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Two-Photon Exitation Cross-Section in Light and Intermediate Atoms

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Using the method of explicit summation over the intermediate states and LS coupling an expression for two-photon absorption cross section in light and intermediate atoms in terms of integrals over radial wave functions is derived. Two selection rules, one exact and one approximate, are derived. In evaluating the radial integrals, for low-lying levels, the Hartree-Fock wave functions, and for high-lying levels hydrogenic wave functions obtained by the quantum defect method have been used. A relationship between the cross section and the oscillator strengths is derived. Cross sections due to selected transitions in nitrogen, oxygen, and chlorine are given. The expression for the cross section should find usefulness in calculating the two-photon absorption in light and intermediate atoms.

I. INTRODUCTION

Multiphoton absorption of laser beams by atmospheric atoms and molecules and subsequent fluorescence of these particles provide a sensitive tool for remote sensing and monitoring of the atmospheric species.[1] To determine the strength of the atomic fluorescence, evaluation of the atomic absorption cross section is necessary.

Several methods for evaluation of the cross section are available.[2] A suitable method often used is a sum rule or inverse Green's function method due to Dalgarno and Lewis[3] which has been applied by several authors[4,5,6] to two-photon absorption in atoms. The method, except in resonance absorptions[5], provides reliable results for the cross sections.

An alternative method is the method of explicit summation over the intermediate states. The convergence of the photoabsorption cross section to its final value with respect to the addition of intermediate states, as will be shown, is rapid. An advantage of the method is that the angular integration of the electric dipole matrices appearing in the expression for the cross section can be carried out in general for atoms, leading to an expression for the cross section in terms of radial integrals.

Here we use the method of explicit summation over the intermediate states. A formula for the cross section in terms of integrals over atomic radial wave functions using LS coupling is given. The method is applied to the two-photon excitation cross section calculation in nitrogen, oxygen, and chlorine.

We restrict ourself to cases where the interaction potential between the radiation field and absorbing atoms is small compared to the atomic Hamiltonian. Then the time dependent perturbation theory can be used to derive the cross section.

The two commonly used forms of the interacting potential, V(t), are the electric dipole form, $V(t) = -e\vec{E}(t).\vec{r}$, with $\vec{E}(t)$ the electric field vector and $\vec{r}$ the position vector of the electron undergoing transition, and the velocity form or the Coulomb gauge form of the potential given by $V(t) = (e/mc)\,\vec{A}\,.\,\vec{p}$, where e, m, c have their usual meanings, $\vec{A}$ is the vector potential, and $\vec{p}$ is the momentum of the transient electron.[7]

Lamb[8] has suggested that the electric dipole form should be used, since this form agrees with measurements. Bassani et al[9] have shown that for the resonance cases, where the difference in energy of atomic levels is a multiple of the photon energies and for 1s→2s transition, the two forms give the same results, but with respect to the inclusion of the intermediate states the velocity form converges much slower.

Kobe[7] has verified Bassani et al results, but has shown that for the non-resonance cases the two results are different. However, Grynberg and Giacobino[10] have shown that by taking into account some small terms neglected by Kobe the differences between the two forms disappear.

In addition to the two distinct forms of the cross section due to the two forms of the interacting potentials, the cross section has three forms depending whether length, velocity, or acceleration forms are used for the electric dipole matrices. These forms give identical results if exact atomic wave functions are used, but in practice where approximate wave functions are used, they can be employed to test the accuracy of the applied approximate wave functions. In this way six different forms for the cross section are found. For reference these cross sections, except the acceleration forms, are derived from the Schoedinger equation in Appendix I, treating the radiation field classically and the atomic field quantum mechanically. The results are identical to results by fully quantum mechanical treatment. Since the

acceleration forms are seldom used they will not be given here. Also in Appendix 1 an order of magnitude formula is given for atomic N-photon absorption cross sections.

In evaluating the electric dipole matrices a choice should be made about the atomic wave functions. It is assumed that LS coupling is valid for light and intermediate atoms under consideration.

However, for transitions involving the ground or the final state and a highly excited state the validity of the LS coupling becomes questionable. It is more appropriate to use jK coupling[11], where the total angular momentum of the core (atom minus the highly excited state electron) is coupled to the orbital angular momentum of the highly excited electron, and the resultant combines with the spin of this electron. This approximation is not being used here.

For evaluation of the radial integrals, for low-lying levels single configuration Hartree-Fock wave functions, and for highly excited states hydrogenic wave functions obtained through the quantum defect method have been used. It has been verified that the result obtained by this method for the excited states agrees within a few percent with the result obtained by the Hartree-Fock calculation. Use of the hydrogenic wave functions leads to considerable savings in the computer's time.

The use of the single configuration wave function is not justified for a precision calculation. The calculated cross section using this function may be off sometimes by factors of two or more from the more accurate multi-configuration wave functions. The task of a more accurate calculation is left for the future.

In this paper contribution of the intermediate states that fall in the continuum have not been taken into account. It has been shown[9,12] that in the electric dipole gauge approximation which will be used here the contribution of the continuum intermediate states is small compared to the discrete inter-

mediate states. While inclusion of this contribution is straightforward, algebraically is cumbersome. It is believed that this contribution should be considered only after other approximations which make comparable contributions to the cross section have been removed.

In Section II that follows angular integration over the electric dipole matrices is carried out, and the cross section is expressed in terms of the radial integrals. Two selection rules are also derived, and a crude method for cross section calculation using the oscillator strength is given. In Section III cross sections for selected transitions in N, O, and Cl are given.

For the specific problem of the two-photon excitation in atomic oxygen, in Appendix II population of the excited and ionized states of the excited atoms as functions of the laser pulse duration, the collision time of the atom with the ambient gas in the atomosphere, and the atmospheric opacity to the probling laser beam have been calculated. Results are presented graphically and through a table.

II. FORMULATION

A. Angular Integration of the Amplitude

We carry out the angular integration over the amplitudes given in the Appendix by Eq. (A14). Since we are dealing with light and intermediate atoms, we assume that LS coupling provides a valid coupling scheme. The state $|a\rangle$ is then given by

$$|a\rangle = |(\alpha_1 S_1 L_1 n\ell) SLJM_J\rangle \tag{1}$$

In this expression $n\ell$ is the principal and angular momentum quantum numbers of the active electron undergoing transition, $S_1 L_1$ is the spin and orbital angular momentum quantum numbers of the residual atom, and α_1 represents all other quantum numbers of the residual atom. $SLJM_J$ are the spin, orbital, and total angular momenta of the atom, and M_J is the projection quantum number of J.

The evaluation of the dipole matrices can easily be accomplished by the use of the powerful method of Racah. In evaluating the matrices in (A14) we make use of (1) to express $|i\rangle$, $|m\rangle$, and $|f\rangle$. We also use the notation

$\Sigma_i \hat{e}.\vec{r}_i = P(10)$ where $\vec{r}_i$ are the position vectors of the atomic electrons, and $P(10)$ is the z-component of $\vec{P} = \Sigma_i \vec{r}_i$ (Ref. 13). It should be noted that summation over m stands for a summation over the principal, azimuthal and magnetic quantum numbers of the intermediate states as well as an average with respect to the initial, and a sum with respect to the final magnetic quantum numbers.

We designate the initial, intermediate, and final states by the unprimed, double primed, and primed symbols, respectively. Then (A14) can be written

$$\sigma_0^{(2)} = 8\pi^3 \gamma^2 E^2 \left| \sum_{n''l''L''J''} \frac{T(nln''l''n'l';L_1;SLJSL''J''SL'J')}{E_i - E(n''l''L''J'') + E} \right|^2 \tag{2}$$

where T is defined in the following.

For the case of non-equivalent electrons in a shell T is given by[14]

$$T_{non-eq.}(nln''l''n'l';L_1;SLJSL''J''SL'J')$$

$$= \frac{1}{2J+1} \sum_{M_J M_{J''} M_{J'}} \langle f | \sum_i \hat{e}.\vec{r}_i | m \rangle \langle m | \sum_i \hat{e}.\vec{r}_i | i \rangle$$

$$= \frac{1}{2J+1} \sum_{M_J M_{J''} M_{J'}} \langle (\alpha,S,L,nl)SLJM_J | P(10) | (\alpha,S,L,n''l'')SL''J''M_{J''} \rangle$$

$$\times \langle (\alpha,S,L,n''l'')SL''J''M_{J''} | P(10) | (\alpha,S,L,n'l')SL'J'M_{J'} \rangle$$

$$= (-)^{l'+l''+2S+L+L'+2J''} [(2L+1)(2L'+1)(2J+1)^{-1}(2J'+1)]^{1/2}$$

$$\times (2L''+1)(2J''+1) \begin{Bmatrix} L_1 & L & l \\ 1 & l'' & L'' \end{Bmatrix} \begin{Bmatrix} L_1 & L' & l' \\ 1 & l'' & L'' \end{Bmatrix} \begin{Bmatrix} S & J & L \\ 1 & L'' & J'' \end{Bmatrix} \begin{Bmatrix} S & J' & L' \\ 1 & L'' & J'' \end{Bmatrix}$$

$$\times \left[\sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \right] \langle nl \| P(1) \| n''l'' \rangle \langle n''l'' \| P(1) \| n'l' \rangle . \tag{3}$$

All symbols have their usual meanings and

$$\langle n\ell \| P(1) \| n'\ell' \rangle = \sqrt{\ell_>} \int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r) r^3 dr \,, \tag{4}$$

where $\ell_>$ is the larger of ℓ and ℓ', and $R_{n\ell}$ and $R_{n'\ell'}$ are single electron radial wave functions.

In the above we have assumed that the residual atom designated by the quantum numbers $\alpha_1 S_1 L_1$ is "frozen", and does not change its state during the transition. Similarly, the total spin angular momentum S does not change during the transition.

If there were n equivalent electrons in a shell, the expression for T becomes[14]

$$T_{eq.} = \sqrt{n} \left(\ell^n \alpha SL \, [\![\ell^{n-1} (\alpha_1 S_1 L_1) \ell SL \right) T_{non-eq.} \tag{5}$$

where $T_{non-eq.}$ is given by (3) and the arguments of $T_{eq.}$ and $T_{non-eq.}$ are the same. The bracketed term is the coefficient of fractional parentage in which $\ell^n \alpha$ SL are the quantum numbers of the shell that has equivalent electrons, and $\ell^{n-1}(\alpha_1 S_1 L_1)$ ℓSL are the quantum numbers of a hypothetical shell with n electrons in which there is an active electron with angular momentum quantum number ℓ, a residual atom with quantum numbers $\ell^{n-1}(\alpha_1 S_1 L_1)$, and the shell has the total spin and orbital angular momenta quantum numbers S and L. Tables of numerical values of the coefficients of fractional parentage are given by Racah[15] and Rohrlich[16].

We can combine (3) and (4) with (2) for the case of non-equivalent electrons, and (3), (4), and (5) with (2) for the case of equivalent electrons to express the cross section in terms of radial integrals.

In addition, since variation of $E(n''\ell''L''J'')$ with respect to J'' for light and intermediate atoms is slight and of the order of the fine

structure constant, we take the average of $E(n''\ell''L''J'')$ with respect to J'', and sum only the numerator in (2) with respect to J''. Then the cross section can be expressed as

$$\sigma(SLJ \rightarrow SL'J') = 8\pi^3 \gamma^2 E^2 \left| \sum_{n''\ell''L''} \frac{C(\ell''L'')R(n\ell, n''\ell'')R(n''\ell'', n'\ell')}{E_i - E(n''\ell''L'') + E} \right|^2, \tag{6}$$

$$R(n\ell, n'\ell') = \int_0^\infty R_{n\ell}(r) R_{n'\ell'}(r)\, r^3 dr \tag{7}$$

where $C(\ell''L'')$ are constants expressed in terms of 3-j, 6-j symbols, and the coefficients of fractional parentage, and are obtained by comparing (6) and (7) with (2) through (5). For the case of non-equivalent electrons it is given by

$$C(\ell''L'') = (-)^{\ell'+\ell''+2S+L+L'} \sqrt{\ell_1 \ell_2}\left[(2L+1)(2L'+1)(2J+1)^{-1}(2J'+1)\right]^{1/2}$$

$$\times (2L''+1)\begin{Bmatrix} L, & L & \ell \\ 1 & \ell'' & L'' \end{Bmatrix}\begin{Bmatrix} L, & L' & \ell' \\ 1 & \ell'' & L'' \end{Bmatrix}\sum_{J''}(-)^{2J''}(2J''+1)\begin{Bmatrix} S & J & L \\ 1 & L'' & J'' \end{Bmatrix}\begin{Bmatrix} S & J' & L' \\ 1 & L'' & J'' \end{Bmatrix}$$

$$\times \sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix}\begin{pmatrix} J' & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \tag{8}$$

where ℓ_1 is the larger of ℓ and ℓ'', and ℓ_2 is the larger of ℓ'' and ℓ'. For the case of equivalent electrons anologous to Eq. (5) the right-hand side of (8) should be multiplied by the coefficient of the fractional parentage.

B. Selection Rules

1. An exact selection rule. We consider the expression in squared bracket on the right-hand side of (3) consisting of a summation with respect to M_J. Since M_J is a demi-variable, the expression does not change in value if we let $M_J \to -M_J$. Making use of the properties of the 3-j symbols[17] it follows that

$$\sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ M & -M_J & 0 \end{pmatrix} = \sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ -M_J & M_J & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ -M_J & M_J & 0 \end{pmatrix} \tag{9}$$

$$= (-)^{-(J+J'+2J''+2)} \sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix}$$

Therefore the expression vanishes unless $J+J'+2J''$ is an even integer. For J, J', and J'' integers this implies that $J'-J$ should be even. Then of all permissible values of J' only $J' = J, J\pm 2$ are allowed.

For J, J', and J'' half odd integers, the condition $J+J'+2J''$ even also implies that $J'-J$ must be even. Then again $J'=J, J\pm 2$. We therefore have the following selection rule:

$$J' - J = 0, \pm 2 \tag{10}$$

This rule is in addition to the usual selection rules for single transitions in which $\Delta\ell = \pm 1$, $\Delta L = 0, \pm 1$, and $\Delta J = 0, \pm 1$, where ℓ, L, and J have their usual meanings.

2. An approximate selection rule. This approximate selection rule arises when we neglect splitting of a level with a given S and L due to different J values, i.e., the fine structure splitting, and applies to the case when $J' = J$. With the neglect of the J splitting the denominator inside the squared bracket on the right hand side of (2) becomes independent of J'', and the sum with respect to J'' in (2) can be done analytically.

For $J' = J$ the sum with respect to M_J on the right-hand side of (3) becomes equal to 1/3 (Ref. 17). Then the sum with respect to J'' in (2), using (3), becomes

$$\sum_{J''} (-)^{2J''} (2J''+1) \begin{Bmatrix} S & J & L \\ 1 & L'' & J'' \end{Bmatrix} \begin{Bmatrix} S & J & L' \\ 1 & L'' & J'' \end{Bmatrix} = (-)^{2(S+L'')} (2L+1)^{-1} \delta(L, L') \tag{11}$$

Eq. (11) was derived using the orthogonalization of the 6-j symbols.[17]

Eq. (11) implies that

$$L' - L = 0 \text{ when } J' - J = 0 \tag{12}$$

i.e., when the initial and final total angular momenta are the same, the initial and final orbital angular momenta should also be the same. It will be shown in the next section that transitions for which $J'=J$ have large cross sections. When (12) holds, (3) reduces to

$$\begin{aligned} &T_{non\text{-}eq.}(n\ell n''\ell'' n'\ell'; L_1; SLJSL''J''SL'J') \\ &\cong (-)^{\ell'+\ell''+L+L'} \times \frac{1}{3} \left[(2L+1)^{-1} (2J+1)^{-1} (2L'+1)(2J'+1) \right]^{1/2} \\ &\times (2L''+1) \begin{Bmatrix} L_1 & L & \ell \\ 1 & \ell'' & L'' \end{Bmatrix} \begin{Bmatrix} L_1 & L' & \ell' \\ 1 & \ell'' & L'' \end{Bmatrix} \langle n\ell \| P(1) \| n''\ell'' \rangle \langle n''\ell'' \| P(1) \| n'\ell' \rangle \end{aligned} \tag{13}$$

Using (2) we see that cross sections due to transitions which are forbidden according to (12) are of the order $(Z^4/\gamma^2)^2$ times smaller than allowed transitions, where Z is the effective charge acting on the transient electron, and γ is the fine structure constant.

C. Method of the Oscillator Strength to Calculate the Cross Section

A method used by McIlrath, Hudson, Aikin and Wilkerson[18] employs the available values of the oscillator strengths to calculate multiphoton

excitation in atoms and molecules. The approximation in the method consists in neglecting all intermediate terms represented by the summation with respect to m in (A14) except one term with the largest oscillator strength. In this way an order of magnitude cross section is calculated. The advantage of the method is that no elaborate calculation is necessary, and use is made of the most accurate oscillator strength values available in the literature. However, when no strong line occurs in the transitions considered, the calculated values may be far off from the true values. Examples will be given for N and O using this method of calculation.

The oscillator strength between two levels α_J and $\alpha_{J'}$ is defined by[19]

$$f(\alpha_J \to \alpha_{J'}) = \Delta E(\alpha_J, \alpha_{J'})$$

$$\times \frac{1}{2J+1} \sum_{M_J M_{J'}} |\langle (\alpha, S, L, n\ell) S L J M_J | \sum_i \hat{e} \cdot \vec{r}_i | (\alpha, S, L, n'\ell') S' L' J' M_{J'} \rangle|^2 \qquad (14)$$

where $\Delta E(\alpha_J, \alpha_{J'})$ is the energy difference between the two levels, and other terms have been defined previously. Eq. (14) can be evaluated from (3) by letting in this equation the primed quantities to become unprimed, and the double primed quantities to become primed, and neglecting the phase factor:

$$f(\alpha_J \to \alpha_{J'}) = \frac{1}{3} \Delta E(\alpha_J, \alpha_{J'})(2L+1)(2L'+1)(2J'+1)$$

$$\times \begin{Bmatrix} L, & L & \ell \\ 1 & \ell' & L' \end{Bmatrix}^2 \begin{Bmatrix} S & J & L \\ 1 & L' & J' \end{Bmatrix}^2 |\langle n\ell \| P(1) \| n'\ell' \rangle|^2 \qquad (15)$$

When equivalent electrons are in a shell, the oscillator strength is obtained by multiplying the right hand side of (15) by the factor $n(\ell^n \alpha SL \prod \ell^{n-1}(\alpha_1 S_1 L_1)(SL)^2$, all notations being defined following eq. (5).

We now introduce the line strength $\mathcal{S}(\mathcal{L})$ and the multiplit strength $\mathcal{S}(\mathcal{M})$ by the following equations[16]:

$$\mathcal{S}(\mathcal{L}) = \frac{(2J+1)(2J'+1)}{2S+1} \begin{Bmatrix} S & J & L \\ 1 & L' & J' \end{Bmatrix}^2 \qquad (16)$$

$$\mathcal{S}(\mathcal{M}) = (2S+1)(2L+1)(2L'+1)\ell_>(4\ell_>^2-1)\begin{Bmatrix} L_1 & L & \ell \\ 1 & \ell' & L' \end{Bmatrix}^2 \tag{17}$$

When equivalent electrons are in a shell, the multiplit strength is obtained by multiplying the right hand side of (17) by the factor $n(\ell^n\alpha SL \,[\![\, \ell^{n-1}(\alpha_1 S_1 L_1)\ell SL)^2$.

The absolute line strength is now defined by[13]

$$S(J\to J') = \mathcal{S}(\mathcal{L})\,\mathcal{S}(\mathcal{M})\left[\ell_>(4\ell_>^2-1)\right]^{-1}\left|\langle n\ell\|P(1)\|n'\ell'\rangle\right|^2 \tag{18}$$

The line strength is normalized such that

$$\sum_{JJ'} \mathcal{S}(\mathcal{L}) = 1 \tag{19}$$

It then follows that the absolute multiplit strength is given by

$$S(L\to L') = \sum_{JJ'} S(J\to J') = \mathcal{S}(\mathcal{M})\left[\ell_>(4\ell_>^2-1)\right]^{-1}\left|\langle n\ell\|P(1)\|n'\ell'\rangle\right|^2 \tag{20}$$

Through Eqs. (15)-(18) the oscillator strength for transitions between two levels could be expressed in terms of the absolute line strength[20]

$$f(\alpha_J\to\alpha_{J'}) = \frac{1}{3}(2J+1)^{-1}\Delta E(\alpha_J,\alpha_{J'})\,S(J\to J') \tag{21}$$

An approximate expression could also be obtained for the oscillator strengths for transitions between two multiplets. The approximation consists in neglecting the energy differences of different levels within a multiplet. Using the definition

$$f(\alpha_L\to\alpha_{L'}) = (2S+1)^{-1}(2L+1)^{-1}\sum_{JJ'}(2J+1)\,f(\alpha_J\to\alpha_{J'}) \tag{22}$$

and Eqs. (20)-(22) we find that

$$f(\alpha_L\to\alpha_{L'}) \cong \frac{1}{3}(2S+1)^{-1}(2L+1)^{-1}\Delta E(\alpha_L,\alpha_{L'})\,S(L\to L') \tag{23}$$

where $\Delta E\ (\alpha_L, \alpha_L')$ is the average value of $\Delta E(\alpha_J, \alpha_{J'})$ with respect to J and J'.

If only one intermediate term is included in the sum in (A14), this equation can be written -

$$\sigma_0^{(2)} = \frac{8\pi^3 \gamma^2 E^2}{(E_i - E_m + E)^2} \cdot \frac{1}{2J+1} \left| \sum_{M_J M_{J''} M_{J'}} \langle \Gamma | P(10) | \Gamma'' \rangle \langle \Gamma'' | P(10) | \Gamma' \rangle \right|^2 \tag{24}$$

where we have averaged with respect to the initial, and summed with respect to the intermediate and final magnetic quantum numbers, and Γ, Γ' and Γ'' stand for $(\alpha_1 S_1 L_1 n\ell) SLJM_J$, $(\alpha_1 S_1 L_1 n'' \ell'') SL'' J'' M_J''$ and $(\alpha_1 S_1 L_1 n' \ell') SL' J' M_{J'}$, respectively.

Eq. (24) can be expressed in terms of the oscillator strengths by making use of (3) and (15):

$$\sigma_0^{(2)} \cong \frac{8\pi^3 \gamma^2 \zeta E^2}{(E_i - E_m + E)^2} \cdot \frac{2J''+1}{2J+1} \cdot \frac{f(\alpha_J \to \alpha_{J''})}{\Delta E(\alpha_J \to \alpha_{J''})} \cdot \frac{f(\alpha_{J''} \to \alpha_{J'})}{\Delta E(\alpha_{J''} \to \alpha_{J'})},$$

$$\zeta = 9 \left[\sum_{M_J} \begin{pmatrix} J & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ M_J & -M_J & 0 \end{pmatrix} \right]^2 \tag{25}$$

In the above ζ is a number of order unity. For J=J', ζ =1. Eq. (25) is the desired equation for calculation of the cross section.

Values of multiplet strengths have been tabulated by Goldberg[21,22]. It is interesting to note that the tables given by Goldberg are contained in the simple expression due basically to Racah given by (17). In the tables, however, values of the multiplet strengths are not listed for separate parents for the case of equivalent electrons in a shell, rather values corresponding to sum over the parents are given, while Eq. (17) gives value of the multiplet strength for individual parent. Also, tables by Goldberg give the square of

the transition amplitudes, while in the present calculation values of the transition amplitudes are necessary. The use of the Racah's formulas for multiphoton absorption cross section calculation then is a necessity.

III. RESULTS AND DISCUSSIONS

Formulas derived in the previous sections have been applied to the two-photon excitations in atomic nitrogen, oxygen, and chlorine. In using the explicit summation method, for low lying intermediate states use has been made of the single configuration numerical Hartree-Fock wave functions[23]. For high-lying levels we use hydrogenic wave functions with non-integer principal quantum numbers fixed by the quantum defect method. This is justified since for highly excited atomic states hydrogenic description of the states are valid.

The hydrogenic wave functions with non-integer principal quantum numbers used here is in the form of an asymptotic expansion discovered by Eddington and Suguira as reported by Bates and Damgaard.[20] This function, not being a hydrogenic eigenfunction, diverges at the origin. However, for exact radial wave functions the value of the integrand in the integral given by (4) vanishes at the origin, and for highly excited states has small values for distances from the origin of the order of the Bohr radius a_o. Then to circumvent the problem of divergence, we introduce a lower limit cutoff in the integral (4) equal to a_o. It can be shown numerically that the value of the integral is insensitive to the slight variation of this cutoff.

In evaluating the radial integrals, states are divided into two groups, according to whether the values of their wave functions are given through Hartree-Fock, or hydrogenic wave functions. It is tested that values of the integral does not change appreciably by switching some states at the boundary of the two groups from one group to the other.

We choose transitions which lead to strong emission lines, since fluorescence from these lines are being detected. The initial state as a rule is the ground state. The final state is chosen depending on the range of the laser frequencies and allowance of the selection rules. In this way only a few suitable transitions can be found for each atom.

For the case of atomic nitrogen we consider the two transitions $2p^3\ {}^4S^o_{3/2} \rightarrow 2p^2({}^3P)3p\ {}^4S^o_{3/2}$, and $2p^3\ {}^4S^o_{3/2} \rightarrow 2p^2({}^3P)3p\,{}^4D^o_{7/2}$. Values of J' in the second transition could be 1/2, 3/2, 5/2, 7/2. However, J' = 1/2 and 5/2 are forbidden by the selection rule (10). Also J' = 3/2 is forbidden by the approximate selection rule (12). Then we are left with J' = 7/2 only. The coefficient $C(\ell''L'')$ from (8) for the first transition are C(01) =-0.19245 and C(21) =-0.38490, and for the second transition are C(01) = 0.14903 and C(20) = 0.029805.

Table I gives values of cross sections for the two transitions. For each case 8 intermediate states have been employed, and contribution of each intermediate state to the total cross section is shown in the table. Addition of more intermediate states would change the cross section in the third significant figure. Expressed in cm^4, we find that for $S_{3/2} \rightarrow S_{3/2}$ transition the cross section is 2.74×10^{-35} cm^4, while for $S_{3/2} \rightarrow D_{7/2}$ transition the cross section is 3.97×10^{-36} cm^4, almost a factor of 7 smaller than the first transition. In all cases considered it seems that the cross section is largest when the initial and final orbital and total angular momenta are the same.

Using the method of the oscillator strength, cross sections for the two transitions by Eq. (23) are 5.2×10^{-36} and 6.9×10^{-36} cm^4.

For the case of atomic oxygen the transitions $2p^4\ {}^3P_2 \rightarrow 2p^3({}^4S^o)\ 3p\ {}^3P_{o,2}$ have been considered. Of the three values of J'=0, 1, 2, the value J'=1 is excluded through the selection rule (10). Using (8) the coefficients $C(\ell''L'')$

for J'=0 are C(00) =-0.036289 and C(22)=0.1283, and for J'=2 are C(00) =-0.0072578 and C(22)=0.2566.

Table II gives cross sectional values in oxygen for the final angular momenta J'=0 and 2. Similar to Table I, eight intermediate states and their contributions are included. Expressed in cm^4, the cross sections $\sigma_o(0)$, $\sigma_o(2)$ and σ_{oT} are given by 1.71×10^{-37}, 6.60×10^{-36}, and $6.77 \times 10^{-36} cm^4$, where σ_{oT} is the sum of the two cross sections. It is seen that the cross section for the transition in which the total angular momentum does not change is 39 times larger than when it changes by 2 units.

Pindzola[6] has calculated cross sections for the above transitions in atomic oxygen, using the inverse Green's function method of Dalgarno and Lewis.[3] Using the electric dipole form of the interacting potential he obtains a value of $7.62 \times 10^{-36} cm^4$ for σ_{oT}. Considering the many approximations used in the present paper, the agreement between the two independent methods, if not accidental, is striking, and is an indication of the reliability of the cross section.

These cross sections can also be calculated using the method of oscillator strength. Using the value of the oscillator strength[24] for the single intermediate state $3p^3(^4S^o)3s^3S^o$ and Eq. (25) we find for $\sigma_o(0)$, $\sigma_o(2)$, and σ_{oT} the values 1.88×10^{-37}, 2.35×10^{-36}, and $2.54 \times 10^{-36} cm^4$ respectively. Therefore the value of σ_{oT} by this method is by a factor of 2.7 smaller than the value of σ_{oT} obtained by the method of explicit summation.

The value of σ_{oT} using the method of oscillator strength given by McIlrath et al[18] for σ_{oT} is $7.13 \times 10^{-36} cm^4$ which is by a factor of 2.81 larger than σ_{oT} given here. The discrepancy is due to the neglect of some weighting factors in (25) by these authors.

In the case of atomic chlorine the transition considered is $3p^5\ {}^2P^o_{3/2} \rightarrow 3p^4({}^3P)4p\,{}^2P^o_{3/2}$. Using (8) the coefficients $C(\ell''L'')$ for the 3 intermediate series are $C(01)=-1/9$, $C(21)=-1/18$, and $C(22)=-1/6$. Table III lists 11 intermediate states and their contribution to the total cross section. In terms of cm^4 the total cross section is $1.89\times10^{-36}cm^4$.

IV. SUMMARY AND CONCLUSIONS

Using Racah's formulas an expression for two-photon absorption cross section for light and intermediate atoms in terms of integrals over radial wave functions is derived. An exact and an approximate selection rules, in addition to known selection rules, are found. The formulation is applied to selected transitions in atomic nitrogen, oxygen, and chlorine.

When oscillator strengths calculated using single configuration Hartree-Fock approximation are tested against more accurate tabulated values, on occasions they are different by factors as large as 2-3. This suggests that cross sections calculated here may also be different from their accurate values by these factors.

In a more accurate calculation in the future multiconfiguration Hartree-Fock wave functions should be employed, jK coupling scheme should be considered for the excited states, and continuum intermediate states should be included. In addition, length and velocity forms of the cross sections as given in Appendix I should be employed to test the accuracy of the wave functions employed.

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APPENDIX I: DEVIATION OF TWO PHOTON ABSORPTION CROSS SECTION

The transition probability for a particle to go from an initial state $|i\rangle$ to a final state $|f\rangle$ when the interaction potential is turned on from time t_o to time t is given by[27]

$$W(i \to f) = |\langle f|U(t,t_o)|i\rangle|^2 \tag{A1}$$

where $U(t, t_o)$ is the evolution operator. The transition amplitude in different orders of the interaction potential can be expanded in the following way[27]:

$$\langle f|U(t, t_o)|i\rangle = \sum_{n=1}^{\infty} \langle f|U^{(n)}(t, t_o)|i\rangle \tag{A2}$$

The two-photon absorption process corresponds to the second order amplitude given by[27]

$$\langle f|U^{(2)}(t,t_o)|i\rangle = -\hbar^{-2}\sum_m \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 \left[e^{-i\omega_f(t-t_1)} \times V_{fm}(t_1)\, e^{-i\omega_m(t_1-t_2)} V_{mi}(t_2)\, e^{-i\omega_i(t_2-t_o)}\right], \tag{A3}$$

where we have introduced $\omega_k = E_k/\hbar$, E_k being the eigenvalue of the eigenstate $|k\rangle$, and $V_{ij}(t)$ are the expectation values of the time dependent interaction potential V(t).

In empty space the vector potential of the radiation field is given by

$$\vec{A} = \vec{A}_o\left[\exp(i(\vec{k}\cdot\vec{r}-\omega t)] + \exp[-i(\vec{k}\cdot\vec{r}-\omega t)]\right.$$
$$\cong \vec{A}_o\left[\exp(-i\omega t) + \exp(i\omega t)\right] \tag{A4}$$

where $\vec{k}$ is the propagation vector, and ω is the frequency of the field. The approximate equality in (A4) results from the fact that in the visible range of the spectrum $\vec{k}\cdot\vec{r} \ll 1$.

The first term on the right hand side of (A4) corresponds to the absorption of photons from the field, and the second to the emission of photons into the field.

Since we are dealing with absorption only, the first term will be used in the calculation. The interaction potential in the length form is then given by

$$V(t) = -e\sum_i \vec{E}(t)\cdot\vec{r}_i = \frac{e}{c}\sum_i \frac{\partial \vec{A}}{\partial t}\cdot\vec{r}_i = V_0\, e^{-i\omega t},$$

$$V_0 = -ie\hbar\sum_i \vec{A}_0\cdot\vec{r}_i, \tag{A5}$$

where $\vec{r}_i$ is the position vector of the ith atomic electron. Substituting the potential given by (A5) in (A3) and making the plausible assumption that $t_0 \to \infty$ we find that

$$\langle f|U^{(2)}|i\rangle = -\hbar^2\sum_m e^{-i\omega_f t}\langle f|V_0|m\rangle\langle m|V_0|i\rangle$$

$$\times\int_{-\infty}^{t} dt_1\int_{-\infty}^{t_1} dt_2\, \exp\left[i(\omega_f-\omega)t_1+\epsilon t_1 - i\omega_m(t_1-t_2) - i(\omega_i+\omega)t_2+\epsilon t_2\right]$$

$$= \sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle \exp(2\epsilon t - i\omega_i t - 2i\omega t)}{\hbar^2(\omega_i-\omega_m+\omega+i\epsilon)(\omega_i-\omega_f+2\omega+2i\epsilon)}, \tag{A6}$$

where we have introduced the converging factor ε. At the end we let $\varepsilon\to 0$. The choice $t_0\to-\infty$ while convenient is not valid when the perturbative time is comparable to the periods of atomic orbitals (Of the order $10^{-17}/Z^2$ sec, where Z is the effective charge acting on the transient electron).

Let us assume that the first order transition is zero. Then by letting $2\varepsilon\to\varepsilon$ we obtain from (A1) and (A6)

$$W(i\to f) = \frac{1}{\hbar^4}\left|\sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle}{\omega_i-\omega_m+\omega-i\epsilon/2}\right|^2 \frac{e^{2\epsilon t}}{(\omega_i-\omega_f+2\omega)^2+\epsilon^2} \tag{A7}$$

Using the definition of the transition rate and by letting $\varepsilon \to 0$ we obtain

$$R = \frac{dw}{dt} = \frac{1}{\hbar^4} \left| \sum_m \frac{\langle f | V_0 | m \rangle \langle m | V_0 | i \rangle}{\omega_i - \omega_m + \omega + i\epsilon} \right|^2 \frac{2\epsilon}{(\omega_i - \omega_f + 2\omega)^2 + \epsilon^2} \tag{A8}$$

or,

$$R = \frac{2\pi}{\hbar^4} \left| \sum_m \frac{\langle f | V_0 | m \rangle \langle m | V_0 | i \rangle}{\omega_i - \omega_m + \omega + i\epsilon} \right|^2 \delta(\omega_i - \omega_f + 2\omega) . \tag{A9}$$

We now substitute the value of V_0 from (A5), but first we relate A_0 to the average field intensity $\bar{I}$ which is an observable quantity, while A_0 is not. From the definition of the Poynting vector we have that

$$\bar{I} = \frac{c}{4\pi} \overline{\vec{E} \times \vec{H}} = \frac{\omega^2}{2\pi c} A_0^2 \tag{A10}$$

Making use of (A5) and (A10) in (A9) leads to

$$R = \frac{8\pi^3 e^4 \bar{I}^2}{\hbar^4 c^2} \left| \sum_m \frac{\langle f | \sum_i \hat{e} \cdot \vec{r}_i | m \rangle \langle m | \sum_i \hat{e} \cdot \vec{r}_i | i \rangle}{\omega_i - \omega_m + \omega + i\epsilon} \right|^2 \delta(\omega_i - \omega_f + 2\omega) \tag{A11}$$

$\hat{e}$ being a unit vector in the direction of the polarization vector $\vec{A}_0$.

The transition rate is related to the two-photon absorption generalized cross section $\sigma^{(2)}$ by

$$R = \sigma^{(2)} (\bar{I}/\hbar\omega)^2 \tag{A12}$$

Combination of (A11) and (A12) leads to

$$\sigma^{(2)} = \sigma_0^{(2)} \delta(\omega_i - \omega_f + 2\omega) \tag{A13}$$

$$\sigma_o^{(2)} = 8\pi^3 \gamma^2 E^2 \left| \sum_m \frac{\langle f | \sum_i \hat{e}\cdot\vec{r}_i | m \rangle \langle m | \sum_i \hat{e}\cdot\vec{r}_i | i \rangle}{E_i - E_m + E} \right|^2 \tag{A14}$$

where γ is the fine structure constant and $E = \hbar\omega$ is the energy of the photons. We notice that $\sigma_o^{(2)}$ has the dimension of 4th power of length while $\sigma^{(2)}$ has the dimension of 4th power of length multiplied by time, and R has the dimension of inverse of time.

The converging factor ε introduced in (A6) has a physical meaning. It is proportional to the width of the final state. The δ-function in (A13) can then be shown to be approximately equal to $2\tau_f/\pi$, where τ_f is the lifetime of the final state.[26]

Equations (A13) and (A14) are identical to similar equations derived by fully quantum mechanical methods.[26]

Making use of the commutator relationship

$$\langle b | \hat{e}\cdot \mathrm{grad} | a \rangle = a_o^{-2} (E_{ab} / \mathrm{ryd}) \langle b | \hat{e}\cdot\vec{r} | a \rangle \tag{A15}$$

where $E_{ab} = E_a - E_b$ is the energy difference between states $|a\rangle$ and $|b\rangle$ in rydberg units, and a_o is the Bohr's radius, (A14) can be written in the alternative form

$$\sigma_o^{(2)} = 8\pi^3 (a_o^2 \mathrm{ryd})^4 \gamma^2 E^2 \left| \sum_m \frac{\langle f | \sum_i \hat{e}\cdot\nabla_i | m \rangle \langle m | \sum_i \hat{e}\cdot\nabla_i | i \rangle}{E_{im} E_{mf} (E_{im} + E)} \right|^2 \tag{A16}$$

Energies in (A16) are expressed in rydberg. While for exact atomic wave functions the two expressions (A14) and (A16) are equivalent, they differ for approximate wave functions. The degree of the difference is usually taken as a measure of the accuracy of the approximate wave functions used.

If we had to use the velocity form or Coulomb gauge form of the potential given by

$$V(t) = (e/mc)\,\vec{A}\cdot\vec{p} \quad , \tag{A17}$$

we would obtain the following value for $\sigma_o^{(2)}$:

$$\sigma_o^{(2)} = 8\pi^3 (a_o^2 r_y d)^4 \gamma^2 E^{-2} \left| \sum_m - \frac{\langle f | \sum_i \hat{e}\cdot\nabla_i | m\rangle \langle m | \sum_i \hat{e}\cdot\nabla_i | i\rangle}{E_i - E_m + E} \right|^2 \tag{A18}$$

Making use of the commutator relationship (A[illegible]), (A18) can be written

$$\sigma_o^{(2)} = 8\pi^3 \gamma^2 E^{-2} \left| \sum_m \frac{E_{fm} E_{mi} \langle f | \sum_i \hat{e}\cdot\vec{r}_i | m\rangle \langle m | \sum_i \hat{e}\cdot\vec{r}_i | i\rangle}{E_i - E_m + E} \right|^2 \tag{A19}$$

We therefore have four equivalent forms for the cross section. These forms can be used to test the accuracy of the wave functions used.

According to the principle of microreversibility if the total Hamiltonian remain invariant under the time reversal, the transition probability in the reverse direction is the same as the direct transition.

$$H(-t) = H(t) \Longrightarrow R(f,i) = R(i,f) \tag{A20}$$

It is seen from (A4) that the time dependent part of the Hamiltonian is invariant under the time reversal. The reverse transition corresponds to the emission into the field, and the creation operator $\vec{A}_o \exp(i\omega t)$ should be used. The cross section for the reverse process is obtained by letting in (A14) $i \rightleftarrows f$ and $\omega \to -\omega$. Then (A14) is transformed into

$$\sigma_o^{(2)} = 8\pi^3 \gamma^2 E^2 \left| \sum_m \frac{\langle f | \sum_i \hat{e}\cdot\vec{r}_i | m\rangle \langle m | \sum_i \hat{e}\cdot\vec{r}_i | i\rangle}{E_f - E_m - E} \right|^2 \tag{A21}$$

Eq. (A21) is however not an independent equation, since by the conservation of energy $E_f - E_m - E = E_i - E_m + E$, and (A21) is the same as (A14).

Making use of the closure relationship, an upper bound and an order of magnitude value can be found for $\sigma_0^{(2)}$. According to this relationship

$$\sum_m \langle f | \hat{e} \cdot \vec{r} | m \rangle \langle m | \hat{e} \cdot \vec{r} | i \rangle = \frac{1}{3} \langle f | r^2 | i \rangle \tag{A22A}$$

where $|j\rangle$ represents the total wave function of all electrons in the atom or the molecule. However, when one electron wave functions are used, as usually is the case, (22A) should be replaced by

$$\sum_m \langle f | \hat{e} \cdot \vec{r} | m \rangle \langle m | \hat{e} \cdot \vec{r} | i \rangle = \frac{1}{3} \langle f | r^2 | i \rangle - \sum_M \langle f | \hat{e} \cdot \vec{r} | M \rangle \langle M | \hat{e} \cdot \vec{r} | i \rangle , \tag{A22B}$$

where M stands for occopied atomic or molecular shells inaccessible to the transient electron. Eq. (A14) can then be written

$$\sigma_0^{(2)} \langle 2\pi (2\pi\gamma a_0^2)^2 \left[\frac{E}{(E_i - E_m + E)_{min}} \right]^2$$

$$\times \left| \frac{1}{3a_0^2} \langle f | r^2 | i \rangle - \sum_M \frac{1}{a_0^2} \langle f | \hat{e} \cdot \vec{r} | M \rangle \langle M | \hat{e} \cdot \vec{r} | i \rangle \right|^2 \tag{A23}$$

where in $(E_f - E_m - E)_{min}$, E_m corresponds to an intermediate eigenvalue which is closest to $1/2\ (E_i - E_f)$.

Since the energy ratio and terms inside the bars in (A23) are of the order unity, the two-photon absorption cross sections in atoms and molecules are expected to be of the order of $2\pi(2\pi\gamma a_0^2)^2 \approx 1.035 \times 10^{-35} cm^4$. For the three atoms N, O, and Cl considered here, indeed the calculated cross sections differ from the above number within a factor of 5. The energy denominator

in (A14) as a rule does not vanish, since E_m for any m can only accidentally fall halfway between E_i and E_f.

The above order of magnitude calculation can be generalized to N-photon absorption cross section calculation. Using the formula for this cross section[2] the order of magnitude expression will be given by

$$O(\sigma_o^{(N)}) \approx 2\pi(2\pi\gamma a_o^2)^N(\hbar/ryd)^{N-2}$$
$$\approx 2\pi(1.28\times10^{-18})^N(4.84\times10^{-17})^{N-2}\,cm^{2N}/sec^{N-2} \quad \text{(A24)}$$

Thus for the three and four photon absorption cross sections we get respectively $6.41\times10^{-70}cm^6$ sec and $3.97\times10^{-104}cm^8sec^2$ (Compare Table I of Ref. 2). On the other hand the single photoabsorption cross section is of the order of $4\pi^2\gamma a_o^2 = 8.04\times10^{-18}cm^2$.

Since the derivation in this section was based on perturbation theory, it is in order to find the validity of the theory in dealing with intensities of short pulsed laser beams. The validity criterion is that $eE_o\langle r\rangle_a \ll V_a$, where E_o is amplitude of the electric field of the laser beam, $\langle r\rangle_a$ is the average atomic radius, and V_a is the atomic potential. From (A5) and (A10) we find that $|E_o| = \sqrt{2\pi\bar{I}/c}$. We also assume that $\langle r\rangle_a$ is of the order of the Bohr radius a_o. If we then express the energy of the laser beam ε in mJ, its cross sectional area A in cm^2, and its pulse duration τ_L in n sec, the value of $|E_o|\langle r\rangle_a$ in volt will be given by

$$|E_o|\langle r\rangle_a(V) \cong 0.725\times10^{-4}\sqrt{\frac{\epsilon(mJ)}{A(cm^2)\,\tau_L(n\,sec)}} \quad \text{(A25)}$$

Since the atomic potential is of the order of electron-volt, for the perturbation theory to be valid we must have $|E_o|\langle r\rangle_a \ll 1$. As an example, for a typical case of ε = 1 mJ, A = $10^{-4}cm^2$, and τ_L = 10 n sec, we find the laser interacting potential to be 0.00229 eV, indicating the validity of the perturbation theory.

APPENDIX II: POPULATION DYNAMICS

A. Rate Equations. With the knowledge of cross sections for different processes, we can calculate population of different states at the end of a laser pulse. For simplicity we assume a three level atom consisting of the ground, excited, and ionized states. The processes that should be taken into account in the rate equations are the following: (a) Resonance two-photon absorption by the ground state, (b) Resonance two-photon emission by the excited state, (c) Spontaneous emission of the excited state, (d) Photo-ionization of the excited state, (e) Triple and higher multiphoton coherent ionization of the ground state, (f) Radiative recombination of electrons and ions which follows ionizations, and finally (g) Population and depopulation of atomic states through collisions with the ambient gas.

It will be shown in Section B that for laser duration of interest (e) can be neglected. Similarly, radiative recombination lifetimes are too long compared to the short-pulsed laser beams, and (f) can be neglected. In dealing with more complex atoms than those dealt with here a fast recombination process, namely dielectronic recombination, occurs which should be taken into account. In this case autoionizing processes should also be accounted for. Here we neglect these processes.

Finally it will be shown in Section C that for gas densities less than $10^{17}/cm^3$ corresponding to the atmospheric conditions above 30 Km the collision effects can be neglected.

Additional assumptions are that the two-photon excitation is the only mode of excitation of the ground state, and all electrons that cascade by the sponteneous emissions end up in the ground state, i.e., no metastable states exist.

We are then left with four processes (a) through (d). Let N_1, N_2, N_3 represent the instantaneous population of the ground, excited, and ionized states, and N_o the initial population of the ground state. Then $N_1+N_2+N_3 = N_o$. The rate equations for these states are given by

$$\begin{cases} dN_1/dt = -\alpha_{11}N_1 + \alpha_{12}N_2 \quad , \quad \alpha_{11} = \alpha_{21} = R_{2r} \\ dN_2/dt = \alpha_{21}N_1 - \alpha_{22}N_2 \quad , \quad \alpha_{12} = R_{2r} + \sum_m A(f,m) \\ dN_3/dt = \alpha_{32}N_2 , \quad \alpha_{22} = R_{2r} + R_1 + \sum_m A(f,m) , \quad \alpha_{32} = R_1 \end{cases} \tag{A26}$$

In these equations $R_{2r} = \sigma_o^{(2)} \tau_S I_N^2$ is the rate for two-photon absorption or emission. τ_S is the smaller of the inverse of the laser's band width or the atomic Doppler width[18], and I_N is the number intensity of the laser's beam in units of $cm^{-2}sec^{-1}$. $R_1 = \sigma_1 I_N$ is the rate of single photoionization of the upper state with σ_1 the photoionization cross section, and finally A(f,m) are the Einstein's transition probabilities for going from the upper state f to the intermediate states m, where $E_m<E_f$.

The initial conditions at t=0 are that $N_1=N_o$, $N_2=N_3=0$. Strictly speaking the values of N_2 and N_3 at t=0 are determined by the Boltzman factors. However, for conditions of interest in the laboratory and stratosphere the error due to the neglect of these factors is extremely small.

Subject to the above initial conditions (A26) can be solved by the standard methods leading to

$$\begin{cases} \dfrac{N_1}{N_o} = \dfrac{1}{A^+ - A^-}\left[-(A^- - \alpha_{11})e^{-A^+\tau} + (A^+ - \alpha_{11})e^{-A^-\tau}\right] \\ \dfrac{N_2}{N_o} = \dfrac{\alpha_{11}}{A^+ - A^-}\left[-e^{-A^+\tau} + e^{-A^-\tau}\right] \\ \dfrac{N_3}{N_o} = -\dfrac{\alpha_{11}R_1}{A^+ - A^-}\left[\dfrac{1}{A^+}\left(1 - e^{-A^+\tau}\right) - \dfrac{1}{A^-}\left(1 - e^{-A^-\tau}\right)\right] \\ A^{\pm} = \dfrac{1}{2}\left\{\alpha_{11} + \alpha_{22} \pm \left[(\alpha_{11} - \alpha_{22})^2 + 4\alpha_{12}\alpha_{21}\right]^{1/2}\right\} , \end{cases} \tag{A27}$$

τ being the duration of the laser's pulse. From the above it is easily verified that $N_1+N_2+N_3 = N_o$.

Since the validity of (A27) is based on the validity of the perturbation theory, τ or the duration of the laser's beam must be much larger than the orbital period of the running atomic electron (Cf. Appendix I).

The above equations are applied to find the state population of atomic oxygen due to interaction with a laser beam of energy 1 Joule, a radius of the cross sectional area at the position of interaction of 18 cm, and a variable pulse length.

The parameters needed to evaluate (A27) are $\sigma_o^{(2)}$, σ_1 and $\Sigma_m A(f,m)$. Values of $\sigma_o^{(2)}$ are given in Table II. Since σ_1 is the photoionization cross section of the excited state, the quantum defect method[25] employing hydrogenic wave functions can be used to find its values.

In calculating σ_1 we notice that initially the electron is in the state $2p^3(^4S^o)3p^3P$. The final states then should be $2p^3(^4S^o)\varepsilon s^3S^o$ and $2p^3(^4S^o)\varepsilon d^3D^o$, where ε is the energy of ejected electrons. Using tables of energy levels[24] we find by extrapolation that the quantum defects of εs and εd are approximately 1 and 0. Then the photoionization cross sections for these two states and their sum can be calculated and are given by $0.972\text{x}10^{-19}$, $0.119\text{x}10^{-19}$, and $0.109\text{x}10^{-18}\text{cm}^2$.

Using the values of $\sigma_o^{(2)}$ and σ_1 we find that $R_{2r} = 8.45\text{x}10^{-6}\tau_S/\tau^2$, and $R_1 = 3.16\text{x}10^{-4}/\tau$.

In calculating $\Sigma_m A(f,m)$, with good approximation we can replace this sum by the transition probability for the strong line $2p^33p^3P \rightarrow 2p^33s^3S$ with an oscillator strength of 0.898 (Ref. 24), leading to a transition probability of $8.42\text{x}10^7$/sec.

With R_{2r}, R_1 and $\Sigma_m A(f,m)$ so determined, (A27) can be evaluated for the cases $\tau_S = \tau$, and $\tau_S = \tau_D$, τ_D being the inverse of the Doppler width. Results are presented in Figures 1 and 2.

In Figure 1 the form $R_{2r}=\sigma_o^{(2)}\tau I_N^2$ has been used for the two-photon rate. As is seen both N_2/N_o and N_3/N_o have constant values for very short pulses up to $\tau=10^{-10}$ sec, then they fall off exponentially. In the regions that these ratios are constants, (A27) take a simple form. For $\tau<<10^{-7}$, it can be shown that $A^{\pm}\tau<<1$, and (A27) reduces to

$$\begin{cases} N_1/N_o \approx 1 - R_{2r}\tau\left[1-\frac{1}{2}(A^+ + A^- - R_1)\tau\right] \\ N_2/N_o \approx R_{2r}\tau\left[1-\frac{1}{2}(A^+ + A^-)\tau\right] \\ N_3/N_o \approx \frac{1}{2}R_{2r}R_1\tau^2 \end{cases} \tag{A28}$$

showing that N_2/N_o and N_3/N_o approach constant values for short pulses.

The expression for N_2/N_o given by (A28) is in full agreement with a similar expression given by McIlrath et al[18], since their expression is the limiting value of N_2/N_o given by (A27).

In Figure 2 the alternative form $R_{2r}=\sigma_o^{(2)}\tau_D N_N^2$ has been used. In this figure three distinct regions are noted. For $\tau<10^{-15}$ both ratios are constants. For $10^{-14}<\tau<10^{-9}$ the ratios fall as the inverse of τ, and for $\tau>10^{-7}$ the ratios decrease as $1/\tau^2$. These behaviors can be seen from (A27) as follows:

When $\tau_S=\tau_D$, $R_{2r}=1.07\times10^{-15}/\tau^2$, while R_1 and $\Sigma_m A(f,m)$ have the same values as before. The following cases follow:

(i) $\tau<10^{-15}$. Eq. (A27) shows that $A^+\tau>>1$ and $A^-\tau<<1$, leading to the following limiting forms:

$$N_1/N_o \approx 1/2,\quad N_2/N_o \approx 1/2,\quad N_3/N_o \approx \frac{1}{2}R_1\tau\left(1-1/2R_{2r}\tau\right) \tag{A29}$$

Then to first order the three ratios have constant values in agreement with Figure 2.

(ii) $10^{-14}<\tau<10^{-9}$. In this case $A^{\pm}\tau<<1$, leading to the following limiting forms:

$$N_1/N_0 \approx 1, \quad N_2/N_0 \approx R_{2r}\tau, \quad N_3/N_0 \approx \frac{1}{2} R_{2r} R_1 \tau^2 \tag{A30}$$

Then N_2/N_0 and N_3/N_0 fall as $1/\tau$ in agreement with Figure 2.

(iii) $\tau>10^{-7}$. In this case $\sum_m A(f,m)>>R_1>>R_{2r}$, leading to the following limiting forms:

$$N_1/N_0 \approx 1, \quad N_2/N_0 \approx R_{2r}/\sum_m A(f,m), \quad N_3/N_0 \approx R_{2r} R_1 \tau / \sum_m A(f,m) \tag{A31}$$

Then N_2/N_0 and N_3/N_0 fall as $1/\tau^2$ in agreement with Figure 2.

Case (ii) for N_2/N_0 is in agreement with the result of McIlrath et al.[18] Therefore their result is valid for $10^{-14}<\tau<10^{-9}$, which is the important range of τ in application.

The results for N_2/N_0 and N_3/N_0 given in Figures 1 and 2 are combined in Figures 3 and 4. It is seen that the ratios N_2/N_0 and N_3/N_0 have almost constant values for $\tau<1.266\times10^{-10}$ sec. Then they fall off rapidly. The constant values are 0.845×10^{-5} for N_2/N_0 and 1.335×10^{-9} for N_3/N_0.

B. Effect of Three-Photon Ionizations

The energy of the laser beam is sufficient to ionize the ground state through three-photon ionization. This process is different from the two-photon excitation of the ground state and the photoionization of the excited state in two respects. The former is a coherent, while the latter is a non-coherent process. In addition the former process depends on the population of the ground state, while the latter depends on population of both the ground and the excited states.

When the three-photon ionization of the ground state is included, the last equation in (A26) should read

$$dN_3/dt = R_1N_2 + R_3N_1 \tag{A32}$$

where R_3 is the rate of three-photon ionization. We substitute N_1 and N_2 from (A27) into (A32) and carry out an integration with respect to t. The following result follows:

$$\frac{N_3}{N_0} = \frac{1}{A^+ - A^-}\left\{-\alpha_{11}R_1\left[\frac{1}{A^+}\left(1-e^{-A^+\tau}\right) - \frac{1}{A^-}\left(1-e^{-A^-\tau}\right)\right] + R_3\left[\frac{\alpha_{11}-A^-}{A^+}\left(1-e^{-A^+\tau}\right) - \frac{\alpha_{11}-A^+}{A^-}\left(1-e^{-A^-\tau}\right)\right]\right\} \tag{A33}$$

For short pulses, similar to the derivation of (A28), $A^{\pm}\tau<<1$, and (A33) reduces to

$$N_3/N_0 \approx \frac{1}{2}\alpha_{11}R_1\tau^2 + R_3\tau \tag{A34}$$

Realizing that $R_3=\sigma_0^{(3)}\tau I_N^3$, the ratio of the second term to the first on the right-hand side of (A34) is given by $2\sigma_0^{(3)}/\sigma_0^{(2)}\sigma_1\tau$. Making use of (A24) and the fact that σ_1 is of the order of $4\pi\gamma a_0^2 \approx 2.56\times10^{-18}\text{cm}^2$, the value of this ratio is given by $4.84\times10^{-17}/\tau$.

We therefore conclude that for $\tau>>10^{-17}$ sec, the three-photon ionization can be neglected. Similarly, higher order processes can be neglected.

C. Collision Time. Collisions of molecules under study with the ambient gas have dual effects. They broaden the absorption and emission lines, and have quenching effects on the excited states.

To obtain a rough estimate of the collision time we use the classical picture that molecules are made up of hard spheres. Then the collision rate is given by[28]

$$\Theta = \sqrt{2}\,\pi n_2 (r_1 + r_2)^2 \left(\bar{v}_1^2 + \bar{v}_2^2\right)^{1/2} \tag{A35}$$

where r_1 and $\bar{v}_1$ are the radius and average velocity of the molecule under study, and n_2, r_2, and $\bar{v}_2$ are the density, radius and the average velocity of the ambient gas.

We use (A35) to calculate the collision rate of the excited state $2p^3(^4S^o)3p^3P$ of oxygen with the ambient gas. The average value of the radius of the excited state of oxygen according to the Hartree-Fock calculation is given by 3.67×10^{-8}cm. For simplicity we assume that the ambient gas is made up of 80 percent of N_2 and 20 percent of O_2. Based on the hard sphere model and the viscosity data, and neglecting a slow varying temperature factor, the radii of N_2 and O_2 are given respectively by 1.88×10^{-8}cm and 1.81×10^{-8}cm (Ref. 28). Using (A35), the rate coefficient k, and the collision time τ_c are given by

$$\begin{cases} k = \Theta/n_2 \approx 0.437 \times 10^{-10} \sqrt{T} \\ \tau_c = 1/\Theta \approx 2.29 \times 10^{10}/n_2\sqrt{T} \end{cases} \tag{A36}$$

Using the atmospheric data for densities and temperatures[29], (A36) have been evaluated. Results for τ_c as functions of altitude are given in Table IV and Figure 5. It is seen that in the range of 20-120 Km the collision time is larger than the Doppler time $\tau_D \approx 1.266 \times 10^{-10}$sec. However, for altitudes less than 30 Km, the collision time becomes comparable to the average lifetime of the excited states. For these altitudes the rate equations in Section A should be modified.

D. Opacity Calculation

It is of interest to estimate the absorption of the probing laser beam before it reaches its target. The main absorbing processes are the resonant two photon absorption by atomic oxygen, and the single photo-absorption by O_2 and O_3. The effect of these three processes will be calculated below.

The intensity at any height h is given by

$$I_h = I_o e^{-\Lambda} \tag{A37}$$

where I_o is the initial intensity and Λ is the optical depth. For single photo-absorption Λ is given by

$$\Lambda = \int_0^h \left[\sum_i n_i \sigma_i \right] dx \tag{A38}$$

where n_i are the densities of different constituents in the atmosphere and σ_i are the corresponding photo-absorption cross sections.

We consider laser radiation of wavelength 2256Å. The single photo-absorption cross sections for O_2 and O_3 are given by[30]

$$\sigma(O_2) = 4\text{x}10^{-24}\text{cm}^2, \ \sigma(O_3) = 2.75\text{x}10^{-18}\text{cm}^2$$

Using the density profile for O_2 and O_3 (Ref. 29) and the above cross sections the ratio I_h/I_o can be calculated. This ratio is plotted versus the altitude in Figure 6. It is seen that below 50 Km the laser beam in substantially absorbed by the ozone.

In calculating the two photon absorption by O, it should be kept in mind that part of the radiation absorbed are given back to the field through the two-photon stimulated emission. Stimulated emission should also be taken into account for single photo-absorption, but due to the weakness of the intensity the effect can be neglected. It can then be shown that

$$\Lambda = 2\int_0^h \frac{R_{2r}(1-2P)n}{I_N} dx \approx 2\sigma_o^{(2)} \tau_s I_N \int_0^h n \, dx \tag{A39}$$

where $P = N_2/N_o$ is a small number (Cf. Fig. 3), and has been neglected. n is the density of atomic oxygen.

Using values for column density of atomic oxygen[29], the ratio I_h/I_o for absorption of atomic oxygen is plotted in Figure 6. It is seen that

in the range 120-20 Km this absorption is less than 2 percent and is negligible compared to absorption by O_3 and O_2.

In Table IV distances in horizontal directions equivalent to unit optical depth for various altitudes due to absorption of λ=2256Å radiation by ozone are given.

References

1. E. D. Hinkley, Laser Monitoring of the Atmosphere (Springer-Verlag, New York, 1976).
2. For a review see P. Lambropoulos, Advances in Atomic and Molecular Physics, 12, (Academic, New York, 1976).
3. A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A233, 70 (1956).
4. E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967).
5. T. N. Chang and R. T. Poe, Phys. Rev. A 16, 606 (1977).
6. M. S. Pindzola, Phys. Rev. A 17, 1021 (1978).
7. D. H. Kobe, Phys. Rev. Lett. 40, 538 (1978).
8. W. E. Lamb, Jr., Phys. Rev. 85, 259 (1952).
9. F. Bassani, J. J. Forney, and A. Quatropani, Phys. Rev. Lett. 39, 1970 (1977).
10. G. Grynberg, and E. Giacobino, J. Phys. B: Atom. Molec. Phys. 12, L93 (1979).
11. G. Racah, Phys. Rev. 61, 537 (1942).
12. W. Heitler, The Quantum Theory of Radiation (Clarendon Press, Oxford 1970), Ch. V.
13. E. U. Condon, and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1951).
14. G. Racah, Phys. Rev. 62, 438 (1942), Eq. (44).
15. G. Racah, ibid. 63, 367 (1943), Eq. (27).
16. F. Rohrlich, Ap. J. 129, 441 (1959).
17. A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton University Press, Princeton, 1960).
18. T. J. McIlrath, R. D. Hudson, A. Aikin, and T. D. Wilkerson, Applied Optics 18, 316 (1979).

19. H. A. Bethe and E. E. Salpeter, Quantum Mechanics of one-and two-electron atoms (Academic Press Inc., New York, 1957).

20. D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. A242, 101 (1949).

21. L. Goldberg, Ap. J. 82, 1 (1935).

22. L. Goldberg, ibid 84, 11 (1936).

23. C. Froese Fischer, Computer Phys. Commun. 4, 107 (1972).

24. W. L. Wiese, M. W. Smith, and B. M. Glennon, Atomic Transition Probabilities U.S. Government Printing Office, Washington, DC, 1966).

25. A. Burgess and M. J. Seaton, M.N. 120, 121 (1960).

26. R. Loudon, The Quantum Theory of Light (Clarendon Press, Oxford, 1973).

27. A. Messiah, Quantum Mechanics II (North-Holland Publishing Co., Amsterdam, 1966).

28. E. H. Kennard, Kinetic Theory of Gases (MdGraw-Hill Book Co., Inc., New York, 1938).

29. U.S. Standard Atmosphere, 1976, NOAA, NASA, USAF (U.S. Government Printing Office, Washington, DC 20402, 1976)

30. R. D. Hudson, Can. J. Chem. 52, 1465 (1974).

Table I. Two-photon excitation in atomic nitrogen for the transitions $2p^3\ {}^4S^o_{3/2} \rightarrow 2p^2\ ({}^3P)3p\,{}^4S^o_{3/2}$ and $2p^3\ {}^4S^o_{3/2} \rightarrow 2p^2({}^3P)3p\,{}^4D^o_{7/2}$. For both cases the allowed intermediate states are $2p^2({}^3P)n''s\,{}^4P$ and $2p^2({}^3P)n''d\,{}^4P$, $n'' = 3,4,5, \ldots$, and the continuum. Here and in the following tables n'' is truncated at 6. $\sigma_o(S)$ and $\sigma_o(D)$ are cross sections in units of a_o^4 due to the first and second transitions. Cross tions under $n'' = 3$, $l'' = 0$ are due to the intermediate state $n'' = 3$, $l'' = 0$; those under $n'' = 3$, $l'' = 2$ are due to the states $n'' = 3$, $l'' = 0,2$, etc. The same arrangement holds for other tables. The total cross sections in cm^4 are $\sigma_o(S) = 2.74\times10^{-35}$ and $\sigma_o(D) = 3.97\times10^{-36}$. The required laser wave lengths for the two transitions are 2067.15Å and 2107.86Å, respectively.

n''	3	3	4	4	5	5	6	6
l''	0	2	0	2	0	2	0	6
$\sigma_o(S)$	1.27-2	3.99-2	3.16-2	3.50-2	3.39-2	3.49-2	3.45-2	3.49-2
$\sigma_o(D)$	6.90-3	7.99-3	5.43-3	5.54-3	5.22-3	5.19-3	5.08-3	5.07-3

Table II. Two-photon excitation in atomic oxygen for the transition $2p^4\ ^3P_2 \rightarrow 2p^3(^4S^o)3p\,^3P_{o,2}$. The allowed intermediate states are $2p^3(^4S^o)\ n''s\ ^3S_1{}^o$ and $2p^3(^4S^o)\ n''d^3D_{1,2,3,}$. In the table $\sigma_o(0)$ and $\sigma_o(2)$ are cross sections in units of $a_o{}^4$ for the final states $J' = 0$ and 2. In units of cm^4 the total cross sections for $J'=0$ and 2 are 1.71×10^{-37} and 6.60×10^{-36}, and the required laser wave lengths for their excitation are 2256.546Å and 2256.550Å respectively. The transition corresponding to $J'=1$ is not allowed.

n''	3	3	4	4	5	5	6	6
l''	0	2	0	2	0	2	0	2
$\sigma_o(0)$	3.23-4	3.63-4	2.33-4	2.36-4	2.22-4	2.24-4	2.18-4	2.18-4
$\sigma_o(2)$	4.04-3	1.01-2	7.63-3	8.45-3	8.13-3	8.40-3	8.29-3	8.41-3

Table III. Two-photon excitation for atomic chlorine for the transition $3p^5\ {}^2P^o_{3/2} \rightarrow 3p^4({}^3P)4p\,{}^2P^o_{3/2}$. The allowed intermediate states are $2p^4({}^3P)n''s\,{}^2P$, $2p^4({}^3P)n''d\,{}^2p$, and $2p^4({}^3P)n''d\,{}^2D$. σ_o is the cross section in units of a_o^4. The total cross section in cm^4 is 1.89×10^{-36}. The required laser wave length for this transition is 2340.878Å.

n''	4	5	6	3	4	5	6	3	4	5	6
l''	0	0	0	2	2	2	2	2	2	2	2
L''	1	1	1	1	1	1	1	2	2	2	2
σ_o	1.59-3	9.14-4	8.48-4	2.06-3	1.92-3	1.86-3	1.82-3	2.39-3	2.41-3	2.41-3	2.41-3

TABLE IV. Temperature, column densities for O, O_2, and O_3, the total column density, the collision time τ_c, and distances equivalent to unit optical depth for absorption of λ=2256Å radiation by ozone, X_o, as functions of the altitude.

		N(cm^{-2})					
h(Km)	T(°K)	O	O_2	O_3	Total	τ_c(sec)	X_o(Km)
120	360	1.68+17	3.92+16	1.18+8	6.01+17		
115	300	2.25+17	7.26+16	4.93+8	1.23+18	1.06-3	4.85+9
110	240	3.21+17	1.56+17	2.06+9	2.50+18	5.79-4	1.16+9
105	209	4.64+17	3.90+17	8.58+9	5.11+18	3.03-4	2.79+8
100	195	6.45+17	1.06+18	3.58+10	1.04+19	1.55-4	6.69+7
95	188	8.73+17	2.91+18	1.49+11	2.12+19	7.76-5	1.60+7
90	187	1.04+18	7.72+18	6.23+11	4.32+19	3.79-5	3.84+6
85	189	1.12+18	1.96+19	2.60+12	9.35+19	1.66-5	9.20+5
80	199	1.15+18	4.72+19	1.09+13	2.25+20	6.17-6	2.20+5
75	208	1.16+18	1.08+20	4.52+13	5.14+20	2.74-6	5.29+4
70	220	1.17+18	2.36+20	1.89+14	1.13+21	1.26-6	1.27+4
65	233	1.17+18	4.94+20	7.96+14	2.36+21	6.09-7	2.99+3
60	247	1.18+18	9.92+20	2.97+15	4.73+21	3.07-7	8.37+2
55	261	1.18+18	1.92+21	9.29+15	9.16+21	1.60-7	2.88+2
50	271	1.18+18	3.61+21	2.86+16	1.72+22	8.64-8	9.41+1
45	264	1.19+18	6.76+21	8.94+16	3.22+22	4.69-8	2.99+1
40	250	1.19+18	1.30+22	2.74+17	6.20+22	2.44-8	9.87+1
35	237	1.19+18	2.60+22	7.41+17	1.24+23	1.20-8	3.88
30	227	1.19+18	5.38+22	1.68+18	2.57+23	5.72-9	1.94
25	222	1.19+18	1.15+23	3.34+18	5.46+23	2.66-9	1.10
20	217	1.19+18	2.48+23	5.61+18	1.18+23	1.22-9	8.00-1

FIGURE CAPTIONS

Figure 1. Fraction of atomic oxygen in the excited $2p^3(^4S^o)3p^3P$ and ionized states, N_2/N_o and N_3/N_o, as functions of the laser pulse duration τ using the relationship $R_{2r} = \sigma_o^{(2)}\tau I_N^2$. The laser pulse has the characteristic $\varepsilon/A=9.82$ joule/m^2, where ε is the laser's energy, and A is its cross sectional area. The calculated values are valid for $\tau<\tau_D$ shown by the solid curves. τ_D is the inverse of the Doppler broadening ν_D and is taken to be 1.27×10^{-10}sec, corresponding to 300°K. The position of τ_D is shown by the vertical solid line.

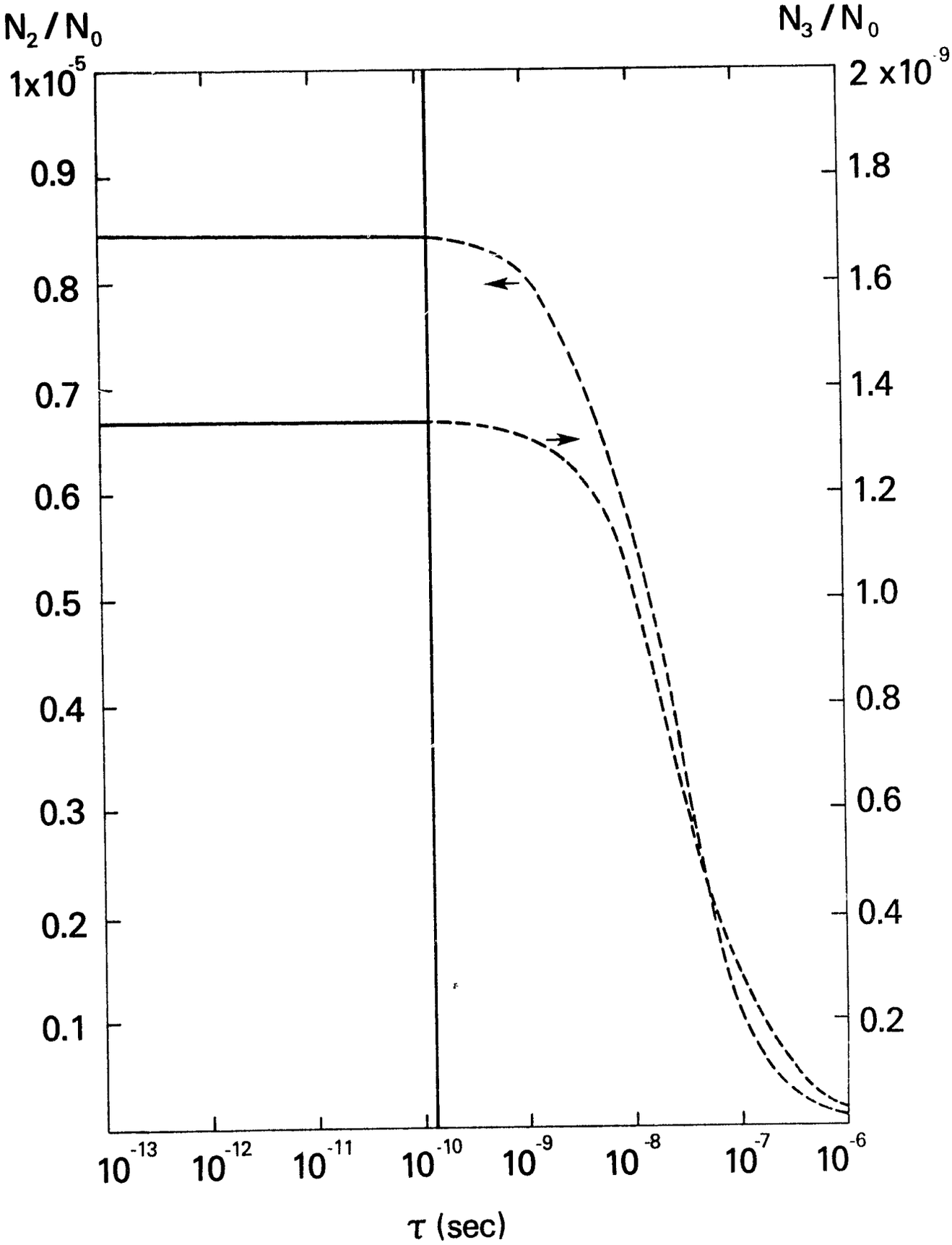
Figure 2. Similar to Figure 1, but for $R_{2r} = \sigma_o^{(2)}\tau_D I_N^2$. The calculated values are valid for $\tau>\tau_D$.

Figure 3. Combination of Figures 1 and 2 for N_2/N_o values. N_2/N_o is also the fraction of atoms at the end of each pulse that undergo spontaneous emission.

Figure 4. Combination of Figures 1 and 2 for N_3/N_o values. N_3/N_o is also the fraction of atoms that are ionized.

Figure 5. Collision time of the excited state $(3p^3P)$ of oxygen with the atmospheric gas as functions of altitude using gas kinetic cross sections.

Figure 6. Atmospheric absorption for λ=2256Å radiation due to O_3, O_2, and O as functions of the altitude for rays that propagate vertically downward. I_o and I_h are intensities at 120 and at the height h, respectively. Absorption by O is due to two-photon processes.


N2 / N0
N3 / N0
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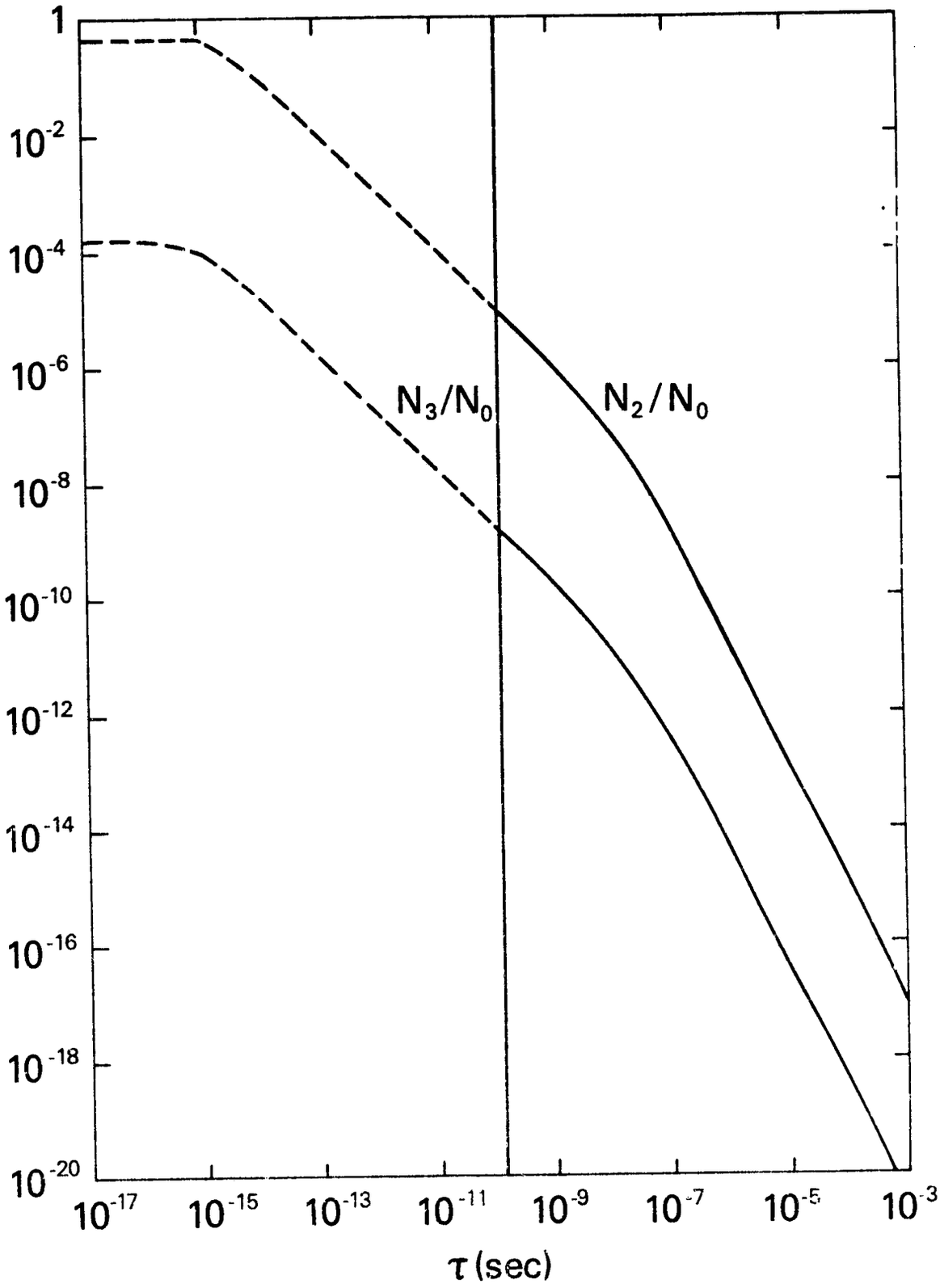
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
2 x10-9
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
10-13
10-12
10-11
10-10
10-9
10-8
10-7
10-6
τ (sec)

Figure 1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10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
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10^{-20}
N_3/N_0
N_2/N_0
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10^{-11}
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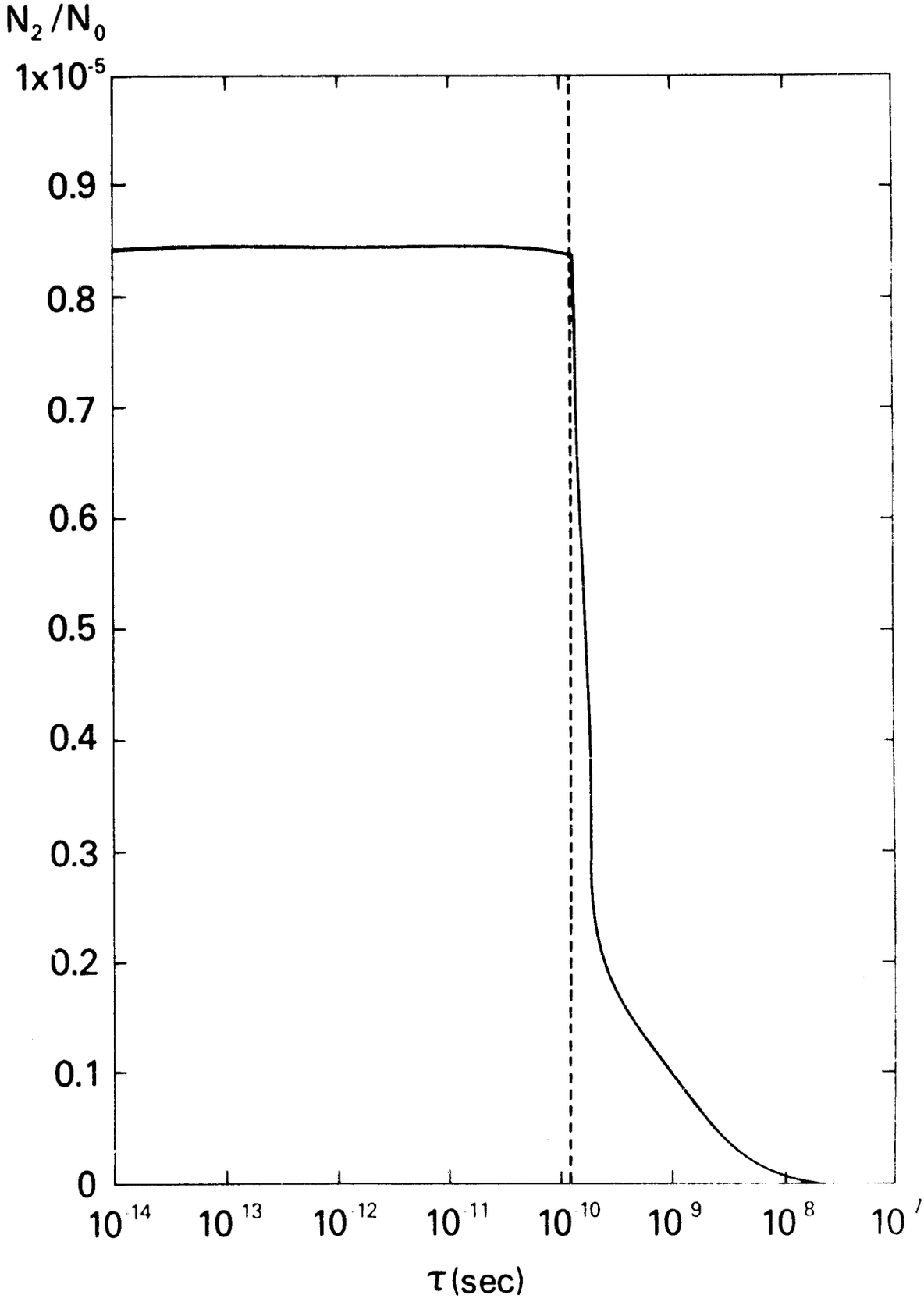
10^{-7}
10^{-5}
10^{-3}
τ (sec)

Figure 2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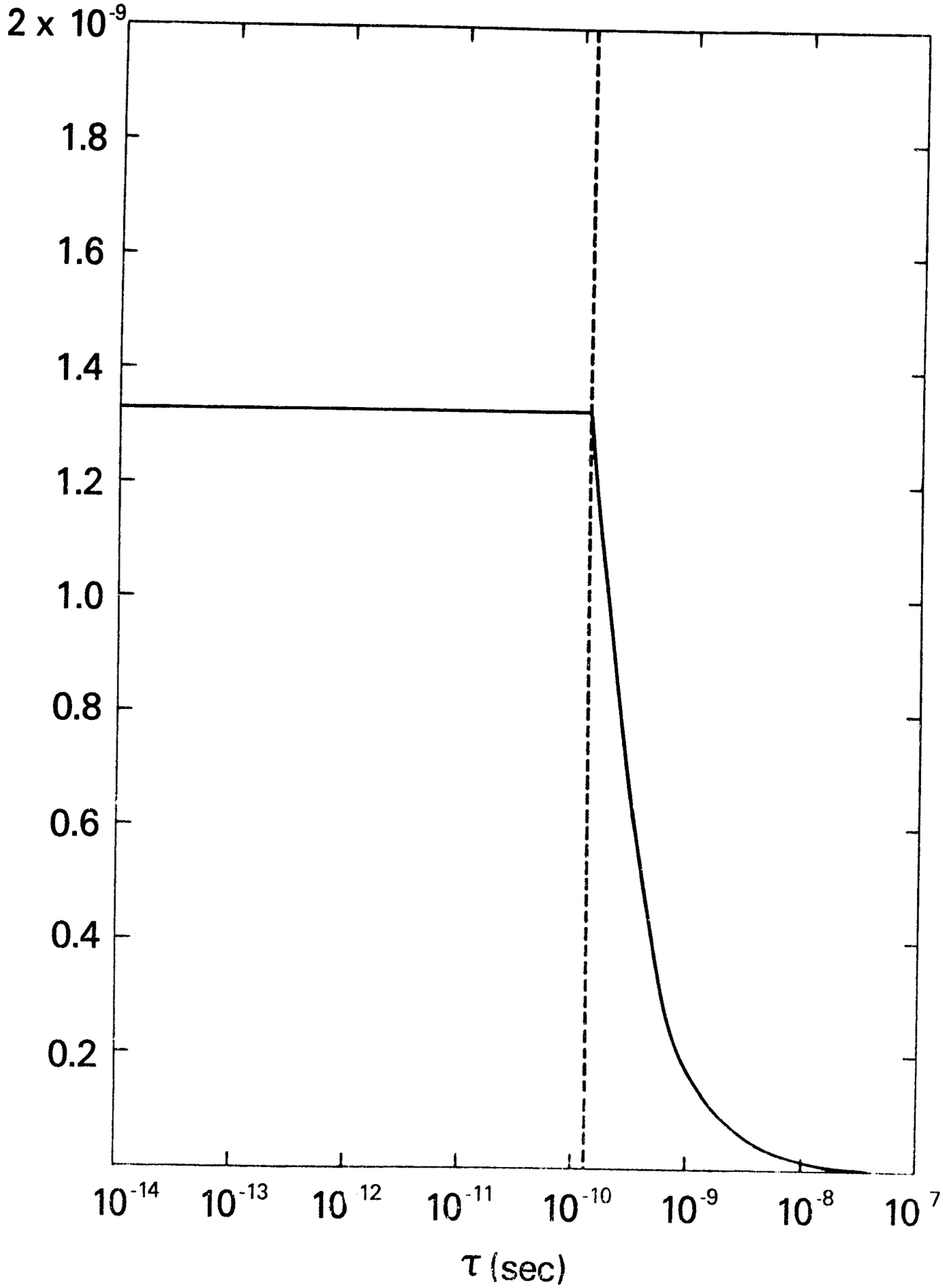
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10 -14
10 -13
10 -12
10 -11
10 -10
10 -9
10 -8
10 -7
τ (sec)

Figure 3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1.6
1.4
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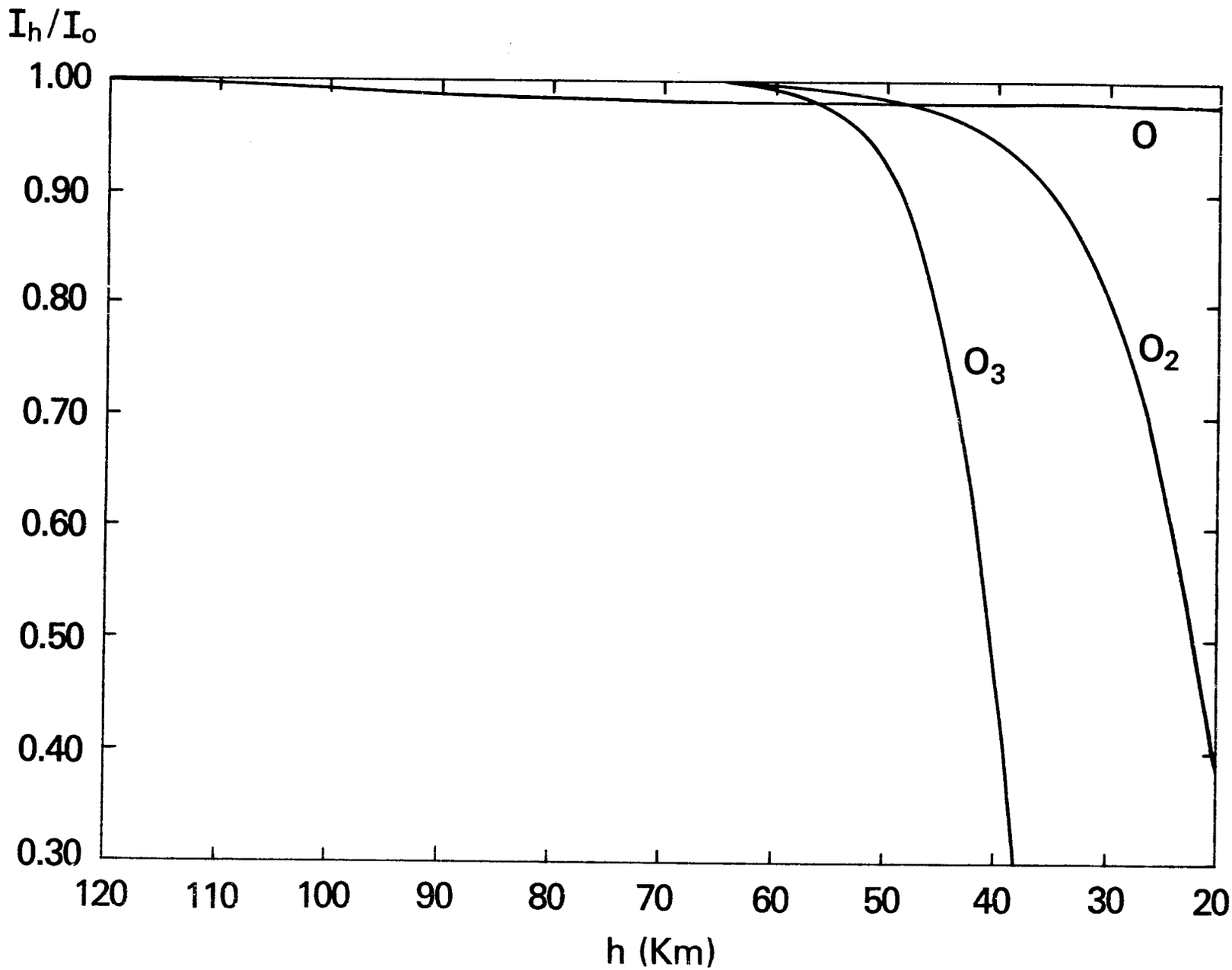
0.8
0.6
0.4
0.2
10-14
10-13
10-12
10-11
10-10
10-9
10-8
10-7
τ (sec)

Figure 4


I_h/I_o
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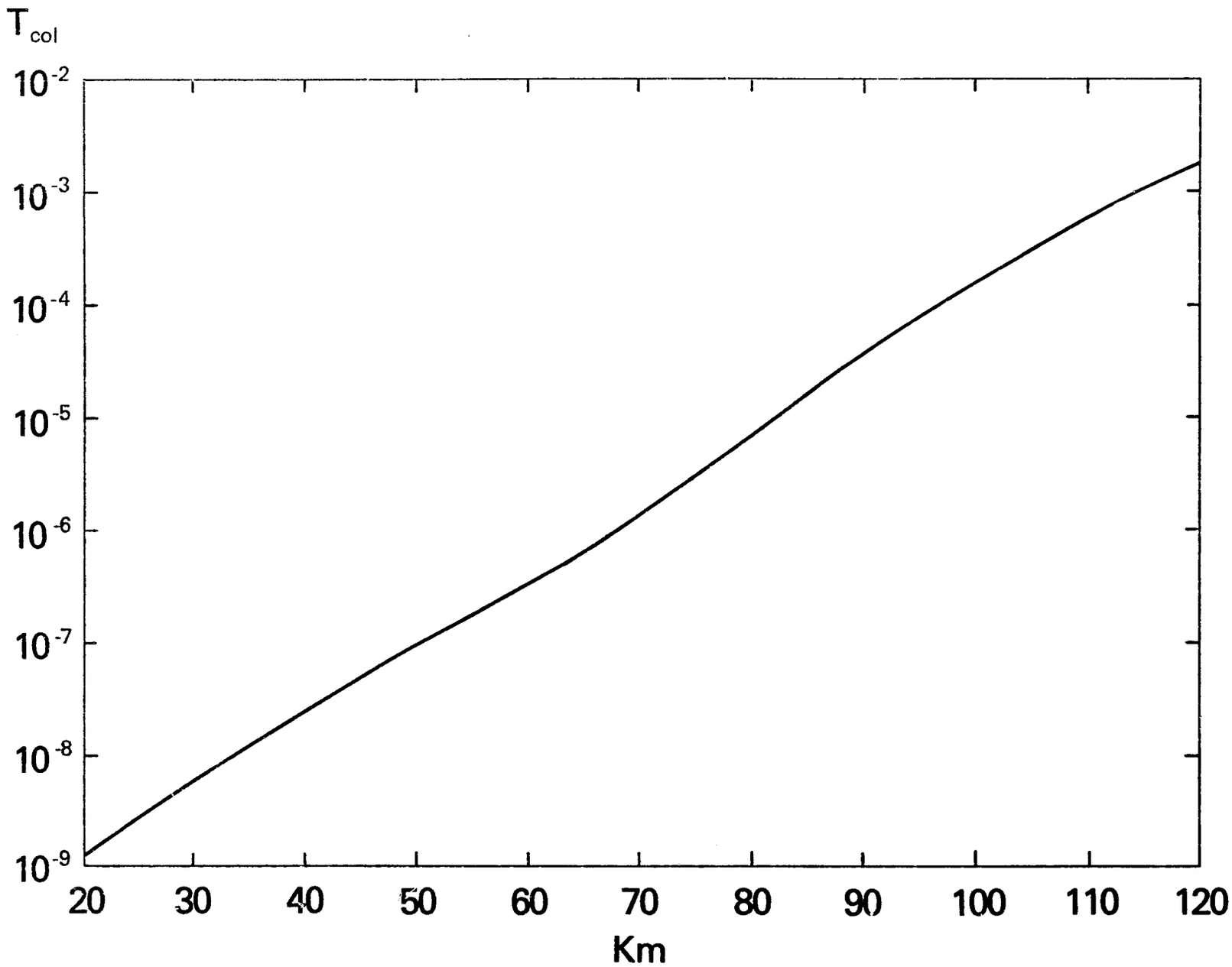
0.90
0.80
0.70
0.60
0.50
0.40
0.30
120
110
100
90
80
70
60
50
40
30
20
h (Km)
O
O_2
O_3

Figure 5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10^{-3}
10^{-4}
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10^{-6}
10^{-7}
10^{-8}
10^{-9}
20
30
40
50
60
70
80
90
100
110
120
Km

Figure 6

BIBLIOGRAPHIC DATA SHEET

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16. Abstract

Using the method of explicit summation over the intermediate states and LS coupling an expression for two-photon absorption cross section in light and intermediate atoms in terms of integrals over radial wave functions is derived. Two selection rules, one exact and one approximate, are derived. In evaluating the radial integrals, for low-lying levels, the Hartree-Fock wave functions, and for high-lying levels hydrogenic wave functions obtained by the quantum defect method have been used. A relationship between the cross section and the oscillator strengths is derived. Cross sections due to selected transitions in nitrogen, oxygen, and chlorine are given. The expression for the cross section should find usefulness in calculating the two-photon absorption in light and intermediate atoms.

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