The term M denotes the total number of states included in the close-coupling expansion at each wavelength λ. The asymmetry parameter is in good agreement with the tabulated results of Starace *et al.*[5] over the entire spectral region.

To judge the effect of retaining the final-state coupling, consider the $(d\sigma/d\Omega)(^4S^0)$ distribution given in Table II. We see that the coupling does not necessarily bring the length and velocity forms of the cross section into closer agreement. Since it is not possible to decide which of the forms is more accurate, a simple mean is adopted. As a result, we see that the difference between the mean cross sections obtained with and without coupling can be as much as 20% in this case. Next, we see that the coupling has a smaller effect on the β asymmetry parameter. Also, the length and velocity forms for β are in good agreement for wavelengths smaller than 500 Å.

In Tables III–VI, the parameters of the remain-

TABLE IV. $(d\sigma/d\Omega)(^2P^0)$ angular distribution. The photoelectron makes a transition from the $O(2p^4;\,^3P)$ state into the continuum relative to the $O^+(2p^3;\,^2P^0)$ state. See text for a description of the columns.

M	λ	σ^L	σ^V	β^L	β^V
3	660	2.53	1.61	−0.110	−0.0468
	658	2.54	1.62	−0.0989	0.0602
	654	2.58	1.64	−0.0724	0.0889
	650	2.60	1.67	−0.0433	0.119
	640	2.68	1.72	0.0334	0.194
	630	2.75	1.77	0.111	0.267
	620	2.82	1.82	0.185	0.336
	600	2.92	1.91	0.325	0.463
	570	3.05	2.01	0.511	0.627
	550	3.11	2.05	0.619	0.721
	530	3.15	2.08	0.718	0.806
	500	3.17	2.11	0.849	0.918
	450	3.10	2.07	1.03	1.07
4	433.34	2.61	1.74	0.995	1.04
	425	2.59	1.73	1.02	1.06
	400	2.51	1.68	1.08	1.12
	360	2.33	1.55	1.18	1.21
	340	2.22	1.48	1.22	1.25
	320	2.09	1.40	1.26	1.29
5	309.09	1.88	1.24	1.29	1.35
	300	1.82	1.20	1.31	1.37
	280	1.67	1.11	1.35	1.41
	250	1.44	0.959	1.40	1.47
	220	1.18	0.794	1.46	1.52
	200	0.998	0.680	1.49	1.56
	150	0.556	0.393	1.55	1.63
	100	0.201	0.150	1.58	1.66
	80	0.106	0.0809	1.56	1.64
	50	0.0239	0.0191	1.48	1.51
	30	0.004 06	0.003 39	1.27	1.28

TABLE V. $(d\sigma/d\Omega)(^4P)$ angular distribution. The photoelectron makes a transition from the $O(2p^4;\,^3P)$ state into the continuum relative to the $O^+(2s2p^4;\,^4P)$ state. See text for a description of the columns.

M	λ	σ^L	σ^V	β^L	β^V
4	433.34	1.08	0.732	−0.255	−0.369
	430	1.07	0.723	−0.225	−0.351
	425	1.07	0.710	−0.180	−0.321
	420	1.06	0.697	−0.141	−0.293
	415	1.06	0.684	−0.100	−0.263
	410	1.05	0.671	−0.0626	−0.234
	400	1.04	0.646	0.0142	−0.171
	380	1.01	0.600	0.169	−0.0286
	360	0.981	0.559	0.329	0.139
	340	0.951	0.523	0.493	0.331
	320	0.920	0.494	0.662	0.545
5	309.09	0.840	0.436	0.925	0.914
	300	0.833	0.433	0.991	1.01
	280	0.817	0.428	1.14	1.22
	250	0.780	0.426	1.33	1.49
	220	0.728	0.424	1.50	1.70
	200	0.681	0.417	1.60	1.80
	150	0.511	0.363	1.77	1.93
	100	0.281	0.233	1.88	1.97
	80	0.189	0.167	1.91	1.97
	50	0.0735	0.0720	1.96	1.99
	30	0.0236	0.0249	1.98	1.99

ing angular distributions are given in both the length and velocity forms from threshold to 30 Å. In comparing the present total cross section with the corresponding results of Henry[8] below the $O^+(^4P)$ threshold, we find that the length forms agree to within about 4% and the velocity forms agree to within about 12%. The discrepancies probably arise as a result of the different discrete orbitals that were used to describe the various bound states. Next, the $\sigma(^4P)$ and $\sigma(^2P)$ cross sections are quite different than those obtained by Dalgarno *et al.*[23] and modified by Henry.[8] One reason for this difference is that they did not include the $O(2s\,2p^5;\,^3P^0)$ correlation state to compensate for the $2p$-orthogonality constraint. In the present calculation, if the correlation term is neglected in the $^3P^0$ partial wave, the resulting cross sections are found to change considerably and are in better agreement with cross sections given by Henry.[8] Therefore, the present $\sigma(^4P)$ and $\sigma(^2P)$ cross sections represent an improvement over the previous results.

The three asymmetry parameters given in Tables I, III, and IV exhibit the same shape with increasing photoelectron energy and are in good agreement with the results of Starace *et al.*[5] The $\beta(^4P)$ parameter given in Table V also exhibits a similar behavior, except at higher energies it approaches a fixed value of 2.0 (i.e., a $\sin^2\theta$

TABLE VI. $(d\sigma/d\Omega)(^2P)$ angular distribution. The photoelectron makes a transition from the $O(2p^4;\,^3P)$ state into the continuum relative to the $O^+(2s2p^4;\,^2P)$ state. See text for a description of the columns.

M	λ	σ^L	σ^V	β^L	β^V
5	309.09	1.41	0.608	1.94	1.90
	300	1.43	0.620	1.95	1.90
	290	1.44	0.630	1.95	1.91
	280	1.43	0.635	1.95	1.91
	270	1.41	0.634	1.95	1.92
	260	1.38	0.630	1.95	1.92
	250	1.34	0.620	1.95	1.92
	220	1.17	0.570	1.96	1.94
	200	1.03	0.520	1.96	1.95
	150	0.631	0.358	1.97	1.97
	100	0.276	0.182	1.98	1.99
	80	0.168	0.120	1.98	1.99
	50	0.0571	0.0460	1.98	2.00
	30	0.0157	0.0147	1.98	2.00

shape). The $\beta(^2P)$ parameter given in Table VI remains approximately fixed at a value of 2.0. Therefore, with the exception of the $\beta(^2P; k^2)$ distribution, we see that the shapes of the photoelectron angular distributions do change significantly over the entire spectral range.

B Influence of autoionization states

The close-coupling method was shown by Feshbach[24] to give rise to resonances when some of the channels are energetically closed, for a given partial wave. For autoionization to take place, there must exist at least one continuum into which an O^* autoionization state can decay by electron emission. The interference between the indirect autoionization process and the direct photoionization process gives rise to a dispersion formula for the absorption cross section (Shore[25]), namely,

$$\sigma(E) = C + DE + \frac{A(E-E_r) + B\Gamma/2}{(E-E_r)^2 + (\Gamma/2)^2}, \tag{33}$$

where A, B, C, D, E_r, and Γ are energy-independent parameters. Two parameters used in this dispersion formula are the resonance energy E_r and the resonance width Γ. They can be obtained using a Breit-Wigner resonance fit of the scattering phase shifts associated with the e^--O^+ system (Burke, McVicar, and Smith[26]).

In the previous work by Henry,[9] resonances in the total absorption cross section below the $O^+(^2D^0)$ and $O^+(^2P^0)$ thresholds were analyzed in detail. The resonance locations were in reasonable agreement with the experimental results of Huffman *et al.*,[27] who obtained various Rydberg series from the absorption spectrum of atomic oxygen. We can expect resonance structure to be confined within a small energy region, only a few eV wide, just below each ionization threshold.

Within the *LS*-coupling scheme, let us examine the behavior of the $(d\sigma/d\Omega)(^4S^0)$ angular distribution through its first resonance below the $O^+(^2D^0)$ threshold. From an observation of Table VII, we see that the cross section exhibits the appropriate profile as given by the dispersion formula in Eq. (33). Also, the asymmetry parameter has a rather distinctive resonance profile itself. The resonance is located at $E_r = 0.118404$ Ry and its half-width is $\Gamma = 0.6883(-5)$ Ry, which is in excellent agreement with Smith, Henry, and Burke.[28]

TABLE VII. $(d\sigma/d\Omega)(^4S^0)$ angular distribution through the first resonance below the $O^+(^2D^0)$ threshold. The photoelectron makes a transition from the $O(2p^4; {}^3P)$ state into the continuum relative to the $O^+(2p^3; {}^4S^0)$ state. See text for a description of the columns.

λ	σ^L	σ^V	β^L	β^V
818.815	2.53	2.61	−0.0939	0.0481
815.882	2.73	2.76	−0.0457	0.0831
815.152	2.98	2.95	0.0006	0.116
814.424	4.74	4.27	0.215	0.272
814.278	7.93	6.53	0.402	0.419
814.206	16.6	12.4	0.598	0.588
814.162	57.6	38.4	0.796	0.778
814.140	400.1	244.6	0.934	0.926
814.133	2580	1524	0.989	0.987
814.130	6329	3682	1.01	1.01
814.126	1613	916.3	1.05	1.06
814.118	248.4	135.2	1.11	1.13
814.104	39.8	19.6	1.25	1.31
814.082	8.22	3.33	1.50	1.64
814.060	2.65	0.885	1.73	1.77
814.046	1.43	0.479	1.79	1.29
814.024	0.704	0.358	1.48	−0.0920
814.009	0.531	0.396	0.943	−0.606
813.987	0.460	0.510	0.0466	−0.784
813.973	0.474	0.597	−0.366	−0.757
813.951	0.534	0.727	−0.677	−0.671
813.936	0.587	0.809	−0.754	−0.612
813.915	0.672	0.923	−0.779	−0.535
813.842	0.944	1.22	−0.662	−0.361
813.697	1.32	1.58	−0.465	−0.206
813.334	1.75	1.96	−0.291	−0.0847
812.971	1.94	2.12	−0.232	−0.0442
810.080	2.21	2.34	−0.154	0.008 14

IV. CONCLUDING REMARKS

The angular distribution of a photoelectron from atomic oxygen has a shape which can be strongly dependent upon the energy of the ejected electron. In particular, the shapes of the $(d\sigma/d\Omega)(^4S^0; {}^2D^0; {}^2P^0; {}^4P)$ angular distributions vary strongly with photoelectron energy, while the shape of the $(d\sigma/d\Omega)(^2P)$ angular distribution remains nearly fixed at $\sin^2\theta$ ($\beta = 2$). The shapes of the present $(d\sigma/d\Omega)(^4S^0; {}^2D^0; {}^2P^0)$ angular distributions agree well with the results given by Starace *et al.*[5]

The coupling between the final states is important in calculating the photoelectron angular distributions. When the final-state coupling is included, the length and velocity forms of the cross section (σ) or the asymmetry parameter (β) are not necessarily brought into closer agreement. If a simple mean of the two forms is adopted, the cross section (asymmetry parameter) at a specified wavelength can change by as much as 20% (16%), when the coupling is included. However, at high photoelectron energies, the asymmetry parameter changes little, when the coupling is included. Finally, in attempting to bring the length and velocity forms into better agreement, it would be worthwhile to investigate such effects as short-range correlation in the initial and final bound states and long-range polarization of the O^+ ion.

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[1] K. Takayanagi and Y. Itikawa, Space Sci. Rev. 11, 380 (1970).

[2] R. C. Whitten and I. G. Popoff, *Fundamentals of Aeronomy* (Wiley, New York, 1971).

[3] J. R. Jasperse, Planet. Space Sci. (to be published).

[4] S. T. Manson, D. J. Kennedy, A. F. Starace, and D. Dill, Planet. Space Sci. 22, 1535 (1974).

[5] A. F. Starace, S. T. Manson, and D. J. Kennedy, Phys. Rev. A 9, 2453 (1974).

[6] D. R. Bates, Mon. Not. R. Astron. Soc. 106, 432 (1946).

[7] J. Cooper and R. N. Zare, *Lectures in Theoretical Physics*, edited by S. Geltman, K. Mahanthappa, and W. Brittin (Gordon and Breach, New York, 1969), Vol. 11, p. 317.

[8] R. J. W. Henry, Planet. Space Sci. 15, 1747 (1967).

[9] R. J. W. Henry, Planet. Space Sci. 16, 1503 (1968).

[10] W. Heitler, *The Quantum Theory of Radiation*, 3rd ed. (Oxford U.P., New York, 1954).

[11] H. Bethe and E. Salpeter, *Quantum Mechanics of One and Two Electron Systems* (Academic, New York, 1957).

[12] B. W. Shore and D. H. Menzel, *Principles of Atomic Spectra* (Wiley, New York, 1968).

[13] E. Clementi, IBM J. Res. Dev. 9, 2 (1965).

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

[15] K. Smith and L. A. Morgan, Phys. Rev. 165, 110 (1968).

[16] P. G. Burke and M. J. Seaton, *Methods in Computation Physics*, edited by B. Alder, S. Fernbach, and M. Rotenburg (Academic New York, 1971), Vol. 10, p. 1.

[17] K. Smith, *The Calculation of Atomic Collision Processes* (Wiley, New York, 1971).

[18] E. R. Smith and R. J. W. Henry, Phys. Rev. A 7, 1585 (1973); 8, 572 (1973).

[19] E. R. Smith, J. Comput. Phys. 18, 201 (1975).

[20] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[21] G. Breit and H. A. Bethe, Phys. Rev. 93, 888 (1954).

[22] C. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) No. 467 (U.S. GPO, Washington, D. C., 1949).

[23] A. Dalgarno, R. J. W. Henry, and A. L. Stewart, Planet. Space Sci. 12, 235 (1964).

[24] H. Feshbach, Ann. Phys. (Leipz.) 19, 287 (1962).

[25] B. W. Shore, Rev. Mod. Phys. 39, 439 (1967).

[26] P. G. Burke, D. D. McVicar, and K. Smith, Proc. Phys. Soc. Lond. 84, 749 (1964).

[27] R. E. Huffman, J. C. Larrabee, and Y. Tanaka, J. Chem. Phys. 46, 2213 (1967).

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