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Theoretical calculation of two-photon absorption cross sections in atomic oxygen

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Two-photon absorption cross sections for transitions from the O(^3P) ground electronic state to the $3p\ ^3P$, $4p\ ^3P$, and the autoionizing O$^+$(^2D)$3p'$ and O$^+$(^2P)$3p''$ states have been calculated by explicit evaluation of the perturbation-theory summation using matrix elements calculated from configuration-interaction wave functions and sum rules to correct for truncation. The role of different contributions in the summation has been analyzed. For the $3p\ ^3P$ state, a cross section of $\sum_{J'}\sigma_0^{(2)}(J' \leftarrow J)$ of $(1.319\pm0.2)\times10^{-35}$ cm^4 has been obtained, which is in excellent agreement with the experimental value for the quantity $\sum_{J'}\sigma_0^{(2)}(J'\leftarrow 2)G^{(2)}=(2.66\pm0.80)\times10^{-35}$ cm^4, given in the companion paper, if the photon statistical factor, $G^{(2)}$, is evaluated in the chaotic field limit ($G^{(2)}=2$).

I. INTRODUCTION

While multiphoton ionization is a powerful and sensitive technique for the detection of atoms and molecules, its quantitative application requires knowledge of absolute cross sections. A recent set of experiments has been carried out by Bamford, Jusinski, and Bischel[1] to obtain absolute cross sections for the two-photon resonant, three-photon ionization of atomic oxygen. Rates for both two-photon absorption and excited-state photoionization have been obtained for the $3p\ ^3P \leftarrow {}^3P$ transition. However, these experiments pose significant challenges, requiring determination of absolute ground-state and excited-state number densities and accurate spatial and temporal characterization of the laser pulse. Thus, it would be highly desirable to compare experimental and theoretical determinations of absolute cross sections.

Two perturbation-theory calculations of two-photon excitation of the O($3p\ ^3P$) state have been reported by Omidvar[2] and Pindzola.[3] Omidvar[2] used the method of explicit summation over intermediate states while Pindzola[3] solved the equivalent inhomogeneous differential equation. While the results are in reasonable agreement with each other, both authors invoked the frozen-core approximation and used Hartree-Fock (or for the high-lying levels quantum-defect) wave functions.

Therefore, we have performed *ab initio* calculations of two-photon absorption for the $3p\ ^3P \leftarrow {}^3P$ transition in atomic oxygen for comparison with the recent experimental results.[1] In this work, the perturbation-theory matrix elements have been obtained by extensive configuration-interaction calculations and no coupling restrictions have been imposed. Cross sections for transitions to the $4p\ ^3P$ as well as to the autoionizing states, O$^+$(^2D)$3p'$ and O$^+$(^2P)$3p''$, have also been obtained. In Sec. I the formulas that have been evaluated and the off-diagonal sum rules described by Huo and Jaffe[4] that have been used to correct for truncation are presented. The configuration-interaction calculations are briefly described and the results are presented and evaluated in the following sections.

II. THEORY

There seems to be no question that the perturbation-theory formulation of multiphoton absorption applies up to quite strong photon intensities.[5] Since the experiments of Bamford *et al.*,[1] with which we will compare results, deliberately are conducted far from the saturation region, perturbation theory is clearly applicable. Derivations of the perturbation-theory expressions have been clearly given elsewhere.[3,5,6] In this section, we briefly set out the form evaluated in this work.

The rate for two-photon absorption W in sec^{-1} may be written in terms of a two-photon rate coefficient $\hat{\sigma}^{(2)}$, in cm^4 sec, and the square of the photon flux as

$$W=\hat{\sigma}^{(2)}(I/\hbar\omega)^2 , \tag{1}$$

where I is the laser intensity in W/cm^2. This cross section may be conveniently expressed as the product of a lineshape-independent cross section $\sigma_0^{(2)}$ in cm^4, which depends only on the properties of the absorbing species, the line-shape function $g(\omega)$ expressed in sec, and a photon statistical factor $G^{(2)}$, as

$$\hat{\sigma}^{(2)}=\sigma_0^{(2)}g(\omega)G^{(2)} . \tag{2}$$

The line-shape function and photon statistical factor, which accounts for photon coherence effects in a multimode laser, are discussed further in Sec. IV. Experimental results for two-photon absorption are often given in terms of the quantity α in cm^4/W which is related as

$$\alpha=\hat{\sigma}^{(2)}/\hbar\omega . \tag{3}$$

The fundamental quantity $\sigma_0^{(2)}$ is obtained from perturbation theory by the expression[5,6]

$$\sigma_0^{(2)}=(2\pi)^3\left[\frac{e^2}{\hbar c}\right]^2(\hbar\omega)^2P^2 , \tag{4}$$

where

$$P=\sum_k \frac{\langle f\,|\,r^\lambda\,|\,k\rangle\langle k\,|\,r^\lambda\,|\,g\rangle}{E_g-E_k+\hbar\omega}\ , \tag{5}$$

ω is the photon energy, g denotes the initial state, f denotes the final state, E_g and E_k denote the energies of the initial and intermediate states, respectively, $r^\lambda=\mathbf{r}\cdot\boldsymbol{\epsilon}_\lambda$, and $\boldsymbol{\epsilon}_\lambda$ is the laser polarization. The evaluation of the quantity P can be accomplished either by explicitly carrying out the, in principle infinite, summation in Eq. (5) over a suitably large number of intermediate states, e.g., as described in Ref. 2, or by using a variational or variation-perturbation method, which requires, instead, the solution of a suitable inhomogeneous differential equation (e.g., Ref. 3). In either case, the quality of the result depends on the quality of the wave functions used in the calculation, i.e, on the completeness of the atomic basis set and the extent of electron correlation included.

Truncation of the perturbation theory sum is a major source of error in these calculations. However, we have used two off-diagonal sum rules introduced by Huo and Jaffe,[4]

$$S_{fg}(0)=\sum_k (2E_k-E_g-E_f)\langle f\,|\,r^\lambda\,|\,k\rangle\langle k\,|\,r^\lambda\,|\,g\rangle=0\ , \tag{6}$$

$$S_{fg}(-1)=\sum_k \langle f\,|\,r^\lambda\,|\,k\rangle\langle k\,|\,r^\lambda\,|\,g\rangle=\langle f\,|\,(r^\lambda)^2\,|\,g\rangle\ , \tag{7}$$

to check convergence. Furthermore, it can be shown that even when the intermediate states are a finite set of approximate wave functions, the sum rules will hold for appropriately chosen states. It is very reasonable to assume that if Eqs. (6) and (7) are satisfied, the summation in Eq. (5) will also converge. In fact, in the sum rules, the high-lying states are weighted more heavily than in P, so that the sum rules provide a stringent convergence test and enable us to approximately correct for the error due to lack of convergence.

To explicitly evaluate the matrix elements in P, the initial and final states, indicated schematically as $|\,g\rangle$ and $\langle f\,|$, must be specified in a particular angular momentum coupling scheme. Because we are using a configuration-interaction code in linear symmetry, in this work, we have found it convenient to describe the states in terms of their L, M_L, S, and M_S quantum numbers and obtain the cross sections between J states by appropriate angular momentum algebra. The sum rules are interpreted, therefore, for LS coupled states. For linearly polarized light, the appropriate operator is the z operator. We then expect $S(-1)=\langle f\,|\,r^2\cos^2\theta\,|\,g\rangle$.

For the evaluation of the two-photon cross section, there are only two unique quantities to be calculated. Denoting the states as $|\,LM_L\,\rangle$ since S and M_S are conserved in the absorption, we define $A(M_L)$ as

$$A(M_L)=\sum_k \frac{\langle L'M_L\,|\,r\cos\theta\,|\,L_kM_L\,\rangle\langle L_kM_L\,|\,r\cos\theta\,|\,LM_L\,\rangle}{E_{LM_L}-E_{L_kM_L}+\hbar\omega}\ , \tag{8}$$

which is the quantity P evaluated for particular M_L projections. The sum extends over intermediate states with the same M_L. Note that $A(1)=A(-1)$.

All of the cross sections connecting individual J states can be expressed in terms of $A(0)$ and $A(1)$ as derived in the Appendix. Explicit formulas for initial and final states of ${}^3P$ symmetry are given in Table I. Writing the J levels explicitly as $\sigma_0^{(2)}(J'\leftarrow J)$, from Table I, some relationship are immediately obvious:

$$\sigma_0^{(2)}(2\leftarrow 0):\sigma_0^{(2)}(2\leftarrow 1):\sigma_0^{(2)}(1\leftarrow 2):\sigma_0^{(2)}(0\leftarrow 2)$$
$$=2.222:1.667:1.000:0.444\ .$$

Furthermore, it can be shown in general for all initial and final L states that the cross sections for transitions from a particular initial J level summed over all final J levels are independent of initial J. This has been observed previously for the ${}^3P\leftarrow{}^3P$ transition in atomic oxygen.[7] The summed cross section may be written as

$$\sum_{J'}\sigma_0^{(2)}(J'\leftarrow J)=(2\pi)^3\left[\frac{e^2}{\hbar c}\right]^2(\hbar\omega)^2\left[\frac{1}{2L+1}\sum_{M_L}A(M_L)^2\right]\ . \tag{9}$$

For the ${}^3P\leftarrow{}^3P$ transition, the quantity in brackets is $\frac{1}{3}A(0)^2+\frac{2}{3}A(1)^2$.

TABLE I. Cross sections in terms of $A(0)$ and $A(1)$ for ${}^3P\leftarrow{}^3P$ transitions.

J'_{final}	J_{initial}	$\bar{\sigma}_{J'\leftarrow J}$ [a]
0	0	$\frac{1}{9}[A(0)+2A(1)]^2$
1	0	$\equiv 0$
2	0	$\frac{2}{9}[A(0)-A(1)]^2$
0	1	$\equiv 0$
1	1	$\frac{1}{3}[\frac{1}{2}A(0)^2+\frac{3}{2}A(1)^2 + A(0)A(1)]$
2	1	$\frac{1}{6}[A(0)-A(1)]^2$
0	2	$\frac{2}{45}[A(0)-A(1)]^2$
1	2	$\frac{1}{10}[A(0)-A(1)]^2$
2	2	$\frac{1}{5}[\frac{17}{18}A(0)^2+\frac{47}{18}A(1)^2 +\frac{13}{9}A(0)A(1)]$

[a] Cross section $\sigma_{J'\leftarrow J}^{(2)}=(2\pi)^3(e^2/\hbar c)^2(\hbar\omega)^2\bar{\sigma}_{J'\leftarrow J}$.

III. CALCULATIONS

The major computational effort in calculating the two-photon absorption cross section lies in evaluating the dipole matrix elements in $A(0)$ and $A(1)$ [Eq. (8)]. In this

TABLE II. Comparison of calculated matrix elements in atomic units with values derived from experimental lifetimes.

			$\langle M_L=0 \mid z \mid M_L=0\rangle$		
Transition	λ (nm)	Expt. τ (ns)[a]	From expt. τ	Calculated $n=5$ basis	Calculated $n=4$ basis
$O^+(^4S)3s\ ^3S-^3P$	130.4	1.8±0.2[b]	0.449	0.4576	0.4591
$O^+(^4S)3p\ ^3P-O^+(^4S)3s\ ^3S$	844.6	34.7±3.7[c]	2.944	3.0753	3.0646
$O^+(^4S)4s\ ^3S-^3P$	104.0	4 ±0.6	0.22	0.1673	0.1680
$O^+(^4S)5s\ ^3S-^3P$	97.7	6 ±0.9	0.16	0.0956	
		17 ±3	0.10[e]		
			$\langle M_L=1 \mid z \mid M_L=1\rangle$		
			From expt. τ	Calculated $n=5$ basis	Calculated $n=4$ basis
$O^+(^4S)3d\ ^3D-^3P$	102.6	9 ±1.4	0.17	0.1402	0.1405
$O^+(^4S)4d\ ^3D-^3P$	97.2	20±3.0	0.11	0.0977	0.1224
$O^+(^4S)5d\ ^3D-^3P$	94.9	30±4.5	0.08	0.2224[d]	
$O^+(^2D)3s'\ ^3D-^3P$	98.9	5±0.8	0.22	0.1411[d]	0.2342

[a] Lifetime data from Ref. 9 except as noted.
[b] References 10–12.
[c] Reference 1.
[d] Both states show substantial configuration mixing.
[e] Reference 13.

work, they have been obtained from large configuration-interaction (CI) wave functions expanded in an atomic basis set of Slater functions. The final basis set, which consists of 9*s*, 7*p*, and 5*d* functions, explicitly includes two Rydberg 3*s* and 3*p* functions and one Rydberg 3*d*, 4*s*, 4*p*, 4*d*, 5*s*, 5*p*, and 5*d* function. Denoted here $n=5$, it was obtained from previous work[8] on O_2 with the addition of functions of principal quantum number 4 and 5. Exponents, ζ, for these functions were taken from the spectroscopic energies of the lowest appropriate Rydberg state according to the quantum-defect-theory expressions $\Delta E_{IP}=0.5(n^*)^{-2}$, $\zeta=1/n^*$, where ΔE_{IP} is the energy difference from the ionization limit. A reasonable physical description of Rydberg states through $n=5$ is expected from calculations with this basis set. For comparison, results of calculations with a smaller basis set (8*s*6*p*4*d*) that included Rydberg functions only through $n=4$ and is so designated are also presented.

The CI expansions included all single and double excitations with respect to the $O(^3P)$ ground state, keeping the 1*s* orbital doubly occupied, resulting in 6788 configurations for the $M_L=0$ (Σ) symmetry and 11 535 for the $M_L=1$ (Π) symmetry with the $n=5$ basis (4618 and 7820 configurations, respectively, for the smaller basis). Atomic orbitals from a self-consistent field (SCF) calculation on $O^+(^4S)$ were used.

For Rydberg states that could be explicitly identified (i.e, up to $n=5$ for calculations with the $n=5$ basis), spectroscopic energies were used in the energy denominators in the evaluation of $A(0)$ and $A(1)$. For the higher virtual states that do not correspond to real physical states but contribute to the sum-rule convergence, calculated energies were used.

In order to evaluate the reliability of the calculated matrix elements, in Table II, we have compared a number of matrix elements with those deduced from experimentally determined lifetimes according to the relationships between lifetime, oscillator strength, and matrix elements given by Eqs. (A3) and (A5b) of the Appendix. For the $3p\ ^3P \leftarrow ^3P$ two-photon transition, the most important intermediate state is the $3s\ ^3S$ state. The calculated matrix element connecting this state to the ground state shows a discrepancy of only 2%. This amounts to a discrepancy of 4% in the oscillator strength for the 130.4-nm reso-

TABLE III. Comparison of calculated matrix elements in atomic units for autoionizing transitions.

			$\langle M_L=1 \mid z \mid M_L=1\rangle$	
Transition	λ (nm)	Expt. f[a]	From expt. f	Calculated $n=5$ basis
$O^+(^2P)3s''\ ^3P-^3P$	87.8	0.0206	0.1283	0.4556[b]
$O^+(^2D)4s'\ ^3D-^3P$	81.7	0.0062	0.0710	0.0772
$O^+(^2D)3d'\ ^3P-^3P$	81.1	0.0039	0.0723	0.1581
$2s2p^5\ ^3P-^3P$	79.2	0.0234	0.1745	0.1389[b]
$O^+(^2D)5s'\ ^3D-^3P$	77.5	0.0021	0.0400	0.0379

[a] Reference 17. Data have been renormalized as explained in the note added in proof in that reference.
[b] Both states show substantial configuration mixing.

TABLE IV. Sum-rule quantities $A(0)$ and $A(1)$ in atomic units for $3p\ {}^3P \leftarrow {}^3P$ and $4p\ {}^3P \leftarrow {}^3P$ transition.

	$3p\ {}^3P$		$4p\ {}^3P$	
	$M_L=0$	$M_L=1$	$M_L=0$	$M_L=1$
$S(0)$	-0.0804	-0.2273	0.0940	-0.1132
$S(-1)$	-1.1989	-0.4780	-0.4815	-0.1800
$\langle r^2\cos^2\theta \rangle$	-1.1890	-0.2957	-0.5838	-0.1221
$A(M_L)$ uncorrected	9.4218	1.9918	3.5531	0.4856
$A(M_L)$ corrected	9.422[a]	1.566	3.720	0.342

[a] Discrepancy in $S(-1)$ too small to correct meaningfully.

nance transition. The $3s\ {}^3S$–$3p\ {}^3P$ matrix element shows a discrepancy of 5% leading to a deviation of 7% in the product of matrix elements in the numerator of $A(0)$ [Eq. (8)]. Larger discrepancies are observed for the smaller matrix elements. The comparison becomes difficult to make when substantial configuration mixing is observed in the calculations.

Results for both $n=5$ and $n=4$ basis sets are listed in Table II. As expected, little difference is observed between them; addition of $n=5$ functions allows matrix elements to be obtained for states of principal quantum number 5. Limited calculations were also performed with larger basis sets designed to span the space of the dipole operator as described in Ref. 4 and with larger CI expansions to include additional correlation. For the resonance transition, changes in matrix element of less than 4% were observed in all cases. Matrix elements for autoionizing transitions are compared with those deduced from experimental oscillator strengths in Table III. Except for problems due to configuration mixing, satisfactory agreement is obtained considering the small magnitude of these values.

IV. RESULTS

A. Intermediate quantities $A(0)$ and $A(1)$

The 40 lowest roots of the CI expansion were obtained for both $M_L=0$ and $M_L=1$ resulting in 24 and 22 dipole-connected intermediate states, respectively. All values reported below have been summed over these states. A detailed example of sum-rule convergence for transitions to the lowest two states considered, the $3p\ {}^3P$ and $4p\ {}^3P$, is given in Table IV. The quantity $S(0)$, Eq. (6), should be equal to zero; $S(-1)$, Eq. (7), should equal $\langle r^2\cos^2\theta \rangle$, which is also given. The intermediate results $A(0)$ and $A(1)$, Eq. (8), as obtained directly from the truncated summation are denoted as "uncorrected."

In order to correct for the truncation error manifesting itself as the deviation of $S(-1)$ from $\langle r^2\cos^2\theta \rangle$, we have added the difference between these quantities divided by the energy denominator to the uncorrected $A(M_L)$, assuming the energy E_k to be the energy of the highest state in the truncated sum. Excellent convergence is achieved for the $3p\ {}^3P$ $A(0)$, no correction being necessary, and the maximum correction for these two transitions is 30%. In the remainder of the paper and in Tables V–X, we have consistently used the corrected values. While the phase between $A(0)$ and $A(1)$ is significant, the overall phase is arbitrary.

The role of the different contributions to the summations may be analyzed as follows. The p^3 oxygen-ion core can exist in three states: ${}^4S$, which is the lowest in energy, followed by the ${}^2D$ and ${}^2P$. For linear polarization, the $M_L=0$ projection of the ${}^3P$ ground state is dipole connected to the $({}^4S)s,d$, the $({}^2D)s,d$ and the $({}^2P)d$ Rydberg states, which may potentially contribute to $A(0)$. The $({}^4S)d$ state and the s and d Rydberg states of the excited cores may contribute to $A(1)$. Note that the strong resonance transition to the $({}^4S)3s$ state does not contribute to $A(1)$.

The intermediate states which actually were calculated to be most significant for all the transitions studied here are reported in Table V. For the $3p\ {}^3P$ $A(0)$, the contribution of the resonance state is strongly dominant while the smaller contributions due to the $4s$ and $3d$ states are opposite in sign and nearly cancel. The concentration of oscillator strength in a single transition explains the excellent sum-rule convergence obtained for the $M_L=0$ projection. The fact that the contributions from the only other significant states cancel in $A(0)$ and that $A(0)$ is substantially larger than $A(1)$ means that for the two-photon transition to the $3p\ {}^3P$ state, the single intermediate-state approximation[7,14] is anomalously successful.

For all transitions, the quantity $\bar{P}^2 = \frac{1}{3}A(0)^2 + \frac{2}{3}A(1)^2$, which is proportional to the cross section from a single initial J state summed over final J' states [Eq. (9)], is listed in Table VI. Use of the spectroscopic energies for the in-

TABLE V. Dominant intermediate states.

Final state	$M_L=0$	$M_L=1$
$O^+({}^4S)3p$	$O^+({}^4S)3s,4s,3d$	$O^+({}^4S)3d,4d$
$O^+({}^4S)4p$	$O^+({}^4S)4s,5s,3d,4d,5d$	$O^+({}^4S)3d,4d,5d$ $O^+({}^2D)3s$
$O^+({}^2D)3p$	$O^+({}^4S)5s$ $O^+({}^2D)3s,4s,3d$	$O^+({}^4S)5d$ $O^+({}^2D)3s,4s,3d$ $2s2p^5$
$O^+({}^2P)3p$	$O^+({}^2D)4d,5d$ $O^+({}^2P)3d$	$O^+({}^2D)5s,3d,4d$ $O^+({}^2P)3s,4s$ $2s2p^5$

TABLE VI. $A(0)$, $A(1)$, and $\bar{P}^2$ in atomic units.

Final state	$A(0)^{\mathrm{a}}$	$A(1)^{\mathrm{a}}$	$\bar{P}^{2\,\mathrm{a,b}}$	$\Delta\bar{P}^2/\bar{P}^{2\,\mathrm{c}}$
$\mathrm{O}^+(^4S)3p\,^3P$	9.422	1.566 (1.992)	31.226 (32.237)	0.03
$\mathrm{O}^+(^4S)4p\,^3P$	3.720 (3.553)	0.342 (0.486)	4.691 (4.365)	0.07
$\mathrm{O}^+(^2D)3p'\,^3D$		1.102 (1.242)	0.810 (1.028)	0.27
$\mathrm{O}^+(^2D)3p'\,^3F$	2.225 (2.499)	1.770 (1.965)	3.776 (4.656)	0.23
$\mathrm{O}^+(^2D)3p'\,^3P$	4.048 (4.410)	2.414 (3.067)	9.347 (12.754)	0.36
$\mathrm{O}^+(^2P)3p''\,^3D$		1.504 (1.628)	1.508 (1.767)	0.17
$\mathrm{O}^+(^2P)3p''\,^3P$	1.691 (2.454)	2.078 (2.301)	3.832 (5.537)	0.44

[a] Uncorrected values given below in parentheses.

[b] $\bar{P}^2=\frac{1}{3}A(0)^2+\frac{2}{3}A(1)^2$.

[c] $\Delta\bar{P}^2$ is difference between corrected and uncorrected values.

termediate states rather than the calculated energies raises $\bar{P}^2$ by $\sim 20\%$ since the calculated energy differences tend to be larger than the spectroscopic values. The percentage change in $\bar{P}^2$ due to the truncation correction is also given in Table VI. As expected, larger sum-rule corrections (up to 44%) are required for the autoionizing transitions which have important contributions from higher states. The quantity $\bar{P}^2$ has also been calculated with the smaller $n=4$ atomic basis set. Agreement with the results of Table VI is excellent (within 10%) with the exception of the $4p\,^3P$ state, which has an important contribution from a $5s$ level, and the highest autoionizing level. Furthermore, although fewer intermediate states were summed in the $n=4$ calculation, agreement in the corrected values is significantly better than for the raw data, which supports the validity of the correction procedure.

B. Cross sections

In order to calculate cross sections that may be directly compared with experimental observations, the line-shape factor $g(\omega)$ and statistical factor $G^{(2)}$ in Eq. (2) need to be specified. We will present cross sections assuming a laser that is narrower than the Doppler width and is tuned to the peak of the room-temperature Doppler profile. The line-shape factor may be represented as a normalized Gaussian distribution with a full width at half maximum (FWHM) equal to the Doppler width. The peak value is given by the expression

$$g(\Delta\omega=0)=2\left[\frac{\ln 2}{\pi}\right]^{1/2}\frac{1}{\Delta\omega_D}=\frac{0.939\,44}{\Delta\omega_D}\,, \tag{10}$$

where the Doppler width may be written

TABLE VII. Two-photon absorption cross sections for atomic oxygen summed over final J' assuming a single-mode laser [calculated with line-shape factor of Eq. (10)].

Final state	Wavelength (nm)	$\sum_{J'}\sigma_0^{(2)}(J'\leftarrow J)$ (10^{-35} cm^4)	$\sum_{J'}\hat{\sigma}^{(2)}_{J'\leftarrow J}$ (10^{-46} cm^{4}sec)	$\sum_{J'}\alpha_{J'\leftarrow J}$ (10^{-28} cm^4/W)
$\mathrm{O}^+(^4S)3p\,^3P$	225.6	1.319±0.2	2.392±0.4	2.717±0.5
$\mathrm{O}^+(^4S)4p\,^3P$	200.6	0.251±0.06	0.404±0.1	0.408±0.1
$\mathrm{O}^+(^2D)3p'\,^3D$	176.5	0.056±0.02	0.079±0.03	0.070±0.03
$\mathrm{O}^+(^2D)3p'\,^3F$	175.9	0.262±0.1	0.371±0.1	0.329±0.1
$\mathrm{O}^+(^2D)3p'\,^3P$	175.9	0.650±0.2	0.919±0.3	0.813±0.3
$\mathrm{O}^+(^2P)3p''\,^3D$	157.1	0.131±0.04	0.166±0.05	0.131±0.04
$\mathrm{O}^+(^2P)3p''\,^3P$	157.1	0.334±0.15	0.422±0.18	0.333±0.15

TABLE VIII. Fine-structure cross sections $\hat{\sigma}^{(2)}_{J'\leftarrow J}$ for two-photon absorption from $O(^3P)$ in units of 10^{-47} cm^4sec assuming single-mode laser.

J'_{final}	J_{initial}	$3p\,^3P$	$4p\,^3P$	$O^+(^2D)3p'\,^3D$	$O^+(^2D)3p'\,^3F$	$O^+(^2D)3p'\,^3P$	$O^+(^2P)3p''\,^3D$	$O^+(^2P)3p''\,^3P$
0	0	13.415	1.857			8.604		4.179
1	0			0.476			0.995	
2	0	10.507	2.185		3.710	0.583		0.037
3	0			0.317			0.664	
4	0				0.001			
0	1							
1	1	16.042	2.403	0.119		8.750	0.249	4.188
2	1	7.880	1.639	0.463	1.237	0.437	0.968	0.028
3	1			0.211	2.474		0.442	
4	1				0.001			
0	2	2.101	0.437			0.117		0.007
1	2	4.738	0.983	0.119		0.262	0.249	0.017
2	2	17.093	2.621	0.198	0.107	0.808	0.415	4.192
3	2			0.476	0.743		0.995	
4	2				2.862			

$$\Delta\omega_D = \frac{2\omega}{c} 2\sqrt{2R\ln 2}\left[\frac{T}{\mu}\right]^{1/2},$$

where R is the gas constant, T the temperature, μ the mass, and the frequency 2ω corresponding to the transition energy has been used.

For a single-mode laser, i.e., a purely coherent state, the photon statistical factor $G^{(2)}=1$. However, many laboratory devices actually have a complicated multimode structure which would most nearly correspond to the incoherent or chaotic limit. In this case, as discussed, by Lambropolous,[5] photon bunching effects lead to $G^{(2)}=2$.

Assuming a single-mode laser, $G^{(2)}=1$ and the line-shape factor of Eq. (10), the three common expressions for two-photon absorption cross sections in Eqs. (2)–(4) evaluated for transitions from the oxygen ^3P ground state to the $3p\,^3P$, $4p\,^3P$, and the autoionizing states, $O^+(^2D)3p'$ and $O^+(^2P)3p''$ are listed in Table VII. The autoionizing states have been assumed to have natural linewidths narrower than the Doppler width. This is probably an excellent assumption for the ^3D and ^3F states whose energy is known precisely. However, since both the autoionizing ^3P states have not been observed spectroscopically,[15,16] they are likely to be broader. Using the estimate that when autoionization is allowed by symmetry, it can be several orders of magnitude faster than dipole radiation,[17] the autoionization linewidth could be an order of magnitude larger than the Doppler width. This width would replace the Doppler width in the denominator of Eq. (10) and the tabulated values of $\hat{\sigma}^{(2)}_{J'\leftarrow J}$ and α would be reduced accordingly.

The transition energy from the lowest ground-state fine-structure level $^3P_2$ to the average of the upper-state fine-structure levels, which are much more closely spaced, has been used; i.e., in Table VII, the upper states are assumed degenerate in energy. Uncertainties have been estimated based primarily on the truncation error and on the discrepancies in calculated matrix elements examined in Tables II and III, although some cancellation of error may be anticipated in the sum of a large number of matrix elements. No attempt has been made to estimate the error due to omitting basis functions of principal quantum number higher than 5 from the basis set. However, even for the autoionizing transitions, the difference between the $n=4$ and $n=5$ basis results was less than or on the order of the truncation error.

Cross sections between individual fine-structure levels calculated from Eq. (A2), or explicitly for $^3P\leftarrow{}^3P$ transitions from Table I, are listed in Table VIII. Comparing only the ^3P final states, because of differences in the relative magnitudes of $A(0)$ and $A(1)$, fairly different distributions among the final-state fine-structure levels for transitions from a given initial level are observed. This is carried to the extreme in Table IX, where the calculated relative cross sections for the $3p\,^3P\leftarrow{}^3P$ transition are compared with those obtained assuming a single intermediate state $[A(1)=0]$. As discussed above, although the single-state value for $\sum_{J'}\sigma^{(2)}_{J'\leftarrow J}$ is smaller by less than 4%, the relative distributions show significant discrepancies.

The calculated value for the quantity $\sum_{J'}\sigma^{(2)}_0(J'\leftarrow J)G^{(2)}$, reported in the companion experimental paper for the $3p\,^3P\leftarrow{}^3P$ transition, is given in Table X along with the results of previous calculations.[2,3]

TABLE IX. Relative cross sections for $3p\,^3P\leftarrow{}^3P$ transition.

J'_{final}	J_{initial}	Full sum	Single intermediate state
0	0	0.561	0.333
1	0		
2	0	0.439	0.668
0	1		
1	1	0.671	0.500
2	1	0.329	0.500
0	2	0.088	0.133
1	2	0.198	0.300
2	2	0.714	0.567

TABLE X. Comparison of cross sections for $3p\ ^3P\leftarrow {}^3P$ for multimode laser (calculated with $G^{(2)}=2$).

	$\sum_{J'} \sigma_0^{(2)}(J'\leftarrow J)G^{(2)}$ (10^{-35} cm^4)
This work	2.638 ± 0.4
Experiment (Ref. 1)	2.66 ± 0.80
Omidvar (Ref. 2)	2.174
Pindzola (Ref. 3)	
Dipole velocity	2.054
Dipole length	1.524

In making this comparison, the photon statistical factor $G^{(2)}=2$, appropriate for the chaotic field limit, has been assumed. The present value of $(2.638\pm0.4)\times10^{-35}$ cm^4 is in remarkable agreement with the experimental value of $(2.66\pm0.80)\times10^{-35}$ cm^4. The present value is about 25% larger than that of Omidvar and that of Pindzola obtained with dipole-velocity matrix elements. Pindzola's dipole length results, the form used in this work and by Omidvar, are significantly smaller. Considering the uncertainties inherent in the theoretical calculations, reasonable agreement has been obtained. The main improvements in the present work are the inclusion of electronic correlation and the relaxation of the frozen-core approximation.

V. SUMMARY AND CONCLUSIONS

Two-photon absorption cross sections for seven transitions in atomic oxygen have been calculated by explicitly evaluating the perturbation-theory sum over dipole matrix elements. Extensive CI calculations have been performed to obtain these matrix elements and off-diagonal sum rules have been evaluated to obtain a correction for the error due to truncation of the summation. Reasonable agreement with the experimental determination of the absolute cross section for the $3p\ ^3P\leftarrow {}^3P$ transition has been obtained.

While the effect of enlarging the atomic basis set in these calculations could be further explored and higher states in the summation could be approximately treated by the quantum-defect-theory approximation, the main improvement to these calculations would most likely be achieved by eliminating the explicit summation using the variational method of Huo[18] that has been developed within a CI framework.

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APPENDIX

The two-photon absorption cross section $\sigma^{(2)}_{J'\leftarrow J}$ may be written

$$\sigma_0^{(2)}(J'\leftarrow J)=(2\pi)^3\left[\frac{e^2}{\hbar c}\right]^2(\hbar\omega)^2\bar{\sigma}_{J'\leftarrow J}\ ,$$

where

$$\bar{\sigma}_{J'\leftarrow J}=\frac{1}{2J+1}\sum_{MM'}\left|\sum_k\frac{\langle J'M'\,|\,z\,|\,k\rangle\langle k\,|\,z\,|\,JM\rangle}{E_{JM}-E_k+\hbar\omega}\right|^2 \tag{A1}$$

and $|\,k\rangle$ is any complete set of states. Expanding in $|\,LM_LSM_S\rangle$ states

$$\begin{aligned}|\,JM\rangle &= |\,(LS)JM\rangle\\ &=\sum_{M_LM_S}\langle LM_LSM_S\,|\,JM\rangle\,|\,LM_LSM_S\rangle\ ,\end{aligned}$$

where the quantity in brackets is the standard Clebsch-Gordan coefficient, and noting that $M_L=M_{L'}$, $S=S'$, $M_S=M_{S'}$, which requires $M=M'$,

$$\bar{\sigma}_{J'\leftarrow J}=\frac{1}{2J+1}\sum_M\left|\sum_{M_L}\langle LM_LS(M-M_L)\,|\,JM\rangle\langle L'M_LS(M-M_L)J'M\rangle\sum_k\frac{\langle L'M_L\,|\,z\,|\,k\rangle\langle k\,|\,z\,|\,LM_L\rangle}{E_{LM_L}-E_k+\hbar\omega}\right|^2 . \tag{A2}$$

The summation over k is the quantity $A(M_L)$ defined in Eq. (8). In deriving Eq. (A2) we have not considered fine-structure splitting in energy. Equation (A2) has been evaluated for $^3P\leftarrow{}^3P$ transitions in Table I.

Using Herzberg's definition of oscillator strength which implies an average over initial M state and sum over final M state, and Einstein's A coefficient, $A=\tau^{-1}$ where τ is the upper-state lifetime, the oscillator strength $f_{J'\leftarrow J}$ may be written

$$f_{J'\leftarrow J}=\frac{\mu c\lambda^2}{8\pi^2e^2}\frac{g_{J'}}{g_J}\frac{1}{\tau}\ ,$$

where μ is the mass, and g_J and $g_{J'}$ are the initial- and final-state degeneracies. For atomic oxygen,

$$f_{J'\leftarrow J}=1.499\,195\times10^{-14}\lambda^2(\text{nm})\frac{g_{J'}}{g_J}\frac{1}{\tau(\text{sec})}\ . \tag{A3}$$

The matrix elements in (A1) and (A2) are related to the oscillator strength by the expression

$$|\,\langle J'M\,|\,z\,|\,JM\rangle\,|^2=\frac{3}{2\Delta E}\langle JM10\,|\,J'M\rangle^2\frac{2J+1}{2J'+1}f_{J'\leftarrow J} \tag{A4}$$

and

$$|\langle L'M_L|z|LM_L\rangle|^2=\frac{3}{2\Delta E(2J'+1)(2L'+1)}\times\frac{\langle LM_L10|L'M_L\rangle^2}{\begin{Bmatrix}L & J & S\\ J' & L' & 1\end{Bmatrix}^2}f_{J'\leftarrow J}\ , \tag{A5a}$$

where the curly brackets denote the conventional 6j symbol, or equivalently

$$|\langle L'M_L|z|LM_L\rangle|^2 =\frac{3}{2\Delta E}\frac{2L+1}{2L'+1}\langle LM_L10|L'M_L\rangle^2\sum_{J'}f_{J'\leftarrow J}\ , \tag{A5b}$$

where ΔE is the energy difference between the initial and final states, $\Delta E=hc/\lambda$.

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