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TWO PHOTON EXCITATION OF ATOMIC OXYGEN

Michael S. Pindzola

June 1977

Goddard Space Flight Center
Greenbelt, Maryland
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Michael S. Pindzola*

Theoretical Studies Group
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, Maryland 20771

ABSTRACT

A standard perturbation expansion in the atom-radiation field interaction is used to calculate the two photon excitation cross section for the 1s² 2s² 2p³ 3P to 1s² 2s² 2p³(4S) 3P transition in atomic oxygen. The summation over bound and continuum intermediate states is handled by solving the equivalent inhomogeneous differential equation. We find that our exact summation results differ by a factor of 2 from a rough estimate obtained by limiting the intermediate state summation to one bound state. Higher order electron correlation effects are also examined.

*National Research Council Research Associate
I. INTRODUCTION

Atmospheric remote sensing systems are currently being developed which will take advantage of the remarkable properties of high-energy lasers.\(^1\) With detection and ranging systems based on optical frequencies one may obtain information on atmospheric pressure, temperature, and water vapor altitude profiles as well as particulate number densities. For certain projected applications\(^2\) the height distribution of trace atomic and molecular gases in the stratosphere may be obtained by knowing their various two-photon excitation cross sections.

Recent multiphoton work\(^3\) has shown that the validity of standard perturbation theory extends to quite strong photon intensities. For two photon absorption the sum over intermediate bound and continuum states found in the second order expression for the cross section may be handled by solving the equivalent inhomogeneous differential equation.\(^4\)\(^,\)\(^5\) This technique has been applied to two photon ionization of hydrogen\(^6\)\(^,\)\(^7\) and the alkali atoms\(^8\)\(^-\)\(^10\), as well as recent studies of double photoionization\(^11\) and the hyperfine interaction.\(^12\)

In this paper we use perturbation theory to calculate the two photon excitation cross section for the \(1s^2 2s^2 2p^3 3p\) to \(1s^2 2s^2 2p^3 (^4S) 3p 3P\) transition in atomic oxygen. We find that our exact summation results using the differential equation technique differ by a factor of 2 from a rough estimate obtained by limiting the intermediate state summation to one bound state. Certain higher order electron correlation corrections to the second order expression are also investigated. In Sec. II we present the perturbation theory for the two photon excitation of an atom; Sec. III contains the results of the oxygen calculation; and Sec. IV is a brief summary.
II. THEORY

The photoexcitation cross section for an atom may be calculated using time dependent perturbation theory. The non-relativistic Hamiltonian for an N electron atom is given by

\[ H_{\text{atom}} = H_0 + H_1, \]  

where

\[ H_0 = \sum_{i<j} \left( -\frac{\hbar^2}{2m} \nabla_i \cdot \nabla_j - \frac{Ze^2}{r_{ij}} + V_i \right), \]

and

\[ H_1 = \sum_{\lambda=1}^{N} v_{ij} - \sum_{\lambda=1}^{N} V_{\lambda}. \]

The single particle potential \( V_i \) is generally the Hartree-Fock potential, while \( v_{ij} \) is the Coulomb interaction between pairs of electrons. In Eq. (2) \( m \) is the electron mass, \( e \) is the magnitude of the electronic charge, and \( Z \) is the atomic number.

The unperturbed Hamiltonian \( H_0 \) for the atom-radiation field system is obtained by combining \( H_{0a} \) of Eq. (2) with the Hamiltonian for the quantized electromagnetic field. The eigenstates \( |\phi_j^\lambda \rangle \) of \( H_0 \) are products of an electronic state \( |j\rangle \) and a radiation state with \( n_\lambda \) photons per mode \( \lambda \) such that \( n = \sum_\lambda n_\lambda \). The eigenenergy \( E_j^\lambda \) equals \( E_j + \sum_\lambda n_\lambda \omega_\lambda \), where \( E_j \) is the unperturbed energy of the \( j \)th electronic state and \( \omega_\lambda \) is the angular frequency of the \( \lambda \)th mode.

The perturbation Hamiltonian \( H_1 \) is given by

\[ H_1 = H_{\text{int}} + H_{1a}, \]

where

\[ H_{\text{int}} = \sum_{j=1}^{\tilde{N}} \left( -\frac{ie\hbar}{mc} \hat{A}(\vec{r}) \cdot \nabla_j + \frac{e^2}{2mc^2} |\hat{A}(\vec{r})|^2 \right), \]

\[ \hat{A}(\vec{r}) = \sum_{\lambda} \left( \hat{a}_\lambda e^{i\hat{k}_\lambda \cdot \vec{r}} + \hat{a}_\lambda^* e^{-i\hat{k}_\lambda \cdot \vec{r}} \right), \]
and the annihilation and creation operators for the quantized vector potential $\vec{A}(\vec{r})$ may be defined by

$$ a_\lambda |n_\lambda\rangle = \sqrt{\frac{2\pi c^2 n_\lambda}{\omega_\lambda}} |n_\lambda - 1\rangle, \quad (7) $$

and

$$ a_\lambda^* |n_\lambda\rangle = \sqrt{\frac{2\pi c^2 (n_\lambda + 1)}{\omega_\lambda}} |n_\lambda + 1\rangle. \quad (8) $$

The solution $\psi(t)$ of the time-dependent Schrödinger equation with Hamiltonian $H = H_0 + H_1$ is given by

$$ \psi(t) = \lim_{\gamma \to 0} \exp\left[-i \frac{H_1}{\gamma} \right] U_\gamma(t) |\Phi_0\rangle, \quad (9) $$

where

$$ U_\gamma(t) = 1 + \frac{i}{\gamma} \int_{-\infty}^{t} \int_{-\infty}^{\tau} \exp \left[-i \frac{H_1(\tau)}{\gamma} \right] H_1(\tau') \text{d}\tau' \text{d}\tau, \quad (10) $$

$$ H_1(t) = \exp\left[i \frac{H_0 t}{\hbar} \right] H_1 \exp\left[i \frac{\gamma t}{\hbar} - i \frac{H_0 t}{\hbar} \right], \quad (11) $$

and the parameter $\gamma$ allows $\psi(t)$ to be adiabatically developed from the initial state $|\Phi_0\rangle$. By projecting $\psi(t)$ of Eq. (9) onto the final state $|\Phi_f\rangle$ and then carrying out the time integrations in Eq. (10), the transition rate $R$ is found to be

$$ R = \frac{\text{d}t}{\hbar} \langle \Phi_f | \sum L H_1 ... (E_0 - H_0)^{-1} H_1 | \Phi_0 \rangle ^2 \langle \psi | \psi \rangle. \quad (12) $$

In a many-body diagrammatic expansion evaluation of Eq. (12), the summation $\sum_L$ means only linked diagrams are to be included. For a single beam of light the two photon transition rate for excitation may be evaluated from Eq. (12) by considering a radiation...
field containing only one mode. In the dipole approximation the lowest order expression for \( R \) with \( m = n - 2 \) is given by

\[
R = \frac{8\pi^3 e^4 \hbar^4}{m^2 c^2 \omega^4} \left| \sum_m \frac{\langle f | \mathbf{\hat{a}}_m^\dagger \mathbf{\hat{a}}_m | \mathbf{\hat{v}}_1 \mathbf{\hat{v}}_2 \mathbf{\hat{v}}_3 \mathbf{\hat{v}}_4 | \mathbf{\hat{I}}_m \mathbf{\hat{I}}_m | \mathbf{\hat{E}}_\omega | \mathbf{\hat{E}}_\omega \rangle}{E_\omega - E_m + \hbar \omega} \right|^2 \delta(\omega - \Delta \omega), \tag{13}
\]

where \( F \) is the photon flux (in photons/cm\(^2\) sec) at frequency \( \omega \), \( \Delta \omega = (E_f - E_o)/\hbar \), and \( \mathbf{\hat{J}} \) represents a sum over bound states and an integration over the continuum. If we assume that the final state has some finite lifetime \( \tau_f \), we may replace the delta function in Eq. (13) by \(^1\)

\[
\delta(\omega - \Delta \omega) \rightarrow \frac{1}{2\pi \tau_f \left( (\Delta \omega)^2 + \frac{1}{4 \tau_f^2} \right)} \tag{14}
\]

We may now define a generalized cross section \( \beta \) (in cm\(^4\) sec) for two photon absorption as

\[
\beta = \frac{R}{F^2} \tag{15}
\]

At the peak frequency of the Lorentz distribution, \( \bar{\omega} = \frac{\Delta \omega}{2} \), the generalized cross section in the velocity form of the dipole operator is:

\[
\beta_v = 16\pi^2 e^4 \hbar^4 \frac{\tau_f}{m^2 c^2 \bar{\omega}^4} \left| \sum_m \frac{\langle f | \mathbf{\hat{a}}_m^\dagger \mathbf{\hat{a}}_m | \mathbf{\hat{v}}_1 \mathbf{\hat{v}}_2 \mathbf{\hat{v}}_3 \mathbf{\hat{v}}_4 | \mathbf{\hat{I}}_m \mathbf{\hat{I}}_m | \mathbf{\hat{E}}_\omega | \mathbf{\hat{E}}_\omega \rangle}{E_\omega - E_m + \hbar \bar{\omega}} \right|^2 \tag{16}
\]

while the length form yields:

\[
\beta_L = \frac{16\pi^2 e^4 \bar{\omega}^2}{c^2} \frac{\tau_f}{m^2 \bar{\omega}^4} \left| \sum_m \frac{\langle f | \mathbf{\hat{a}}_m^\dagger \mathbf{\hat{a}}_m | \mathbf{\hat{v}}_1 \mathbf{\hat{v}}_2 \mathbf{\hat{v}}_3 \mathbf{\hat{v}}_4 | \mathbf{\hat{I}}_m \mathbf{\hat{I}}_m | \mathbf{\hat{E}}_\omega | \mathbf{\hat{E}}_\omega \rangle}{E_\omega - E_m + \hbar \bar{\omega}} \right|^2 \tag{17}
\]

The peak cross sections of Eqs. (16) and (17) will not depend on the actual laser bandwidth. A total two photon cross section, however, must be integrated over the frequency distribution of the particular light source. We should also point out that our cross section equations have been derived assuming that the laser produces photons in a purely coherent state. Any photon statistics effects
or bunching of the photons will increase the probability for absorption by as much as a factor of 2.3.

Higher order electron correlation and radiation field corrections will add to the terms inside the absolute squares of Eqs. (16) and (17). For exact atomic wave functions the velocity and length forms of the dipole operator are of course equivalent, but since we use a perturbation expansion for $H_{\text{atom}}$ they may differ by significant amounts in lowest order.
III. CALCULATION AND RESULTS

In this section we apply the perturbation theory of Sec. II to the calculation of the two photon excitation cross section for the $1s^2 2s^2 2p^4 3P$ to $1s^2 2s^2 2p^3 (4S) 3p 3P$ transition in atomic oxygen. The experimental term separation (weighted average over $J$ levels) is 10.98 eV$^{19}$, thus a laser energy of 5.49 eV (or 2258 Å) is needed for two photon excitation. Unless otherwise indicated we will assume that the incident radiation is linearly polarized.

To obtain the lowest order generalized cross section $\beta$, we must evaluate Eqs. (16) and (17). In the case of the $2p^4 3P$ ground state of oxygen, we calculate $\beta$ for $M_L = 0$ and also for $M_L = \pm 1$ and then average over these values. The single particle core orbitals for the $3P$ ground state were calculated numerically in the Hartree-Fock approximation.$^{20}$

In lowest order the intermediate virtual states allowed by the dipole selection rules are $1s^2 2s^2 2p^3 (4S) ns^3 3S^0$, $1s^2 2s^2 2p^3 (4S) nd^3 3D^0$, and $1s^2 2s 2p^4 (4P) 3p 3P^0$, $3P^0$, $3S^0$. We used the Silverstone$^{21}$-Huzinaga$^{22}$ frozen core potential to construct the orthogonal excited state spectrum. This potential has the property of preserving the Hartree-Fock operator for the core orbitals while at the same time providing a realistic $V^{N-1}$ type operator for the excited states. We assume all single particle states have the product form $P_{ne}(r) Y_{\ell m}(\theta, \phi) \chi_s(m_s)/r$, where $Y_{\ell m}(\theta, \phi)$ is a spherical harmonic and $\chi_s(m_s)$ is the spin function. The potential for the radial $P_{ns}(r)$ orbitals (both bound and continuum) of the $2p^3 (4S) ns^3 3S^0$ intermediate state is then given by:

$$V_{Sh}(l=0) = 2J_{1s}^c - K_{1s}^c + 2J_{2s} - K_{2s}^c$$

$$+ 3J_{2p} + \frac{1}{3} K_{2p}^2 + \prod^c (J_{2p} - K_{2p})^2$$  

(18)
where
\[ \int_{n'\xi'} n_{n'\xi'}(r) \, \frac{e^{+r_{\xi'}}}{r_{\xi'}^{K_{\xi'}}} \, n_{n\xi}(r) \, d\xi \, \xi = \int_{n'\xi'} d\xi \, n_{n'\xi'}(r) \, \frac{e^{+r_{\xi'}}}{r_{\xi'}^{K_{\xi'}}} \, n_{n\xi}(r) \]  
(19)

\[ K_{\xi'}^{K_{\xi}} \, n_{\xi}(r) = \int_{n'\xi'} d\xi \, n_{n'\xi'}(r) \, \frac{e^{+r_{\xi'}}}{r_{\xi'}^{K_{\xi'}}} \, n_{n\xi}(r) \]  
(20)

and the potential for the radial orbitals of the 2p3 (4S) nd 3D0 intermediate state is given by
\[ V_{SN}(l=2) = 2J_{15}^0 - \frac{1}{5} K_{15}^2 + 2J_{25}^0 - \frac{1}{5} K_{25}^2 \]
\[ + 3J_{15}^0 + \frac{2}{15} K_{15}^2 + \frac{3}{15} K_{25}^2 \quad \text{.} \]
(22)

As a first approximation the P_{3p}(r) orbital of the 2p3 (4S) 3p 3p final state of oxygen, with single particle energy e3p, is obtained by solving
\[ \left( T_{1} - 2V_{SN}(l=2) + 2e_{3P} \right) P_{3p}(r) = 0 \quad , \]
(23)

\[ T_{1} = \frac{k^2}{m} \frac{d^2}{dr^2} - \frac{l(l+1)h^2}{mr^2} + \frac{2Ze^2}{r} \quad , \]
(24)

and
\[ V_{SN}(l=1) = 2J_{15}^0 - \frac{1}{5} K_{15}^2 + 2J_{25}^0 - \frac{1}{5} K_{25}^2 \]
\[ + 3J_{15}^0 + \frac{2}{15} K_{15}^2 + \frac{3}{15} K_{25}^2 \]
\[ + \Pi_{k} \left( -\frac{1}{2} K_{15}^2 - \frac{1}{10} J_{25}^0 - \frac{4}{15} K_{25}^2 \right) \quad . \]
(25)

For the cross section \( \beta(\pm 1) \) the dipole selection rules for determinantal states allow only contributions from the 2p3 (4S) nd 3D0 intermediate states in lowest order. After performing the angular integrations, we obtain the following radial form of Eq. (16) for the 2p4 3P to 2p3 (4S) 3p 3p transition in oxygen:
\[ \beta_{\nu}(\pm 1) = \frac{16\pi^3 e^4}{m^6 c^2 \omega^3} \left[ \frac{4}{\sqrt{15}} \langle 3p || D_{\nu} || \Phi_{\nu}(nd) \rangle \right]^2 \quad , \]
(26)
where
\[ \langle n' l' \| D_v \| n l \rangle = \int_0^\infty P_{nl}'(r) D_v P_{nl}(r) \, dr \quad , \quad (27) \]
\[ \phi_v(nl, r) = \sum_{n'l'} \frac{P_{n'l'}(r)}{\epsilon_{n'l'} - \epsilon_{nl} + \hbar \omega} \langle n'l' \| D_v \| 2p \rangle \quad , \quad (28) \]
and \( D_v = \frac{d}{dr} + \left[ \lambda_o (\ell_o + 1) - \lambda_f (\ell_f + 1) \right] / 2r \). One should note that the intermediate sum is now present in the expression for the perturbed bound state function \( \phi_v(nl, r) \) of Eq. (28). For the cross section \( \beta(0) \) the dipole selection rules allow contributions from all three types of intermediate states. The radial form of Eq. (16) is thus:
\[ \beta_v(0) = \frac{16 e^4 \hbar^4}{m^4 c^8 \omega^2} \left[ \frac{\sqrt{27}}{\sqrt{27}} \langle 3p \| D_v \| \phi_v(ns) \rangle + \sqrt{\frac{135}{2\sqrt{27}}} \langle 3p \| D_v \| \phi_v(nl) \rangle + \frac{\sqrt{243}}{\sqrt{243}} \langle 3s \| D_v \| 2p \rangle \langle 3p \| D_v \| 2s \rangle \right] . \quad (29) \]
The radial matrix elements for \( \beta_L(\pm 1) \) and \( \beta_L(0) \) derived from Eq. (17) are the same as those found in Eqs. (26) and (29) except that \( D_v \) is replaced by \( D_L = r \) and \( \phi_v(nl, r) \) is replaced by \( \phi_L(nl, r) \).

The perturbed bound state function \( \phi_v(nl, r) \) of Eq. (28) may be found by solving the inhomogeneous differential equation:
\[ T_e - 2 V_{sh}(k) - \mathbf{\hat{E}} \phi_v(nl, r) = D_v P_{2p}(r) \quad , \quad (30) \]
where \( \mathbf{\hat{E}} = \epsilon_{2p} + \omega \). The experimental energy of \( \epsilon_{2p} = -13.62 \text{ eV} \) is used for functions \( \phi_v(nl, r) \) which represent \( 2p^3(4S) n^1L^0 \) virtual excitations. Similar equations for perturbed functions \( \phi_L(nl, r) \) were also solved. The accuracy of our solutions was checked by computing cross sections for the two photon ionization of argon using perturbed bound state functions and comparing them with results obtained using the radial integration truncation method. The two methods agree to three significant figures in both the length and velocity forms at energies away from resonances.
The lifetime of $\tau_f$ of the $2p^3 ({}^4S) 3p^2 3P$ final state of oxygen may be taken as the natural decay time $\tau_{nf}$ for single photon emission to the $2p^3 ({}^4S) 3s^2 3S^0$ state. This will only be true when the laser pulse time $\tau_L$ is such that $\tau_L > \tau_{nf}$. For laser intensities currently envisioned in atmospheric remote sensing work, the photoionization rate from the $2p^3 ({}^4S) 3p^2 3P$ final state will be much smaller than the natural decay rate. The handbook value of $\tau_{nf} = 3.57 \times 10^{-8}$ sec (accuracy to 10%) is used for all subsequent calculations. If we use Eqs. (A2) and (A3) of the APPENDIX along with $\tau_{nf} = 1/R_{Se}$, we find in lowest order that $\tau_{nf} = 3.31 \times 10^{-8}$ sec in the velocity form and $\tau_{nf} = 2.97 \times 10^{-8}$ sec in the length form.

The lowest order Hartree Fock (HF) results for the generalized cross section $\beta$ for the $2p^4 3P$ to $2p^3 ({}^4S) 3p^2 3P$ transition in oxygen are given in both the length and velocity forms in Table I. Due in part to the inclusion of contributions from the $2p^3 ({}^4S) ns^2 S^0$ intermediate states, $\beta(0)$ is seen to be a factor of 20 to 30 larger than $\beta(\pm 1)$. For $\beta(0)$ the velocity form is 1.4 times larger than the length form, while for $\beta(\pm 1)$ the two forms almost agree. If we transform our wave function representation according to:

$$\Psi(LSJM_J) = \sum_{M_l M_s} C_{1^2(3S)LM_s M_J} L_1 S_{LM_s M_J} \bar{\Psi}(LSLM_s M_J) ,$$

where $C_{1^2(3S)LM_s M_J}$ is the usual Clebsch-Gordan coefficient, we may construct cross section expressions between fine structure levels using the results already obtained for $\beta(0)$ and $\beta(\pm 1)$. The experimental fine structure wave-lengths and our lowest order cross section results are found in Table II. It should be noted that for two photon absorption we may have $\Delta J = \pm 2, \pm 1$ and 0.
The importance of the complete sum over intermediate states in the results for the cross section $B$ may be shown by comparing the matrix element $M^S_\nu = \langle 3p||D_\nu||\phi_y(ns) \rangle$ with

$$
\bar{M}^S_\nu = \frac{\langle 3p||D_\nu||3s\rangle \times 3s||D_\nu||2p \rangle}{\varepsilon_{3p} - \varepsilon_{3s} + \hbar\omega}
$$

where $P_{3s}(r)$ is the radial orbital for the $2p^3\ (^4S)\ 3s\ 3S^0$ state. We found that (in atomic units) $M^S_\nu = 0.671$ and $\bar{M}^S_\nu = 0.443$, while $M^L_\nu = 12.8$ and $\bar{M}^L_\nu = 19.2$. Thus if we use only one intermediate state in the evaluation of $B(0)$, we would find a factor of 2 reduction in the velocity form while the length form would show a factor of 2 increase.

If we assume incident radiation that is circularly polarized, one must perform the angular integrations in Eqs. (16) and (17) using different dipole selection rules. The lowest order Hartree Fock results for the $2p^4\ 3P$ to $2p^3\ (^4S)\ 3p\ 3P$ transition in oxygen are then $<\beta_\nu > = 1.704 \cdot 10^{-43}$ cm$^4$ sec and $<\beta_L > = 0.935 \cdot 10^{-43}$ cm$^4$ sec.

Electron correlation effects may be important in certain multiphoton processes in complex atoms. A many-body diagrammatic expansion of Eq. (12) was developed previously to handle electron correlations in the two photon ionization of argon. The configuration interaction R matrix method has been applied to the calculation of the third-order optical harmonic coefficient for helium. We may also use the multi-configuration Hartree-Fock (MCHF) method to calculate electron correlation corrections for multiphoton processes in a manner similar to that used in recent photo-ionization work.

We therefore examine first the third order electron correlation corrections to the second order two photon cross section for the $2p^4\ 3P$ to $2p^3(4S)\ 3p\ 3P$ transition in oxygen. The complexity of the ground state
correlation problem in oxygen may be appreciated by studying Table IV of a correlation energy paper by Marchetti, Krauss and Weiss. The largest contribution comes from pair excitations of the 2p shell (43%). Since 2p may couple to give $^3P$, $^1D$ and $^1S$ and 3d may couple to give $^3F$, $^3P$, $^1G$, $^1D$, and $^1S$, we have quite a number of allowed ways to attain an overall $^3P$ symmetry. To get a feel for the strength of the ground state correlation correction, we chose the largest angular components among those 2p shell pair excitations given by Marchetti et al. The mixing coefficients of a fixed core MCHF calculation for the configurations $2p^2\ 3p\ (3s^2 \ 1S)\ 3p$, $2p^2\ 3p\ (3d^2 \ 1D)\ 3p$ and $2p^2\ 3p\ (3s3d1D)\ 3p$ are given in Table IIIA. The coefficients $a_i$ of the three excited configurations are all quite small. The contribution of the 2p $^3P\ (3d^2 \ 1D)\ 3p$ configuration to the cross section $\beta_v(\pm 1)$ of Eq. (26) is given explicitly by:

$$\beta_v(\pm 1) = \frac{64\pi^2 e^4 h^4}{m^2 c^2 \hbar^6} \sum_i \left[ \sqrt{\frac{4}{5}} a_i \langle 3p \parallel D_v \parallel \Phi_v(nd) \rangle - \sqrt{\frac{7}{5}} a_3 \langle 3p \parallel D_v \parallel \psi_v(3d^2) \rangle \right]$$

(33)

where

$$\psi_v(3d^2) = \sum_{nd} \frac{P_{nd}(r) \langle nd \parallel 3d \parallel 2p \parallel D_v \parallel 3d \rangle}{\epsilon_{2p} - \epsilon_{nd} + \hbar \omega}.$$

(34)

We may again solve for the perturbed bound state function $\psi_v(3d^2)$ using the inhomogeneous differential equation technique. This two step method of accounting for ground state pair excitations should be equivalent to solving the inhomogeneous pair equation used by Garpman et al. Expressions for $\beta_v(0)$, $\beta_L(\pm 1)$ and $\beta_L(0)$ have forms similar to Eq. (33).

The largest contribution to the electron correlation corrections for the $2p^3\ (^4S)\ 3p\ 3P$ final state of oxygen should come from the mixing
of the 2p³ intermediate couplings. This particular open shell effect was found to be quite strong in recent photoionization work on chlorine.²⁷,²⁸

The mixing coefficients of a fixed core MCHF calculation for the configurations 2p³ (⁴S) 3p ³P, 2p³ (⁰D) 3p ³P, and 2p³ (⁰P) 3p ³P are given in Table IIIIB. The MCHF radial 3p function was found to differ only slightly from the 3p function obtained using Eq. (23). The contribution of the 2p³ (⁰D) 3p ³P configuration to the cross section βv (+ 1) of Eq. (26) is given explicitly by:

\[
\beta_v(± 1) = \frac{16\pi^2 e^4 k^4}{\hbar^4 c^2 m^2} \left[ \sqrt{\frac{4}{75}} b_1 <3p \parallel Dv \parallel \phi_v(n\ell)> - \frac{1}{\sqrt{60}} b_2 <3p \parallel Dv \parallel \phi_v'(n\ell)> - \frac{1}{\sqrt{1500}} b_3 <3p \parallel Dv \parallel \phi_v(n\ell)> \right]^2,
\]

where the perturbed bound state functions \( \phi_v'(n\ell) \) and \( \phi_v'(n\ell) \) are obtained by using Eq. (30) with \( c_{2p} = -16.94 \) eV.¹⁹ Expressions for \( \beta_v(0) \), \( \beta_L(± 1) \) and \( \beta_L(0) \) also have forms similar to Eq. (35).

The multi-configuration Hartree-Fock (MCHF) results for the generalized cross section \( \beta \) for the 2p⁴ ³P to 2p³ (⁴S) 3p ³P transition in oxygen are given in both the length and velocity forms in Table I. Cross sections between fine structure levels are given in Table II. We have included only the excited configurations 2p² ³P (3d² ¹D) ³P, 2p³ (²D) 3p ³P and 2p³ (²P) 3p ³P in our final results. The MCHF values for \( \beta(0) \), \( \beta(± 1) \) and \( <\beta> \) are all lower than the corresponding Hartree-Fock values. We must note that the agreement between length and velocity has not improved. This indicates we have only touched the surface of a very complex electron correlation problem and the continuing difference between the length and velocity forms seems to be a good indicator of this fact. What we have
learned is that the result of a more complete solution of the problem will probably not differ from our lowest order Hartree-Fock values by more than a factor of 2.

As one goes to stronger and stronger photon intensities, the standard perturbation theory begins to break down. In this case the electric component of the radiation field is becoming comparable to the Coulomb field which binds the atom. From previous work we estimate that radiation field corrections, such as the fourth order process involving the absorption of 3 photons and the emission of one, will begin to significantly affect our lowest order results at a flux $F$ of $10^{32}$ photons/cm$^2$ sec. At higher intensities one must use an exact summation of a whole series of higher order radiative terms or go to an alternative formulation of the problem. We should also note that long before this regime is entered (around $10^{25}$ photons/cm$^2$ sec), the Lorentz distribution of Eq. (14) will be modified by either a decrease in laser pulse time ($\tau_L < \tau_{nf}$) or photoionization from the excited state. This in turn will affect the excitation cross sections $\beta$ of Eqs. (16) and (17).
IV. SUMMARY

In this paper we determined a value for a two photon excitation cross section in oxygen of sufficient accuracy for laser atmospheric remote sensing applications. We used the inhomogeneous differential equation technique to handle the sums over bound and continuum intermediate states found in a standard perturbation theory development. Although the electron correlation corrections are found to be quite complex, their overall effect should not significantly alter the lowest order Hartree-Fock results. In the future we hope to extend our work to the study of certain two photon transitions in nitrogen, chlorine, and argon.
ACKNOWLEDGMENTS

I would like to thank Dr. S. L. Carter of the University of Virginia, Dr. A. Temkin and Dr. R. D. Hudson of the Goddard Space Flight Center, and Dr. T. J. McIlrath of the University of Maryland for many helpful discussions. I would also like to thank the National Research Council for their financial support.
APPENDIX

The various single photon emission and absorption transition rates may be obtained from Eq. (12) with \( m = n \pm 1 \). In the dipole approximation the lowest order expression for the absorption rate is given by:

\[
R^\nu_m = \frac{4\pi^2 e^2 \hbar}{m^2 c} \sum \frac{F_\lambda}{\omega_\lambda} \left| \langle \dot{\phi} | \sum_{j=1}^{n} \mathbf{\varepsilon}_j \cdot \mathbf{\nu}_j | 0 \rangle \right|^2 S(\omega_\lambda - \Delta \omega), \tag{A1}
\]

where \( \Delta \omega = (E_f - E_0) / \hbar \). The induced emission rate has a form similar to Eq. (A1) except that \( \Delta \omega = (E_0 - E_f) / \hbar \). For spontaneous emission the flux \( F \) equals \( c/V \), where \( V \) is the volume of the radiation cavity. If the summation \( \sum \) is replaced by an integration over \( \omega \) with the appropriate density \( \rho_\omega \) of modes, we obtain for the spontaneous emission rates at \( \bar{\omega} = \Delta \omega \):

\[
R^\nu_{sc} = \frac{4\pi e^2 \bar{\omega}}{3m^2 c^3} \left| \langle \dot{\phi} \right| \sum_{j=1}^{n} \mathbf{\varepsilon}_j \cdot \mathbf{\nu}_j | 0 \rangle \right|^2, \tag{A2}
\]

and

\[
R^\nu_{sc} = \frac{4\pi e^2 \bar{\omega}}{3k c^3} \left| \langle \dot{\phi} \right| \sum_{j=1}^{n} \mathbf{\nu}_j | 0 \rangle \right|^2. \tag{A3}
\]

The absorption cross section \( \sigma \) (in \( \text{cm}^2 \)) may be obtained from Eq. (A1) by considering an external radiation field containing only one mode and replacing the delta function as in Eq. (14). The cross section \( \sigma \) at \( \bar{\omega} = \Delta \omega \) is then

\[
\sigma^\nu = \frac{8\pi e^2 \bar{\omega}}{m^2 c \bar{\omega}} \frac{\tau_f}{\left| \langle \dot{\phi} \right| \sum_{j=1}^{n} \mathbf{\varepsilon}_j \cdot \mathbf{\nu}_j | 0 \rangle \right|^2}, \tag{A4}
\]

and

\[
\sigma^\nu = \frac{8\pi e^2 \bar{\omega}}{k c} \frac{\tau_f}{\left| \langle \dot{\phi} \right| \sum_{j=1}^{n} \mathbf{\nu}_j | 0 \rangle \right|^2}. \tag{A5}
\]

If we take for \( \tau_f \) the natural lifetime for decay to \( |0\rangle \), we recover the well-known result

\[
\sigma^\nu = \sigma^\nu = \frac{2\pi c^2 \varepsilon_f}{\bar{\omega}^2} \frac{\tau_f}{\bar{\omega}^2}, \tag{A6}
\]
where \( g_i \) is the statistical weight of state \(|i\rangle\).

For two photon emission processes we find an induced emission that is proportional to \( F^2 \), a spontaneous emission that is independent of photon flux, and cross terms that are linear in \( F \). The spontaneous emission rate may also be obtained from Eq. (12) by replacing the summations over modes \( \lambda_1 \) and \( \lambda_2 \) by integrations over frequencies, giving:

\[
R_{sc}^r = \frac{4e^4 \hbar^4}{9\pi m^6 c^4} \int_0^{\omega} \omega \tilde{\omega} d\omega
\left\{ \left| \sum_{\alpha} \left( \frac{\langle \hat{\rho}_{\alpha} \hat{V}_{\alpha} \hat{X}_{\alpha} \hat{V}_{\alpha} \rangle + \langle \hat{\hat{\rho}_{\alpha} \hat{V}_{\alpha} \hat{X}_{\alpha} \hat{V}_{\alpha} \rangle}{E_0 - E_{\alpha} - \hbar\omega} \right) \right|^2 \right\}^{\frac{1}{2}},
\]

and

\[
R_{sc}^L = \frac{4e^4}{9\pi c^4} \int_0^{\omega} \tilde{\omega}^3 d\omega
\left\{ \left| \sum_{\alpha} \left( \frac{\langle \hat{\rho}_{\alpha} \hat{V}_{\alpha} \hat{X}_{\alpha} \hat{V}_{\alpha} \rangle + \langle \hat{\hat{\rho}_{\alpha} \hat{V}_{\alpha} \hat{X}_{\alpha} \hat{V}_{\alpha} \rangle}{E_0 - E_{\alpha} - \hbar\tilde{\omega}} \right) \right|^2 \right\}^{\frac{1}{2}},
\]

where \( \tilde{\omega} = \omega - \omega \). In thermal equilibrium the level populations of states \(|0\rangle\) and \(|f\rangle\) are related by Boltzmann's law. Equating two photon absorption and emission processes at each frequency \( \omega \), we may again recover Planck's law for the frequency distribution of the photon flux.
REFERENCES


TABLE I: The Two Photon Cross Section $\beta$ for the $2p^4 \, ^3p$ to $2p^3 \, (^4S) \, ^3p \, ^3P$ Transition in Oxygen (in units of $10^{-43}$ cm$^4$ sec)

<table>
<thead>
<tr>
<th>Approximation</th>
<th>$\beta(0)$</th>
<th>$\beta(+1)$</th>
<th>$&lt;\beta&gt;_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF velocity</td>
<td>6.538</td>
<td>0.232</td>
<td>2.334</td>
</tr>
<tr>
<td>HF length</td>
<td>4.729</td>
<td>0.234</td>
<td>1.732</td>
</tr>
<tr>
<td>MCHF velocity</td>
<td>6.330</td>
<td>0.155</td>
<td>2.213</td>
</tr>
<tr>
<td>MCHF length</td>
<td>4.566</td>
<td>0.174</td>
<td>1.638</td>
</tr>
</tbody>
</table>

$a \ \ <\beta> = \frac{[2\beta(+1) + \beta(0)]}{3}$
TABLE II: The Fine Structure Components of the Two Photon Cross Section $\beta$ for the $2p^4\, ^3P$ to $2p^3\, (^4S)\, ^3P$ Transition in Oxygen (in units of $10^{-43}\, cm^4$ sec)

<table>
<thead>
<tr>
<th>$J_i$</th>
<th>$J_f$</th>
<th>$\lambda(\AA)$</th>
<th>$\beta_V^{HF}$</th>
<th>$\beta_L^{HF}$</th>
<th>$\beta_V^{MCHF}$</th>
<th>$\beta_L^{MCHF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>2256.5390</td>
<td>0.192</td>
<td>0.127</td>
<td>0.200</td>
<td>0.132</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2256.5430</td>
<td>1.711</td>
<td>1.319</td>
<td>1.562</td>
<td>1.211</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2256.5574</td>
<td>0.431</td>
<td>0.286</td>
<td>0.451</td>
<td>0.296</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2260.5758</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2260.5798</td>
<td>0.718</td>
<td>0.477</td>
<td>0.751</td>
<td>0.493</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2260.5940</td>
<td>1.616</td>
<td>1.256</td>
<td>1.462</td>
<td>1.146</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2262.3328</td>
<td>1.377</td>
<td>1.097</td>
<td>1.211</td>
<td>0.980</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>2262.3368</td>
<td>0.957</td>
<td>0.636</td>
<td>1.001</td>
<td>0.657</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2262.3510</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>
### TABLE III: Multi-Configuration Hartree-Fock Calculations for Oxygen

#### A. Ground State

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Mixing Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p^4,3p$</td>
<td>$a_1 = 0.9989$</td>
</tr>
<tr>
<td>$2p^2,3p,(3s^2,1S),3p$</td>
<td>$a_2 = 0.0191$</td>
</tr>
<tr>
<td>$2p^2,3p,(3d^2,1D),3p$</td>
<td>$a_3 = 0.0398$</td>
</tr>
<tr>
<td>$2p^2,3p,(3s,3d,1D),3p$</td>
<td>$a_4 = 0.0143$</td>
</tr>
</tbody>
</table>

#### B. Final State

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Mixing Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p^3,(^4S),3p,3P$</td>
<td>$b_1 = 0.9958$</td>
</tr>
<tr>
<td>$2p^3,(^2D),3p,3P$</td>
<td>$b_2 = 0.0862$</td>
</tr>
<tr>
<td>$2p^3,(^2P),3p,3P$</td>
<td>$b_3 = -0.0323$</td>
</tr>
</tbody>
</table>