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TWO PHOTON EXCITATION OF ATOMIC OXYGEN

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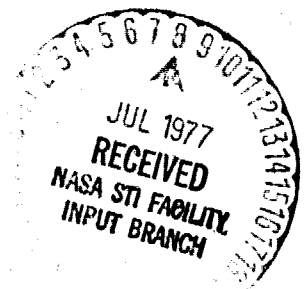
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TWO PHOTON EXCITATION OF ATOMIC OXYGEN

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ABSTRACT

A standard perturbation expansion in the atom-radiation field interaction is used to calculate 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 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.

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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 applications² 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 work³ 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 atoms⁸⁻¹⁰, as well as recent studies of double photoionization¹¹ and the hyperfine interaction.¹²

In this paper we use perturbation theory to calculate the two photon excitation cross section for the $1s^2 2s^2 2p^4 \ ^3P$ 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.¹³ The non-relativistic Hamiltonian for an N electron atom is given by

$$H_{\text{atom}} = H_{0a} + H_1, \quad (1)$$

where
$$H_{0a} = \sum_{j=1}^N \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{Ze^2}{r_j} + V_j \right), \quad (2)$$

and
$$H_{1a} = \sum_{i,j=1}^N v_{ij} - \sum_{j=1}^N V_j. \quad (3)$$

The single particle potential V_j 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.¹³ The eigenstates $|\phi_j^n\rangle$ of H_0 are products of an electronic state $|j\rangle$ and a radiation state with n_λ photons per mode λ such that $n = \sum_\lambda n_\lambda$. The eigenenergy E_j^n equals $E_j + \sum_\lambda n_\lambda \hbar \omega_\lambda$, where E_j is the unperturbed energy of the j th electronic state and ω_λ is the angular frequency of the λ th mode.

The perturbation Hamiltonian H_1 is given by

$$H_1 = H_{\text{int}} + H_{1a}, \quad (4)$$

where

$$H_{\text{int}} = \sum_{j=1}^N \left(-\frac{ie\hbar}{mc} \vec{A}(\vec{r}_j) \cdot \nabla_j + \frac{e^2}{2mc^2} |\vec{A}(\vec{r}_j)|^2 \right), \quad (5)$$

$$\vec{A}(\vec{r}) = \sum_\lambda (\hat{e}_\lambda a_\lambda e^{i\vec{k}_\lambda \cdot \vec{r}} + \hat{e}_\lambda^* a_\lambda^\dagger e^{-i\vec{k}_\lambda \cdot \vec{r}}), \quad (6)$$

and the annihilation and creation operators for the quantized vector potential $\vec{A}(\vec{r})$ may be defined by¹³

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

and

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

The solution $\psi(t)$ of the time-dependent Schrödinger equation with Hamiltonian $H = H_0 + H_1$ is given by¹⁴

$$\psi(t) = \lim_{\gamma \rightarrow 0} \frac{\exp[-iH_0 t/\hbar] U_\gamma(t) |\Phi_0^n\rangle}{\langle \Phi_0^n | U_\gamma(t) | \Phi_0^n \rangle}, \quad (9)$$

where

$$U_\gamma(t) = 1 + \frac{1}{i\hbar} \int_{-\infty}^t d\tau H_1(\tau) \\ + \frac{1}{(i\hbar)^2} \int_{-\infty}^t d\tau \int_{-\infty}^{\tau} d\tau' H_1(\tau) H_1(\tau') + \dots, \quad (10)$$

$$H_1(t) = \exp[iH_0 t/\hbar] H_1 \exp[\gamma t - iH_0 t/\hbar], \quad (11)$$

and the parameter γ allows $\psi(t)$ to be adiabatically developed from the initial state $|\Phi_0^n\rangle$. By projecting $\psi(t)$ of Eq. (9) onto the final state $|\Phi_f^m\rangle$ and then carrying out the time integrations in Eq. (10), the transition rate R is found to be¹⁵

$$R = \frac{2\pi}{\hbar} \delta(E_0^n - E_f^m) \left| \langle \Phi_f^m | \sum_L H_1 \dots (E_0^n - H_0)^{-1} H_1 | \Phi_0^n \rangle \right|^2 \langle \psi | \psi \rangle^{-1}. \quad (12)$$

In a many-body diagrammatic expansion evaluation of Eq. (12), the summation \sum_L means only linked diagrams are to be included.¹⁶

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.¹⁷ In the dipole approximation the lowest order expression for R with $m = n-2$ is given by

$$R = \frac{8\pi^3 e^4 \hbar^4}{m^4 c^2 \omega^2} \left| \sum_m \frac{\langle f | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \nabla_j | m \rangle \langle m | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \nabla_j | 0 \rangle}{E_0 - E_m + \hbar \omega} \right|^2 \delta(2\omega - \Delta\omega), \quad (13)$$

where F is the photon flux (in photons/cm² sec) at frequency ω , $\Delta\omega = (E_f - E_0)/\hbar$, and \sum represents a sum over bound states and an integration over the continuum. If we assume that the final state has some finite lifetime τ_f , we may replace the delta function in Eq. (13) by¹⁸

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

We may now define a generalized cross section β (in cm⁴ sec) for two photon absorption as

$$\beta = \frac{R}{F^2}. \quad (15)$$

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:

$$\beta_v = \frac{16\pi^2 e^4 \hbar^4}{m^4 c^2 \bar{\omega}^2} \tau_f \left| \sum_m \frac{\langle f | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \nabla_j | m \rangle \langle m | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \nabla_j | 0 \rangle}{E_0 - E_m + \hbar \bar{\omega}} \right|^2, \quad (16)$$

while the length form yields:

$$\beta_L = \frac{16\pi^2 e^4 \bar{\omega}^2}{c^2} \tau_f \left| \sum_m \frac{\langle f | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \vec{r}_j | m \rangle \langle m | \sum_{j=1}^N \hat{\mathbf{e}} \cdot \vec{r}_j | 0 \rangle}{E_0 - E_m + \hbar \bar{\omega}} \right|^2. \quad (17)$$

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_{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 \AA) 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 β , we must evaluate Eqs. (16) and (17). In the case of the $2p^4 \ ^3P$ ground state of oxygen, we calculate β 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 $1s^2 2s^2 2p^3 (4S) ns \ ^3S^0$, $1s^2 2s^2 2p^3 (4S) nd \ ^3D^0$, and $1s^2 2s 2p^4 (4P) 3p \ ^3D^0, \ ^3P^0, \ ^3S^0$. We used the Silverstone²¹-Huzinaga²² 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 $P_{nl}(r) Y_{lm}(\theta, \phi) \chi_s(m_s)/r$, where $Y_{lm}(\theta, \phi)$ 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 $2p^3 (4S) ns \ ^3S^0$ intermediate state is then given by:

$$V_{SH}(l=0) = 2J_{1s}^0 - K_{1s}^0 + 2J_{2s}^0 - K_{2s}^0 \\ + 3J_{2p}^0 + \frac{1}{3} K_{2p}^0 + \Pi_0 (J_{2p}^0 - K_{2p}^0), \quad (18)$$

where
$$J_{n'l'}^K P_{nl}(r) = \int_0^\infty dr_1 P_{n'l'}^2(r_1) \frac{e^2 r_1^K}{r_1^{K+1}} P_{nl}(r), \quad (19)$$

$$K_{n'l'}^K P_{nl}(r) = \int_0^\infty dr_1 P_{n'l'}(r_1) P_{nl}(r_1) \frac{e^2 r_1^K}{r_1^{K+1}} P_{n'l'}(r), \quad (20)$$

$$(21)$$

$$\Pi_l = \sum_{n'l'} \delta_{ll'} |n'l'\rangle \langle n'l'|,$$

and $r_< = \min(r_1, r)$ and $r_> = \max(r_1, r)$. The potential for the radial $P_{nd}(r)$ orbitals of the $2p^3 (^4S)$ nd $3D^0$ intermediate state is given by

$$V_{SH}(l=2) = 2J_{2s}^0 - \frac{1}{5} K_{1s}^2 + 2J_{2s}^c - \frac{1}{5} K_{2s}^2 \quad (22)$$

$$+ 3J_{2p}^0 + \frac{2}{15} K_{2p}^1 + \frac{3}{35} K_{2p}^3.$$

As a first approximation the $P_{3p}(r)$ orbital of the $2p^3 (^4S)$ $3p$ $3P$ final state of oxygen, with single particle energy ϵ_{3p} , is obtained by solving

$$(T_l - 2V_{SH}(l=1) + 2\epsilon_{3p}) P_{3p}(r) = 0, \quad (23)$$

where
$$T_l = \frac{\hbar^2}{m} \frac{d^2}{dr^2} - \frac{l(l+1)\hbar^2}{mr^2} + \frac{2Ze^2}{r}, \quad (24)$$

and
$$V_{SH}(l=1) = 2J_{1s}^0 - \frac{1}{3} K_{1s}^1 + 2J_{2s}^0 - \frac{1}{3} K_{2s}^1 \quad (25)$$

$$+ 3J_{2p}^0 + \frac{1}{3} K_{2p}^0 + \frac{2}{15} K_{2p}^2$$

$$+ \Pi_1 \left(-\frac{1}{3} K_{2p}^0 - \frac{2}{10} J_{2p}^2 - \frac{2}{15} K_{2p}^2 \right).$$

For the cross section $\beta(\pm 1)$ the dipole selection rules for determinantal states allow only contributions from the $2p^3 (^4S)$ nd $3D^0$ intermediate states in lowest order. After performing the angular integrations, we obtain the following radial form of Eq. (16) for the $2p^4$ $3P$ to $2p^3 (^4S)$ $3p$ $3P$ transition in oxygen:

$$\beta_v(\pm 1) = \frac{16\pi^2 e^4 \hbar^4}{m^4 c^2 \bar{\omega}^2} \tau_f \left[\sqrt{\frac{4}{15}} \langle 3p || D_v || \phi_v(nd) \rangle \right]^2, \quad (26)$$

where $\langle n'l' || D_v || nl \rangle = \int_0^\infty P_{n'l'}(r) D_v P_{nl}(r) dr$, (27)

$$\phi_v(nl, r) = \sum_{nl} \frac{P_{nl}(r) \langle nl || D_v || 2p \rangle}{\epsilon_{2p} - \epsilon_{nl} + \hbar\omega} \quad (28)$$

and $D_v = d/dr + [\ell_0(\ell_0 + 1) - \ell_f(\ell_f + 1)]/2r$. 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:

$$\beta_v(0) = \frac{16\pi^2 e^4 \hbar^4}{m^4 c^3 \omega^2} \tau_f \left[\frac{\sqrt{4}}{\sqrt{27}} \langle 3p || D_v || \phi_v(ns) \rangle + \frac{\sqrt{64}}{\sqrt{675}} \langle 3p || D_v || \phi_v(nd) \rangle + \frac{\sqrt{4}}{\sqrt{243}} \frac{\langle 2s || D_v || 2p \rangle \langle 3p || D_v || 2s \rangle}{\epsilon_{2s} - \epsilon_{3p} + \hbar\omega} \right]^2. \quad (29)$$

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^{4,5}:

$$(T_L - 2V_{SH}(\ell) + 2\tilde{E}) \phi_v(nl, r) = D_v P_{2p}(r) , \quad (30)$$

where $\tilde{E} = \epsilon_{2p} + \omega$. The experimental energy of $\epsilon_{2p} = -13.62$ eV¹⁹ is used for functions $\phi_v(nl, r)$ which represent $2p^3(^4S)$ $nl\ ^3L^0$ 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.¹⁵ The two methods agree to three significant figures in both the length and velocity forms at energies away from resonances.

The lifetime of τ_f of the $2p^3 (^4S) 3p ^3P$ final state of oxygen may be taken as the natural decay time τ_{nf} for single photon emission to the $2p^3 (^4S) 3s ^3S^0$ state. This will only be true when the laser pulse time τ_L is such that $\tau_L > \tau_{nf}$.² For laser intensities currently envisioned in atmospheric remote sensing work,² the photoionization rate from the $2p^3 (^4S) 3p ^3P$ final state will be much smaller than the natural decay rate. The handbook²³ value of $\tau_{nf} = 3.57 \cdot 10^{-8}$ 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 $\tau_{nf} = 3.31 \cdot 10^{-8}$ sec in the velocity form and $\tau_{nf} = 2.97 \cdot 10^{-8}$ sec in the length form.

The lowest order Hartree Fock (HF) results for the generalized cross section β for the $2p^4 ^3P$ to $2p^3 (^4S) 3p ^3P$ 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 $2p^3 (^4S) ns ^3S^0$ 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:

$$\Psi(LSJ M_J) = \sum_{M_L M_S} C_{M_L M_S M_J}^{LSJ} \Phi(LS M_L M_S) \quad , \quad (31)$$

where $C_{m_1 m_2 m_3}^{l_1 l_2 l_3}$ 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 wavelengths¹⁹ 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 β may be shown by comparing the matrix element $M_V^S = \langle 3p || D_Y || \phi_V(ns) \rangle$ with

$$\bar{M}_V^S = \frac{\langle 3p || D_Y || 3s \rangle \langle 3s || D_Y || 2p \rangle}{E_{2p} - E_{3s} + \hbar\omega}, \quad (32)$$

where $P_{3s}(r)$ is the radial orbital for the $2p^3 ({}^4S) 3s {}^3S^o$ state. We found that (in atomic units) $M_V^S = 0.671$ and $\bar{M}_V^S = 0.443$, while $M_L^S = 12.8$ and $\bar{M}_L^S = 19.2$. Thus if we use only one intermediate state in the evaluation of $\beta(0)$, 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 $\langle \beta_V \rangle = 1.704 \cdot 10^{-43} \text{ cm}^4 \text{ sec}$ and $\langle \beta_L \rangle = 0.935 \cdot 10^{-43} \text{ cm}^4 \text{ sec}$.

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.¹⁵ The configuration interaction R matrix method has been applied to the calculation of the third-order optical harmonic coefficient for helium.²⁴ We may also use the multi-configuration Hartree-Fock (MCHF) method²⁰ to calculate electron correlation corrections for multiphoton processes in a manner similar to that used in recent photo-ionization work.²⁵

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.²⁶

The largest contribution comes from pair excitations of the 2p shell (43%). Since $2p^2$ may couple to give 3P , 1D , and 1S and $3d^2$ 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 $2p^4$ 3P , $2p^2$ 3P ($3s^2$ 1S) 3P , $2p^2$ 3P ($3d^2$ 1D) 3P and $2p^2$ 3P ($3s3d^1D$) 3P are given in Table IIIA. The coefficients a_i of the three excited configurations are all quite small. The contribution of the $2p^2$ 3P ($3d^2$ 1D) 3P configuration to the cross section $\beta_V(\pm 1)$ of Eq. (26) is given explicitly by:

$$\beta_V(\pm 1) = \frac{16\pi^2 e^4 \hbar^4}{m^4 c^2 \tilde{\omega}^2} \chi_f \left[\sqrt{\frac{4}{75}} a_1 \langle 3p || D_V || \phi_V(nd) \rangle - \sqrt{\frac{7}{375}} a_3 \langle 3p || D_V || \psi_V(3d^2) \rangle \right]^2, \quad (33)$$

$$\text{where} \quad \psi_V(3d^2) = \sum_{nd} \frac{P_{nd}(r) \langle nd || 3d \rangle \langle 2p || D_V || 3d \rangle}{\epsilon_{2p} - \epsilon_{nd} + \hbar\omega}. \quad (34)$$

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.¹² 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 $2p^3$ 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 $2p^3$ (4S) $3p$ 3P , $2p^3$ (2D) $3p$ 3P , and $2p^3$ (2P) $3p$ 3P are given in Table IIIB. The MCHF radial $3p$ function was found to differ only slightly from the $3p$ function obtained using Eq. (23). The contribution of the $2p^3$ (2D) $3p$ 3P configuration to the cross section $\beta_V(\pm 1)$ of Eq. (26) is given explicitly by:

$$\beta_V(\pm 1) = \frac{16\pi^2 e^4 \hbar^4}{m^4 c^2 \omega^2} \zeta_f \left[\sqrt{\frac{4}{75}} b_1 \langle 3p || D_V || \phi_V(nd) \rangle - \sqrt{\frac{1}{60}} b_2 \langle 3p || D_V || \phi'_V(ns) \rangle - \sqrt{\frac{121}{1500}} b_2 \langle 3p || D_V || \phi'_V(nd) \rangle \right]^2, \quad (35)$$

where the perturbed bound state functions $\phi'_V(ns)$ and $\phi'_V(nd)$ are obtained by using Eq. (30) with $\epsilon_{2p} = -16.94$ eV.¹⁹ Expressions for $\beta_V(0)$, $\beta_L(\pm 1)$ and $\beta_L(0)$ also have forms similar to Eq. (35).

The multi-configuration Hartree-Fock (MCHF) results for the generalized cross section β for the $2p^4$ 3P to $2p^3$ (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 $2p^2$ 3P ($3d^2$ 1D) 3P , $2p^3$ (2D) $3p$ 3P and $2p^3$ (2P) $3p$ 3P in our final results. The MCHF values for $\beta(0)$, $\beta(\pm 1)$ and $\langle \beta \rangle$ 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 work¹⁵ 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/cm² sec. At higher intensities one must use an exact summation of a whole series of higher order radiative terms²⁸ or go to an alternative formulation of the problem.³ We should also note that long before this regime is entered (around 10^{25} photons/cm² 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 β 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.

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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:

$$R_a^v = \frac{4\pi^2 e^2 \hbar}{m^2 c} \sum_{\lambda} \frac{F_{\lambda}}{\omega_{\lambda}} |\langle f | \sum_{j=1}^N \hat{\epsilon} \cdot \nabla_j | o \rangle|^2 \delta(\omega_{\lambda} - \Delta\omega), \quad (A1)$$

where $\Delta\omega = (E_f - E_o)/\hbar$. The induced emission rate has a form similar to Eq. (A1) except that $\Delta\omega = (E_o - E_f)/\hbar$. For spontaneous emission the flux F equals c/V , where V is the volume of the radiation cavity. If the summation \sum_{λ} is replaced by an integration over ω with the appropriate density ρ_{ω} of modes,¹⁸ we obtain for the spontaneous emission rates at $\bar{\omega} = \Delta\omega$:

$$R_{se}^v = \frac{4e^2 \hbar \bar{\omega}}{3m^2 c^3} |\langle f | \sum_{j=1}^N \nabla_j | o \rangle|^2, \quad (A2)$$

$$\text{and} \quad R_{se}^L = \frac{4e^2 \bar{\omega}^3}{3\hbar c^3} |\langle f | \sum_{j=1}^N \vec{r}_j | o \rangle|^2. \quad (A3)$$

The absorption cross section σ (in 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 σ at $\bar{\omega} = \Delta\omega$ is then

$$\sigma_v = \frac{8\pi e^2 \hbar}{m^2 c \bar{\omega}} \tau_f |\langle f | \sum_{j=1}^N \hat{\epsilon} \cdot \nabla_j | o \rangle|^2, \quad (A4)$$

$$\text{and} \quad \sigma_L = \frac{8\pi e^2 \bar{\omega}}{\hbar c} \tau_f |\langle f | \sum_{j=1}^N \hat{\epsilon} \cdot \vec{r}_j | o \rangle|^2. \quad (A5)$$

If we take for τ_f the natural lifetime for decay to $|o\rangle$, we recover the well-known result¹⁷

$$\sigma_v = \sigma_L = \frac{2\pi c^2}{\bar{\omega}^2} \frac{g_f}{g_o}, \quad (A6)$$

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 λ_1 and λ_2 by integrations over frequencies, giving:

$$R_{se}^V = \frac{4e^4 \hbar^4}{9\pi m^4 c^6} \int_0^{\Delta\omega} \omega \tilde{\omega} d\omega \times \left| \sum_m \left(\frac{\langle f | \sum_{j=1}^N \nabla_j |m\rangle \chi_m | \sum_{j=1}^N \nabla_j |o\rangle}{E_o - E_m - \hbar\omega} + \frac{\langle f | \sum_{j=1}^N \nabla_j |m\rangle \chi_m | \sum_{j=1}^N \nabla_j |o\rangle}{E_o - E_m - \hbar\tilde{\omega}} \right) \right|^2, \quad (A7)$$

$$\text{and } R_{se}^L = \frac{4e^4}{9\pi c^6} \int_0^{\Delta\omega} \omega^3 \tilde{\omega}^3 d\omega \times \left| \sum_m \left(\frac{\langle f | \sum_{j=1}^N \vec{r}_j |m\rangle \chi_m | \sum_{j=1}^N \vec{r}_j |o\rangle}{E_o - E_m - \hbar\omega} + \frac{\langle f | \sum_{j=1}^N \vec{r}_j |m\rangle \chi_m | \sum_{j=1}^N \vec{r}_j |o\rangle}{E_o - E_m - \hbar\tilde{\omega}} \right) \right|^2, \quad (A8)$$

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

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

Approximation	$\beta(0)$	$\beta(+1)$	$\langle \beta \rangle^a$
HF velocity	6.538	0.232	2.334
HF length	4.729	0.234	1.732
MCHF velocity	6.330	0.155	2.213
MCHF length	4.566	0.174	1.638

^a $\langle \beta \rangle = [2\beta(+1) + \beta(0)]/3$

TABLE II: The Fine Structure Components of the Two Photon Cross Section β for the $2p^4\ ^3P$ to $2p^3\ (^4S)\ 3p\ ^3P$ Transition in Oxygen (in units of $10^{-43}\ \text{cm}^4\ \text{sec}$)

J_i	J_f	$\lambda(\text{\AA})$	β_V^{HF}	β_L^{HF}	β_V^{MCHF}	β_L^{MCHF}
2	0	2256.5390	0.192	0.127	0.200	0.132
2	2	2256.5430	1.711	1.319	1.562	1.211
2	1	2256.5574	0.431	0.286	0.451	0.296
1	0	2260.5758	0.000	0.000	0.000	0.000
1	2	2260.5798	0.718	0.477	0.751	0.493
1	1	2260.5940	1.616	1.256	1.462	1.146
0	0	2262.3328	1.377	1.097	1.211	0.980
0	2	2262.3368	0.957	0.636	1.001	0.657
0	1	2262.3510	0.000	0.000	0.000	0.000

TABLE III: Multi-Configuration Hartree-Fock Calculations for Oxygen

A. Ground State

Configuration	Mixing Coefficients
$2p^4\ 3p$	$a_1 = 0.9989$
$2p^2\ 3p\ (3s^2\ 1S)\ 3p$	$a_2 = 0.0191$
$2p^2\ 3p\ (3d^2\ 1D)\ 3p$	$a_3 = 0.0398$
$2p^2\ 3p\ (3s\ 3d\ 1D)\ 3p$	$a_4 = 0.0143$

B. Final State

Configuration	Mixing Coefficients
$2p^3\ (^4S)\ 3p\ 3p$	$b_1 = 0.9958$
$2p^3\ (^2D)\ 3p\ 3p$	$b_2 = 0.0862$
$2p^3\ (^2P)\ 3p\ 3p$	$b_3 = - 0.0323$