Photoexcitation and ionization in ozone: Stieltjes–Tchebycheff studies in the separated-channel static-exchange approximation

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Photoexcitation and ionization in ozone: Stieltjes–Tchebycheff studies in the separated-channel static-exchange approximation

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Theoretical studies are reported of total and partial-channel photoexcitation/ionization cross sections in ozone employing Stieltjes–Tchebycheff (S–T) techniques and the separated-channel static-exchange approximation. As in previously reported investigations of excitation and ionization spectra in diatomic and polyatomic molecules employing this approach, vertical electronic dipole transition spectra for the twelve occupied canonical Hartree–Fock symmetry orbitals in ozone are constructed using large Gaussian basis sets, appropriate computational methods, and noncentral static-exchange potentials of correct molecular symmetry. Experimental rather than Koopmans ionization potentials are employed when available in construction of transition energies to avoid the incorrect ionic-state orderings predicted by Hartree–Fock theory, and to insure that the calculated series have the appropriate limits. The spectral characteristics of the resulting improved-virtual-orbital discrete excitation series and corresponding static-exchange photoionization continua are interpreted in terms of contributions from valence-like 7a,(σ*), 2b2,(π*,*) and 5b, (σ*) virtual orbitals, and appropriate diffuse Rydberg functions. The 2b1,(σ*,*) valence orbital apparently contributes primarily to discrete or autoionizing spectra, whereas the 7a,(σ*) and 5b, (σ*) orbitals generally appear in the various photoionization continua. Moreover, there is also evidence of strong 2p→kd atomiclike contributions to ka2, final-state channels in the photoionization continua. The calculated outer-valence-shell 6a1, 4b1, and 1a1 excitation series are compared with electron impact–excitation spectra in the 9 to 13 eV interval, and the corresponding partial-channel photoionization cross sections are contrasted and compared with the results of previously reported studies of photoionization in molecular oxygen. The intermediate- and inner-valence-shell excitation series and corresponding photoionization cross sections are in general accord with quantum-defect estimates and with the measured electron-impact spectra, which are generally unstructured above ~ 22 eV. Of particular interest in the intermediate-valence-shell spectra is the appearance of a strong σ→* feature just above threshold in the 3b2→kb2 photoionization cross section, in qualitative agreement with previously reported studies of the closely related 3 orbitals, cross section in molecular oxygen. Finally, qualitative comparisons are made of the calculated K-edge excitation and ionization spectra in ozone with recently reported photoabsorption studies in molecular oxygen.

I. INTRODUCTION

Molecular ozone is one of the more important trace constituents of the earth's atmosphere. In spite of this, many aspects of its photoabsorption spectrum and photochemistry are incompletely understood at present. Specifically, although photoabsorption, photoionization, and electron-impact cross sections have been measured, certain regions of the spectrum analyzed, and theoretical investigations of the ground and low-lying excited states reported, very little is known about the higher-lying excited states and the various partial-channel photoionization continua. Theoretical studies of the far UV dipole excitation/ionization spectrum in ozone at a computationally reliable level of approximation would clearly be desirable.

In the present article, theoretical investigations of vertical electronic photoexcitation and ionization in O3 are reported employing static-exchange calculations and the Stieltjes–Tchebycheff (S–T) technique. As in previously reported studies of diatomic (N2, CO, O2, F2) and polyatomic (H2O, H2CO) molecules employing this approach, large Gaussian basis sets, Hartree–Fock canonical orbitals, and appropriate computational methods are used in constructing many-electron wave functions and noncentral static-exchange potentials of correct symmetry for the excitation and ionization of the occupied orbitals in O3. Although the Hartree–Fock approximation provides an incorrect ordering of certain of the low-lying neutral and ionic states in O3 and does not provide a completely adequate description of the biradical character of its ground state, the canonical orbitals should give generally appropriate hole states for calculations of higher-lying discrete spectra and corresponding photoionization continua. Variational solutions of the one-electron excita-
tion/ionization equations provide improved–virtual-orbital (IVO) discrete states and pseudospectral approximations to the static-exchange continua, from which the corresponding photoionization cross sections are obtained using the S–T technique. Experimental rather than Koopmans ionization potentials are employed for the outer-valence orbitals to avoid the incorrect ionic-state orderings indicated above, to allow somewhat for the effects of core relaxation, and to insure that the calculated series and continua have appropriate limits and thresholds. Although the vertical–electron separated-channel static-exchange approximation can be refined and improved upon, experience indicates the approach is generally satisfactory for the excitation and ionization of outer-valence and K–shell orbitals.

When the effects of valence configuration mixing are generally required in these cases to obtain intensity projections, the static-exchange results can fail completely, the static-exchange approach requires modification. Moreover, for inner-valence–shell ionization, in which cases the effects of correlation are more significant and the orbital model can fail completely, the static-exchange results can be employed in conjunction with appropriate ionic-state shakeup amplitudes in obtaining first approximations to the cross sections. Finally, the vertical-excitation results can be combined with bound and dissociative Franck–Condon factors to obtain the yields of molecular ions and ionic-fragment products. Consequently, it is seen that S–T static-exchange calculations provide the initial information necessary for construction of reliable cross sections over the entire allowable ionization spectrum in O₂.

The calculated discrete excitations are found to be comprised of \( n_\alpha n_\beta, n_\alpha p_\beta, n_\beta p_\alpha, \) and \( n_\alpha p_\alpha \) Rydberg series and generally stronger transitions into \( 2\alpha (\pi^*) \) and \( 5\beta (\sigma^*) \) valence-like virtual orbitals. There is general agreement between the predicted \( 6\alpha, 4\beta, 1\alpha_0 = n_\alpha, n_\beta, \) and \( n_\alpha p_\alpha \) outer-valence Rydberg series and quantum-defect estimates, and the positions of strong \( 6\alpha - 5\beta \) (\( \pi^* \)) and \( 1\alpha_0 - 2\beta (\sigma^*) \) intravalence transitions are in accord with prominent features in the electron-impact data. However, as indicated above, the positions of intravalence states can be sensitive to the effects of configuration interaction, and in certain cases the static-exchange approach requires modification.

These aspects of the static-exchange approximation in the case of O₂, and techniques for avoiding the difficulties that can arise are discussed at appropriate points in the text. Although the higher Rydberg excitation series associated with inner-valence orbitals have not been experimentally assigned, the calculated positions and intensities are in general accord with the measured spectra and with estimates based on quantum-defect analysis. Of course, autoionizing line–shape calculations are generally required in these cases to obtain intensity profiles appropriate for detailed comparison with experiment.

Certain of the calculated partial-channel photoionization cross sections exhibit resonancelike structure that can be attributed to contributions from valence-like \( 7\alpha (\sigma^*) \) and \( 5\beta (\sigma^*) \) virtual orbitals in the appropriate continua. In addition, there is evidence of strong atomiclike contributions to the \( k_0 \) final-state photoionization profiles. Although corresponding experimental partial-channel cross sections are not available for comparison with the calculations, the theoretical results are in qualitative accord with previously reported studies of photoionization in other polyatomic molecules (\( \text{H}_2 \) \( \text{O}_2 \), \( \text{H}_2\text{CO} \)) having \( C_2\text{v} \) symmetry and are similar in certain respects to the previously studied partial-channel cross sections in molecular oxygen. Moreover, in spite of the various structures in the partial-channel components, the calculated total photoionization cross section is generally structureless in the 22–30 eV interval, in qualitative accord with the photoabsorption and electron-impact measurements.

Although further computational refinements, including the effects of configuration–interaction on intravalence transitions, incorporation of the biradical nature of the ground state in the calculations, determinations of shakeup amplitudes, explicit treatment of autoionizing intensities, and incorporation of aspects of the vibrational degrees of freedom will presumably alter certain of the quantitative aspects of the present study, the qualitative description provided here of the origins of the prominent features in the discrete and continuous spectra in ozone are likely to remain unchanged.

A brief description of the S–T separated-channel method is given in Sec. II, and the required IVO/static-exchange calculations in ozone are outlined in Sec. III. The resulting partial-channel and total photoexcitation/ionization cross sections are reported and discussed in Sec. IV, and concluding remarks are made in Sec. V.

II. THEORETICAL APPROACH

The Stieltjes–Tchebycheff procedure and the separated-channel static-exchange approximation are described in considerable detail in previous publications. Consequently, only a brief description of the general scheme is presented here.

A ground-state Hartree–Fock function is constructed near the appropriate equilibrium molecular geometry employing Gaussian basis orbitals and appropriate computational methods. Many-electron wave functions and noncentral static-exchange potentials are constructed from the self-consistent-field (SCF) canonical orbitals for each orbital excitation considered, and corresponding one-electron Schrödinger equations are formed for the calculation of excitation spectra. These equations are solved variationally employing basis sets significantly larger than those employed in constructing the ground-state Hartree–Fock function. Consequently, rather long integral files must generally be constructed in such calculations, involving storage and manipulation of many millions of words. This potential difficulty is avoided in the present development by constructing integral files for only those two-electron integrals in which two orbitals are taken from the occupied space and two from the virtual or unoccupied space, since these are the only ones required in the static-exchange calculations.

The one-electron eigenvalues obtained from the static-exchange calculations that are below the occupied–orbital ionization potential, and the corresponding one-electron...
orbits, provide approximations to the appropriate discrete or autoionizing valence and Rydberg states. Those eigenvalues above the ionization potential, and their corresponding orbitals, provide pseudospectra for the Stieltjes–Tchebycheff moment analysis, from which the appropriate photoionization cross sections are obtained. Transition energies and oscillator strengths are formed employing experimental rather than Koopmans ionization potentials to avoid inadequacies in the Hartree–Fock predictions of the energy orderings of the ionic states. This procedure insures that the correct series limits and thresholds are incorporated and allows in some small measure for the effects of core relaxation and correlation-energy differences in initial and final states. It is important to recognize, however, as indicated above, that static-exchange calculations can lead to incorrect positionings of intravalence states in dipole excitation spectra. 42 Valence basis configuration-interaction calculations, which do not involve the rather large basis sets required for a successful S–T analysis, can generally clarify the appropriate positioning of a particular state, and the IVO calculations can be interpreted accordingly.

The S–T approach employs a pseudospectrum of discrete transition frequencies and oscillator strengths, calculated in the present study as indicated in the preceding, in a smoothing procedure in which a continuous approximation to the underlying photoionization cross section is obtained. Conventional spectral power moments, which are convergent in the $L^p$ pseudospectrum of energies and strengths, are generally regarded as intermediaries in the smoothing procedure, providing a basis for establishing the convergence of the overall procedure. In actual calculations, however, the power moments are not used; rather, a highly stable computational algorithm is employed in constructing so-called recurrence coefficients and moment-theory spectra of (principal) frequency points and weights directly from the quantum-mechanically determined pseudospectrum. 35, 34 These points and weights are the generalized Gaussian quadratures corresponding to the photoabsorption/ionization cross section. The moment-theory spectra exhibit useful properties which the original pseudospectrum does not exhibit and, in particular, provide bounds on the cumulative oscillator-strength distribution. 35 The bounds can be differentiated in a variety of ways to provide a final expression for the photoionization cross section. Stieltjes derivatives of various orders are generally employed to obtain a first approximation to the continuous cross section and to establish the range of convergence of the variationally calculated recurrence coefficients. Tchebycheff derivatives and appropriate recurrence-coefficient extension procedures are then used to construct a continuous approximation to the cross section. In addition, specific analytic forms fit to the cumulative Stieltjes histograms provide expressions convenient for differentiation. When very small numbers of recurrence coefficients or spectral moments are available, reference density techniques—in which additional available information is incorporated in the development—can also be employed. 35, 36 Previous investigations indicate the general moment-theory approach is highly satisfactory, provided that the quantum-mechanical pseudostate calculation gives an adequate description of the underlying continuous spectrum. 35–36

III. STATIC-EXCHANGE CALCULATIONS IN OZONE

The ground-state Hartree–Fock (HF) configuration in ozone is written

$$\begin{align*}
(\sigma_1^2 \alpha_1^2 \alpha_2^2 \beta_1^2 \beta_2^2 \gamma_1^2 \gamma_2^2 \delta_1^2 \delta_2^2 \epsilon_1^2 \epsilon_2^2 \zeta_1^2 \zeta_2^2 \eta_1^2 \eta_2^2 \theta_1^2 \theta_2^2 \varphi_1^2 \varphi_2^2)A_1,
\end{align*}$$

where the molecular orbitals are ordered according to the observed photoelectron spectra when available. 11–14 Canonical Hartree–Fock orbitals are constructed in the present development at the experimental equilibrium geometry ($r_{\text{O}O}=2.413 \text{ a.u.}$) in a $(10s, 5p)$ basis, giving a total SCF energy of $-224.098$ a.u., compared to an experimental value of $-225.562$ a.u. 53 The energies and spatial characteristics of the occupied [Eq. (1)] and virtual (2b, 2a) valence orbitals have been given previously 15–25 and are only briefly described at appropriate points in the following. Of course, the single-configurational Hartree–Fock function of Eq. (1) is presumably inadequate for considerations of bond-angle and bond-length energetics 27, 28 and for descriptions of certain of the low-lying states. 37, 38, 29 The major inadequacy of the Hartree–Fock description of the O$_3$ ground state is apparently related to the ionic character of the $1a_1^2$ configuration. 32 This problem does not arise for the $(1a_2^2)^2 A_2$ hole state, 55 however, and the static-exchange potentials associated with other hole states are expected to be dominated in large measure by the spatial characteristics of the vacated orbital. 50 Consequently, the canonical orbitals should provide ionic hole states that are generally appropriate for studies of the higher excitation spectra and associated photoionization continua in O$_3$. Singlet-coupled one-electron excitations of all the occupied orbitals of Eq. (1) are considered here, resulting in excitation/ionization spectra of the forms

$$\begin{align*}
(6\alpha_1^2 \kappa_1 A_1, (6\alpha_1^2 \kappa_1) B_1, (6\alpha_1^2 \kappa_1) B_2) & , \\
(4\alpha_2^2 \kappa_1 A_1, (4\alpha_2^2 \kappa_1) B_1, (4\alpha_2^2 \kappa_1) B_2) & , \\
(2\alpha_2^2 \kappa_2 A_1, (2\alpha_2^2 \kappa_2) B_1, (2\alpha_2^2 \kappa_2) B_2) & , \\
(3\alpha_1^2 \kappa_2 A_1, (3\alpha_1^2 \kappa_2) B_1, (3\alpha_1^2 \kappa_2) B_2) & , \\
(5\alpha_1^2 \kappa_3 A_1, (5\alpha_1^2 \kappa_3) B_1, (5\alpha_1^2 \kappa_3) B_2) & , \\
(4\alpha_2^2 \kappa_3 A_1, (4\alpha_2^2 \kappa_3) B_1, (4\alpha_2^2 \kappa_3) B_2) & , \\
(2\alpha_2^2 \kappa_4 A_1, (2\alpha_2^2 \kappa_4) B_1, (2\alpha_2^2 \kappa_4) B_2) & , \\
(3\alpha_1^2 \kappa_4 A_1, (3\alpha_1^2 \kappa_4) B_1, (3\alpha_1^2 \kappa_4) B_2) & , \\
(2\alpha_2^2 \kappa_5 A_1, (2\alpha_2^2 \kappa_5) B_1, (2\alpha_2^2 \kappa_5) B_2) & , \\
(1\alpha_2^2 \kappa_5 A_1, (1\alpha_2^2 \kappa_5) B_1, (1\alpha_2^2 \kappa_5) B_2) & , \\
(1\alpha_1^2 \kappa_5 A_1, (1\alpha_1^2 \kappa_5) B_1, (1\alpha_1^2 \kappa_5) B_2) & .
\end{align*}$$

corresponding to electric field polarizations in the $x$ (in-plane), $y$ (out-of-plane), and $z$ (in-plane) directions, respectively. It is important to recognize that the one-electron excitation series of Eqs. (2) are not appropriate for descriptions of the low-lying Chappuis, Hartley, and

TABLE I. Supplemental Gaussian basis functions used in O₃ static-exchange calculations.²

<table>
<thead>
<tr>
<th>Location</th>
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<th>Number</th>
<th>Exponents²</th>
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<td>s/dₓₓ</td>
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<td>s/...</td>
<td>4/...</td>
<td>0.15 - 0.025/...</td>
</tr>
<tr>
<td>O₃</td>
<td>pₓ/dₓₓ</td>
<td>4/12</td>
<td>0.1 - 0.0125/1.0 - 0.00156</td>
</tr>
<tr>
<td>O₁ and O₂</td>
<td>.../s</td>
<td>.../3</td>
<td>.../1.0 - 0.1</td>
</tr>
<tr>
<td>O₁ and O₂</td>
<td>pₓ,pₓ,pₓ</td>
<td>4/3,3</td>
<td>2.0 - 0.1/1.0 - 0.1, 1.0 - 0.1</td>
</tr>
<tr>
<td>O₁</td>
<td>pₓ/pₓ</td>
<td>8/7</td>
<td>2.0 - 0.00156/1.0 - 0.00625</td>
</tr>
</tbody>
</table>

²Supplemental basis functions employed, in addition to the (10s, 5p)/[3s, 2p] valence basis (Ref. 40), in solution of the static-exchange equations [Eqs. (3) to (7)].

¹O₃ and O₂ refer to the end atoms; O₁ to the central atom.
²A geometric series variation is employed in the indicated range where appropriate.

Huggins bands, which apparently involve two-electron transitions in a canonical HF basis.²⁷,²⁸

Static-exchange Hamiltonians appropriate for the spectra of Eqs. (2) are constructed in the forms

\[ h_e = T + V + V_r, \]

(3)

where \( T \) and \( V \) are the kinetic- and nuclear-framework potential-energies, and

\[ V_r = \sum_n (2\hat{J}_n - \hat{\mathcal{K}}_n) + \hat{J}_n + \hat{\mathcal{K}}_n, \]

(4)

is the channel potential, written in terms of Coulomb and exchange operators for the doubly occupied \((\hat{J}_n, \hat{\mathcal{K}}_n)\) and singly occupied \((\hat{J}_n, \hat{\mathcal{K}}_n)\) orbitals. The resulting non-local, non-central one-electron Schrödinger equations

\[ \left( \hat{h}_p - \epsilon \right) \Psi_n = 0, \]

(5)

where \( \epsilon \) takes on discrete and continuous values, are solved variationally in the forms

\[ \langle \hat{\Phi}_{ij} | \hat{h}_p | \hat{\Phi}_{ij} \rangle = \epsilon_{ij, \delta_{ij}}, \]

(6a)

\[ \langle \hat{\Phi}_{ij} | \hat{\Phi}_{ij} \rangle = \delta_{ij}, \quad i, j = 1, N \]

(6b)

using the virtual canonical orbitals and the supplemental basis sets shown in Table I. The latter are chosen to augment the (10s, 5p)/[3s, 2p] valence basis so that sufficient numbers of compact and diffuse functions are available in each final-state orbital symmetry considered. The combined basis provides pseudospectra [Eqs. (6)] of dimensionality \( N \) for the four final-orbital symmetries, \( h_{10}(28) \), \( h_{10}(17) \), \( h_{2b}(16) \), and \( h_{2b}(21) \), which are orthogonal to the occupied canonical orbitals of Eq. (1).

Pseudospectra of transition frequencies and oscillator strengths of the dimensionality indicated above are obtained from Eqs. (1)-(6) in the forms

\[ \tilde{\zeta}^i = \epsilon_i - \epsilon_{ij}, \]

(7a)

\[ \tilde{J}^i = \frac{1}{\tilde{\zeta}^i} \langle \hat{\Phi}_{ij} | \mu | \hat{\Phi}_{ij} \rangle^2, \]

(7b)

where \( \Phi_i \) is the appropriate occupied canonical Fock orbital, \( \epsilon_i \) is the corresponding Koopmans or experimental ionization potential, \( \mu \) is the dipole moment operator, and the additional factor of 2 in Eq. (7b) arises from singlet coupling the many-electron eigenstates for the spectra of Eqs. (2). Equations (7) provide transition energies and \( f \) numbers for the discrete and autoionizing states lying below the various thresholds and furnish the pseudospectra necessary for the S-T construction of photoionization cross sections above the ionization thresholds. As indicated above, the resulting static-exchange cross sections can be combined with appropriate ionic-state intensity borrowing calculations in order to include the effects of relaxation, and the necessary Franck-Condon factors can also be introduced if the available PES and partial-channel cross section data warrant. These refinements are not included in the present development, but are appropriate subjects for subsequent investigations.

IV. PHOTOCITCATION AND IONIZATION IN OZONE

A brief qualitative description of the spatial characteristics of the occupied canonical HF symmetry orbitals provides a basis for proper interpretation of the calculated cross sections.¹⁴-²⁵ It will be recalled that \( 6a_1(n) \) and \( 4b_2(n) \) are nonbonding/weakly antibonding orbitals, comprised, respectively, of in-phase and out-of-phase combinations of in-plane \((\pi_e)\) end-atom \(2p_\pi \) orbitals, whereas \( 1a_2(n) \) is nonbonding and comprised of out-of-plane, out-of-plane, end-atom \(2p_\sigma \) orbitals. The \( 1b_1(\pi_e) \) orbital is a \( \pi \) bonding in-phase combination of three out-of-plane \(2p_\sigma \) orbitals, \( 3b_2(\pi_e) \) is nonbonding, comprised primarily of end-atom \(2s-2p_\pi \) hybrids, \( 5a_1(\pi_e) \) is very weakly \( \sigma \) bonding, \( 4a_1(\pi) \) is strongly \( 2s-2p_\sigma \) antibonding, and \( 2b_1(\sigma) \) and \( 3a_1(\sigma) \) are strongly \( 2s-2p_\sigma \) and \( 2s-2p_\sigma \) bonding, respectively. The \( 2a_2(1s) \), \( 1b_3(1s) \), \( 1a_1(1s) \) molecular orbitals are appropriate symmetry combinations of 1s atomic oxygen orbitals.¹⁴-²⁵ The reader is referred to the literature for more complete descriptions of these orbitals.

In addition to the occupied canonical HF symmetry orbitals, \( 2b_1(\pi_e^*) \), \( 7a_1(\sigma^*) \), and \( 5b_2(\sigma^*) \) virtual valence-like orbitals also appear in the ozone spectrum.¹⁴-²⁵ The antibonding \( 2b_2(\pi_e^*) \) molecular orbital is complementary to the \( 1b_1(\pi_e) \) bonding orbital, \( 7a_1(\sigma^*) \) is strongly antibonding and comprised of end- and central-atom \(2s-2p_\sigma \) hybrids, and \( 5b_2(\sigma^*) \) is strongly \( 2s-2p_\sigma \) antibonding. The various calculated excitation and ionization spectra should be comprised of intravalence transitions into these relatively compact virtual orbitals, which can appear either above or below the appropriate ionization thresholds, and transitions into more diffuse Rydberg-like discrete and continuum orbitals formed from the supplemental basis set of Table I.

It is convenient in the following to describe and discuss separately the outer-valence-shell (\( 6a_1, 4b_2, 1a_2 \)), intermediate-valence-shell (\( 1b_1, 3b_2, 5a_1 \)), inner-valence-shell (\( 4a_1, 2b_1, 3a_1 \)), and K-edge (\( 2a_2, 1b_3, 1a_1 \)) cross sections obtained from the present calculations.
A. Outer-valence-shell cross sections

Cross sections for $6\alpha_1(n)$, $4b_2(n)$, and $1\alpha_2(n)$ excitation and ionization are presented in this subsection. Photoelectron spectra indicate the presence of low-lying $2A_1$, $2B_1$, and $2A_2$ states of O$_2$ that can be associated with removal of $6\alpha_1$, $4b_2$, and $1\alpha_2$ canonical orbitals, respectively. Experimental, rather than Koopmans, ionization potentials are employed in the present development to avoid the incorrect ordering predicted by the HF approximation. A semiquantitative description of the calculated outer-valence-shell excitation spectra is given in Fig. 1, in comparison with the measured 300 eV electron impact–excitation profile.

1. $6\alpha_1(n)$ spectra (I.P. = 12.75 eV)

The calculated $6\alpha_1(n) - n\alpha_1$, $n\beta_1$, and $n\beta_2$ excitation series are reported and compared with experimental results and quantum-defect estimates in Table II and Fig. 1, and the corresponding $6\alpha_1(n) - k\alpha_1$, $k\beta_1$, and $k\beta_2$ cross sections are shown in Fig. 2(a).

Evidently the $6\alpha_1(n) - n\alpha_1$ series is comprised of perturbed $n\alpha_1$ and $n\beta_1$ Rydberg transitions. The basis set employed in $\alpha_1$ symmetry (Table I) is apparently not large enough to provide separate well-defined $n\alpha_1$ and $n\beta_1$ Rydberg series. Consequently, agreement with the quantum-defect estimates is only generally satisfactory. It should be noted in this connection that the threshold value of the photoionization cross section required in constructing defect estimates of $f$ numbers is generally uncertain by at least a factor of 2 for profiles that are rapidly varying with energy near threshold. Because the series is relatively weak, unique assignment of corresponding features in the impact spectrum of Fig. 1 is not possible. The expected strong $6\alpha_1(n) - 7\alpha_1(\sigma^*)$ intravalence transition evidently appears ~2 eV above threshold in the $6\alpha_1(n) - k\alpha_1$ cross section of Fig. 2(a) as a relatively sharp resonancelike feature.

### Table II. Outer-valence-shell $6\alpha_1$ (I.P. = 12.75 eV), $4b_2$ (I.P. = 13.03 eV), and $1\alpha_2$ (I.P. = 13.57 eV) excitation spectra in O$_2$.

<table>
<thead>
<tr>
<th>Present results$^a$</th>
<th>Defect estimates$^b$</th>
<th>Present results$^a$</th>
<th>Defect estimates$^b$</th>
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<td>$(4b_2)^1A_1 - (n\beta_2)^1B_1$</td>
<td>$(6\alpha_1)^1A_1 - (n\beta_1)^1B_1$</td>
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<tr>
<td>11.92/0.0066</td>
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<td>13.2/0.00008</td>
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<tr>
<td>12.09/0.0019</td>
<td>12.1/0.0010</td>
<td>12.2/0.0004</td>
<td>12.2/0.0005</td>
<td>12.2/0.0010</td>
<td>12.2/0.0005</td>
</tr>
</tbody>
</table>

$^a$Energies and strengths obtained from the development of Eqs. (1) to (7) and the basis sets described in Sec. III and Table I. The series are made to converge on the experimentally observed vertical photoionization thresholds (Refs. 11–14), as discussed in the text.

$^b$Energies taken from the Rydberg formula $\varepsilon_f = \varepsilon_r - 13,606/(n - 0)^2$, and $f$ numbers from the Coulomb-limit approximation $\varepsilon_f = \varepsilon_r(n - 0)^{-1}$ of D. R. Bates and A. Damgaard, Astrophys. J. 242, 14 (1980), and A. Burgess and M. J. Seaton, Mon. Not. R. Astron. Soc. 120, 121 (1960), with $f(n, u)$ the photoionization oscillator strengths at threshold (Fig. 2). Quantum defects of $\delta = 1.1, 0.7$, and 0 are used for $\alpha, \beta$, and $\delta$ series, respectively.

rate calculations are performed. In the latter case, this intravalence transition could account for the strong feature in the impact spectrum at ~10 eV (Fig. 1). Under the assumption that the \( 6a_1(n) - 5b_2(\sigma^*) \) intravalence transition appears below the ionization threshold, the \( 6a_1 - kb_2 \) photoionization profile of Fig. 2(a) is determined by deleting the intravalence transition from the imaging procedure. The resulting photoionization profile is evidently generally weak, with a broad maximum at ~30 eV.

2. \( 4b_2(n) \) spectra (I.P. = 13.03 eV)

The \( 4b_2(n) - na_1, nb_1, \) and \( na_2 \) excitation series are shown in Table II and Fig. 1, and the corresponding \( 4b_2 - ka_2, kb_2, \) and \( ka_2 \) photoionization cross sections are presented in Fig. 2(b).

Evidently, the \( 4b_2(n) - na_1 \) excitations are comprised of perturbed \( na_1, \) and \( npa_1 \) Rydberg series only in general accord with the defect estimates. The relatively strong resonance in the Rydberg series presumably contributes to the sharp line in the experimental spectrum at ~9 eV.\(^{15} \) The expected strong \( 4b_2(n) - 1a_2(\sigma^*) \) intravalence transition apparently appears ~5 eV above threshold in the \( 4b_2 - ka_2 \) photoionization cross section of Fig. 2(b), similar to the \( 6a_1 - ka_1 \) profile of Fig. 2(a). The small difference in peak position in the two profiles can be attributed to differences in detail in the appropriate static-exchange potentials obtained employing many-electron singlet-coupled states.

The \( 4b_2(n) - nb_2 \) excitations of the Rydberg series is very weak, as might be expected, since \( 4b_2(n) \) is primarily end atom \( 2p \), in character. The corresponding \( 4b_2 - ka_2 \) photoionization cross section of Fig. 2(b) shows evidence of a weak resonancelike structure ~4 eV above threshold, however, that can be attributed to atomiclike \( 2p - kd \) contributions to the continuum.

3. \( 1a_2(n) \) spectra (I.P. = 13.57 eV)

The discrete \( 1a_2 - nb_1, na_1, \) and \( nb_2 \) excitation series are shown in Table II and Fig. 1, and the corresponding \( 1a_2 - kb_1, ka_1, \) and \( kb_1 \) cross sections are presented in Fig. 2(c).

A very strong \( 1a_2(n) - 2b_1(\pi^*) \) intravalence \( n - \pi^* \) transition appears in the \( 1a_2 - nb_1 \) series, since \( 1a_2(n) \) is comprised primarily of out-of-plane, out-of-phase, end-atom \( 2p_\sigma \) orbitals. This transition presumably contributes to the moderately strong and broad feature in the impact spectrum between 8 to 9 eV.\(^{16} \) The rest of the excitations evidently comprise an \( npb_2 \) Rydberg series of moderate intensity, in good accord with the defect estimates. Referring to Fig. 2(c), the \( 1a_2 - kb_1 \) photoionization cross section is correspondingly weak, since much of the total \( f \) number in this channel appears in the resonance transition.

---

**FIG. 2.** (a) Calculated S–T static-exchange cross sections in O\(_3\) for \( 6a_1 \rightarrow ka_1, kb_1 \), and \( kb_2 \) photoionization obtained from the development of Eqs. (1)–(7). Note that the \( 6a_1 - kb_1 \) cross section shown is five times the calculated value. 1 Mb = 10\(^{-18}\) cm\(^2\). (b) As in (a), for \( 4b_2 - ka_1, kb_1, \) and \( kb_2 \) photoionization in O\(_3\). The \( 4b_2 - ka_2 \) cross section shown is twice the calculated value. (c) As in (a), for \( 1a_2 - kb_1, ka_1, \) and \( kb_2 \) photoionization in O\(_3\). The \( 1a_2 - ka_2 \) cross section shown is twice the calculated value.
TABLE III. Intermediate-valence-shell 1b2 (I. P. = 21.51 eV), 3b2 (I. P. = 21.59 eV), and 5a1 (I. P. = 22.78 eV) excitation spectra in O2.

<table>
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<th>Energy (eV)/f number</th>
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<td></td>
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</tr>
<tr>
<td></td>
<td>21.07/0.0001</td>
<td>21.00/0.0001</td>
</tr>
</tbody>
</table>

The 1a2(n) → nda2 Rydberg series is apparently very weak, with the positions in excellent accord with quantum-defect estimates. By contrast, the corresponding 1a2 → nda2 photoionization profile of Fig. 2(c) shows a very broad atomiclike 2p → kd feature ~ 7 eV above threshold. Similar kd orbital features are predicted and observed in the photoionization spectra of diatomic and other polyatomic molecules having C2v symmetry. 35-45

The 1a2(n) → nda2 excitations of Table II evidently form an npb2 Rydberg series, in very good agreement with the quantum-defect estimates, with no evidence of an intra-valence 1a2(n) → 5b2(σ*) transition present. The latter feature evidently appears as a resonancelike contribution ~ 6 eV above threshold in the 1a2 → kb2 photoionization profile of Fig. 2(c), similar to the 4b2 → kb2 profile of Fig. 2(b). By contrast, the 6a1 → 5b2(σ*) intra-valence transition appears in the discrete position of the 6a1 spectrum.

The 1a2 → kb1, kb2, and kb3 photoionization cross sections of Fig. 2(c) and corresponding discrete spectra of Table II are qualitatively similar to the previously reported 1a1 profiles in molecular oxygen, 40,41 apparently as a consequence of the out-of-plane 2p character of the 1a1(n) orbital.

B. Intermediate-valence-shell cross sections

The intermediate-valence-shell 1b1(πν), 3b2(σν), and 5a1(σν) excitation series are shown in Table III and Fig. 1, and the corresponding photoionization cross sections are given in Fig. 3. Photoelectron spectra indicate weak shakeup lines in the 13.6–17.5 eV interval which are not treated here and a stronger line at ~ 20 eV. The latter presumably corresponds to one of the three intermediate-valence-shell orbitals in O2.
appropriate experimental values are unavailable, the Koopmans ionization potentials are employed in these cases in the present development.

1. 1b_{1}(\pi_{a}) spectra (I.P. = 21.51 eV)

The discrete 1b_{1}(\pi_{a}) - na_{2}, nb_{1}, and na_{1} excitation series are shown in Table III, and the corresponding 1b_{1} - ka_{2}, kb_{1}, and ka_{1} photoionization cross sections are shown in Fig. 3(a).

The 1b_{1}(\pi_{a}) - na_{2} excitations evidently comprise a well-defined nda_{2} Rydberg series of weak intensity, in very good agreement with the quantum-defect estimates. Evidently, the corresponding 1b_{1} - ka_{2} cross section of Fig. 3(a) contains a broad but very weak kda_{2} feature at ~32 eV, in accord with the 4b - ka_{2} and 5a - ka_{2} profiles of Figs. 2(b) and 2(c), respectively. Apparently, the out-of-plane 2p_{x} character of the 1b_{1}(\pi_{a}) orbital is inappropriate for the formation of strong overlap charge with the nda_{2}/ka_{2} spectrum.

As expected, there is a strong 1b_{1}(\pi_{a}) - 2b_{1}(\pi_{a}^{*}) \pi - \pi^{*} transition in the 1b_{1} - nb_{1} series, with the other members comprising a well-defined npb_{1} Rydberg series. The associated 1b_{1} - kb_{1} photoionization cross section of Fig. 3(a) is correspondingly weak, similar to the structures of previously reported \pi - k\pi^{*} channels in diatomic molecules.\textsuperscript{35-42}

Finally, the 1b_{1}(\pi_{a}) - na_{1} excitations evidently form perturbed nsa_{1} and npa_{1} Rydberg series, and the corresponding 1b_{1} - ka_{1} photoionization cross section contains a strong 1b_{1}(\pi_{a}) - \tau_{a_{1}}(\sigma^{*}) resonancelike contribution immediately above threshold.

2. 3b_{2}(n) spectra (I.P. = 21.59 eV)

The discrete 3b_{2}(n) - na_{1}, nb_{2}, and na_{2} series are shown in Table III and Fig. 1, and the corresponding ka_{1}, kb_{2}, and ka_{2} cross sections are given in Fig. 3(b).

Evidently, the 3b_{2}(n) - na_{1} excitations of Table III form strong nsa_{1} and npa_{1} Rydberg series, perturbed by a 3b_{2}(n) - \tau_{a_{1}}(\sigma^{*}) intravalence interloper, and the 3b_{2}(n) - ka_{1} photoionization cross section is correspondingly weak and monotonic. By contrast, the 4b_{2} - na_{1}/ka_{1} profile [Table II and Fig. 2(b)] exhibits a \tau_{a_{1}}(\sigma^{*}) photoionization resonance. Calculations somewhat more elaborate than the static-exchange results reported here are required to confirm the positioning of the 3b_{2}(n) - \tau_{a_{1}}(\sigma^{*}) transition in the discrete spectrum, since the positions of intravalence transitions can be sensitive to the details of configuration interaction.\textsuperscript{42}

The 3b_{2}(n) - nb_{2} excitations of Table III form a reasonably well-defined, moderate intensity, npb_{2} Rydberg series, whereas the corresponding 3b_{2}(n) - kb_{2} cross section of Fig. 3(b) has a strong 3b_{2}(n) - 5b_{3}(\sigma^{*}) resonance ~1.5 eV above threshold. The latter is the strongest individual feature present in the O\textsubscript{2} photoionization cross section. It can be attributed to the strong \sigma - \sigma^{*} like transition density arising from the 3b_{2}(n) - 5b_{3}(\sigma^{*}) product and is qualitatively similar to the 3\sigma - ka_{2} resonance in molecular oxygen.\textsuperscript{40,41}

Finally, the 3b_{2}(n) - na_{2} excitations of Table III comprise a well-defined but very weak nda_{2} Rydberg series, in excellent agreement with the quantum-defect estimates. The corresponding 3b_{2}(n) - ka_{2} photoionization cross section of Fig. 3(b) is weak, but shows clear evidence of a broad k\sigma atomiclike contribution, peaking at somewhat higher energy than in the 1b_{1}(\pi_{a}) - ka_{2} profile of Fig. 3(a).

3. 5a_{1}(\pi_{a}) spectra (I.P. = 22.78 eV)

The 5a_{1}(\pi_{a}) - na_{1}, nb_{1}, and nb_{2} excitation series are shown in Table III and Fig. 1, and the corresponding ka_{1}, kb_{1}, and kb_{2} cross sections are given in Fig. 3(c).

The 5a_{1}(\pi_{a}) - na_{1} excitations evidently form perturbed nsa_{1} and npa_{1} Rydberg series of moderate intensity, and the ka_{1} cross section of Fig. 3(c) is monotonically decreasing. There is little evidence in this channel of a 5a_{1} - \tau_{a_{1}}(\sigma^{*}) resonance contribution in either the discrete or continuous spectral regions, although this feature may be mixed in the perturbed Rydberg series. The \pi character of the 5a_{1} orbital is apparently inappropriate for forming a strong transition charge density with the 5a_{1}(\sigma^{*}) virtual valence orbital.

Although the 5a_{1}(\pi_{a}) - nb_{1} series contains an intravalence transition, its intensity is apparently quite weak, as may be expected from the out-of-plane character of the 2b_{1}(\pi_{a}^{*}) orbital. The other 5a_{1} - nb_{2} excitations evidently form a weak npb_{1} Rydberg series, in good agreement with the quantum-defect estimates. The associated 5a_{1} - kb_{1} photoionization cross section of Fig. 3(c) is correspondingly weak and monotonically decreasing, presumably also as a consequence of the out-of-plane character of the kb_{1} orbitals.

Finally, the 5a_{1} - nb_{2} excitations of Table III form an npb_{2} Rydberg series of moderate intensity, with little indication of an intravalence 5a_{1}(\pi_{a}) - 5b_{3}(\sigma^{*}) present in either the discrete spectrum or the 5a_{1} - ka_{1} cross section of Fig. 3(c), although it may contribute to the resonance transition. Apparently the directions of the 5b_{3}(\sigma^{*}) hybrid lobes are such that a strong overlap charge density is not formed with the 5a_{1}(\pi_{a}) orbital.

C. Inner-valence-shell cross sections

The inner-valence-shell 4a_{1}(\sigma^{*}), 2b_{2}(\sigma), and the 3a_{1}(\sigma) excitation spectra are shown in Table IV, and corresponding photoionization cross sections appear in Fig. 4. Koopmans values are employed in the absence of experimentally determined vertical ionization potentials. Because of strong configuration mixing in the inner-valence-shell ionic states of molecules containing first row atoms,\textsuperscript{42} the results of Fig. 4 should be combined with appropriate intensity borrowing calculations prior to making comparison with experiment.

1. 4a_{1}(\sigma^{*}) spectra (I.P. = 29.86 eV)

The 4a_{1}(\sigma^{*}) - nsa_{1} and npa_{1} Rydberg series of Table IV is irregular and weak, and the positions are only in fair agreement with the quantum-defect estimates, apparently due to limitations of the basis set of Table I. The as-
TABLE IV. Inner-valence-shell 4a₁ (I. P. = 29.9 eV), 2b₂ (I. P. = 39.6 eV), and 3a₁ (I. P. = 48.6 eV) excitation spectra in O₃.

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<th>Present results</th>
<th>Defect estimates</th>
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<td>energy (eV)/ number</td>
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3a₁(α³) spectra (I. P. = 49.55 eV)

Evidently, the 3a₁(α³) – nsa₁ excitations of Table IV comprise weak nsa₁ and npa₁ Rydberg series, whereas

...
there is a strong intravalence $3a_1(\sigma) \to 7a_1(\sigma^*)(\sigma \to \sigma^*)$ contribution to the $ka_2$ continuum of Fig. 4(c) at $\sim 70$ eV. The $3a_1 \to nb_2$ excitations comprise a weak Rydberg series, with a moderately strong $3a_1(\sigma) \to 5b_2(\sigma^*)(\sigma \to \sigma^*)$ transition also present. The $kb_2$ continuum is correspondingly weak and monotonically decreasing. Finally, there is a weak low-lying $3a_1(\sigma) \to 2b_1(\tau_2^+)$ transition in the $3a_1 \to nb_1$ excitations and a weak Rydberg series, and the corresponding $kb_1$ continuum shows a broad maximum at $\sim 70$ eV.

D. Valence shell partial-channel cross sections

The various polarization components of the partial-channel cross sections of Figs. 2-4 are combined and presented in Fig. 5. Of the three low ionization potential nonbonding orbitals ($6a_1$, $4b_2$, $1a_2$), the $1a_2$ orbital evidently makes the major contribution to the photoionization cross sections shown in Fig. 5(a). The peak at $\sim 20$ eV in this partial-channel profile is due to $1a_2(n) \to 5b_2(\sigma^*)$ and $1a_2(n) \to a_2kd$ resonancelike contributions [Fig. 2(c)] to the $1a_2(n) \to kb_2$ and $ka_2$ components. As indicated above, the $1a_2(n)$ cross sections are qualitatively similar to the previously reported $1\pi^*_{\gamma}$ results in molecular oxygen,\textsuperscript{40,41} apparently as a consequence of the out-of-plane $2p_y$ character of the $1a_2(n)$ orbital. Although the $6a_1$ and $4b_2$ partial-channel cross sections are weaker, there is evidence of a $6a_1(n) \to 7a_1(\sigma^*)$ resonance contribution in the former [Fig. 2(a)], and $4b_2(n) \to 7a_1(\sigma^*)$ $5b_2(\sigma^*)$, and $a_2kd$ resonances in the latter [Fig. 2(b)]. The $6a_1(n)$ and $4b_2(n)$ results are qualitatively similar to the $1\pi_e$ and $1\pi_e$ cross sections in $O_2$,\textsuperscript{40,41} although less so than in the case of the $1a_2(n)$ orbital indicated above, presumably as a consequence of the in-plane $2p_y$ character of the $6a_1(n)$ and $4b_2(n)$ orbitals. In order to separate the three partial cross sections of Fig. 5(a) for parent O$_3$ ion formation into vibrationally bound and dissociative components, appropriate potential surfaces and Franck-Condon factors must be constructed. These aspects of photoionization in O$_3$ are beyond the scope of the present investigation.

In the spectral interval from $\sim 13$ to $21$ eV there are a series of discrete excitations associated with intravalence and Rydberg transitions converging to the higher ionization thresholds at $\sim 21$ to $22$ eV (Fig. 1 and Table III). These excitations can autoionize into the underlying $6a_1$, $4b_2$, and $1a_2$ photoionization continua, and appropriate line-shape calculations are required to obtain the correct intensity distribution in the $13-21$ eV interval. In the absence of these calculations, estimates of the ionization cross section are obtained by including in the $8$-T analysis all the discrete $f$ numbers of Table III. The profile so obtained corresponds approximately to total ionization from these states, and so gives an upper limit. By contrast, the direct ionization curves for $6a_1$, $4b_2$, and $1a_2$ orbitals provide a lower estimate of the one-electron ionization contribute to the photoabsorption cross section in the $\sim 13-21$ eV interval.

Above $\sim 21$ eV the $1b_1$, $3b_2$, and $5a_1$ partial-channel cross sections shown in Fig. 5(b) contribute to $O_3^+$ parent ion formation. Evidently, the $3b_2$ contribution dominates in this spectral region, due to the $3b_2(n) \to 5b_2(\sigma^*)$ resonance at $\sim 23$ eV in the $3b_2 \to kb_2$ photoionization cross section [Fig. 5(b)]. As indicated above, this feature corresponds closely to the strong $\sigma \to \sigma^*$ resonancelike contribution just above threshold in the $3a_1 \to kb_2$ photoionization cross section in molecular oxygen.\textsuperscript{40,41} Although the $1b_1$ cross section is smaller in magnitude, the $1b_1(n) \to 7a_1(\sigma^*)$ resonancelike contribution to this channel [Fig. 3(a)] is apparent in the partial cross section of Fig. 5(b). Finally, the $5a_1$ cross section of Fig. 5(b) is generally weak and monotonic, apparently as a consequence, as indicated previously, of the out-of-plane $\pi$ character of this orbital, which prevents formation of strong overlap densities with the valencelike virtual orbitals. The total calculated photoionization cross section in the $\sim 22-30$ eV interval is seen to be monotonic and structureless, in general accord with photoabsorption\textsuperscript{4-10} and electron-impact\textsuperscript{15} measurements.

With the exception of the strong intravalence $4a_1(\sigma^*) \to 2b_1(\tau_2^+)$ transition, the discrete transitions of Table IV arising from inner-valence-shell excitation are seen to be relatively weak. Consequently, the total photoionization cross section will be generally structureless up to

![FIG. 5. (a) Outer-valence-shell $6a_1$, $4b_2$, and $1a_2$ partial-channel photoionization cross sections in O$_3$ obtained from Fig. 2. (b) As in (a), for $1b_1$, $3b_2$, and $5a_1$ photoionization in O$_3$ from Fig. 3. (c) As in (a), for $4a_1$, $2b_2$, and $3a_1$ photoionization in O$_3$ from Fig. 4. Note that the energy scale in this case differs from that of (a) and (b).]
TABLE V. K-edge 2a1 (I.P. = 541.5 eV), 1b2 (I.P. = 541.5 eV), and 1a1 (I.P. = 546.2 eV) excitation spectra in O3.

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<tr>
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</table>

The ~30 eV threshold for 4a1 ionization. The partial-channel cross sections for 4a1, 2b2, and 3a1 ionization shown in Fig. 5(c) are evidently weak, although their combined peaks may be evident in the total cross section. Apparently the 4a1 contribution is the largest of the three inner-valence-shell cross sections shown in Fig. 5(c), a consequence of the 4a1(σ*) and 7a1(σ*) resonances in this case [Fig. 4(a)]. The prominent features in the 2b2 and 3a1 cross sections of Fig. 5(c) are due to 2b2(σ) ~ 7a2Dd [Fig. 4(b)] and 3a1(σ) ~ 7a1(σ*) [Fig. 4(c)] resonances, respectively. These features are similar to resonancelike structures appearing in the inner-valence-shell 2a1 and 2b2 cross sections in molecular oxygen. Of course it should be noted, as indicated above, that the Koopmans approximation generally fails in the inner-valence-shell ionization spectrum of molecules containing first row atoms. Consequently, the results of Fig. 5(c) must be combined with appropriate ionic-state amplitudes prior to making comparison with experiment.

E. K-edge cross sections

The K-edge 2a1, 1b2, and 1a1 excitation series are shown in Table V, and the corresponding photoionization cross sections are shown in Fig. 6. Experimental ionization potentials are employed in these three cases. These values are in general accord with other oxygen atom 1s ionization thresholds reported in the ~530~545 eV interval in various oxygen containing compounds. The 1a1 molecular orbital corresponds essentially to a central oxygen atom 1s orbital, whereas the degenerate 2a1 and 1b2 molecular orbitals correspond to appropriate even and odd combinations of end-atom 1s orbitals, respectively.

1. 2a1 spectra (I.P. = 541.5 eV)

The 2a1 → nsa series of Table V evidently contains a strong transition into the 7a1(σ*) orbital and interacting nsa and npb Rydberg series, and the corresponding 2a1 → 1a1 cross section is a broad weak continuum [Fig. 6(a)]. Similarly, the 2a1 → npb1 series contains a very

FIG. 6. (a) As in Fig. 2(a), for 2a1 → ka1 , kb1 , and kb2 photoionization in O3. (b) As in (a), for 1b2 → ka2 , kb2 , and ka2 photoionization in O3. (c) As in (a), for 1a1 → ka1 , kb1 , and kb2 photoionization in O3.
strong transition into the $2b_1(\pi^*)$ valence-like orbital, and a weak Rydberg series in good accord with quantum-defect estimates. The $2a_1-np_2$ series of Table V evidently contains a moderately strong transition into the $5b_2(\sigma^*)$ orbital, and a Rydberg series in good accord with quantum-defect estimates. The corresponding continuum cross section of Fig. 6(a) is correspondingly weak and structureless. The $2a_1-np_2$ series of Table V evidently contains a moderately strong transition into the $5b_2(\sigma^*)$ orbital, and a Rydberg series in good accord with quantum-defect estimates. The corresponding continuum cross section of Fig. 6(a) is correspondingly weak and structureless. The positions of the other members of the $1b_2-np_2$ series are evidently in good agreement with quantum-defect estimates, and the $f$ numbers are relatively weak. Note that the $1b_2-5b_2(\sigma^*)$ resonance is degenerate with the corresponding $2a_1-5b_2(\sigma^*)$ transition close to threshold is in accord with a strong feature in the O$_2$ spectrum just below threshold that can be given a $1a_s-2p_2$ assignment. By contrast, the $2a_1-7a_1(\sigma^*)$ valence-like resonance does not have a counterpart in the O$_2$ K-edge spectra.

2. 1b$_2$ spectra (I. P. = 541.5 eV)

The $1b_2-np_2$ series of Table V evidently contains a strong resonance transition associated with the $5b_2(\sigma^*)$ orbital, whereas the corresponding cross section of Fig. 6(b) is monotonic and structureless. The positions of the other members of the $1b_2-np_2$ series are evidently in good agreement with quantum-defect estimates, and the $f$ numbers are relatively weak. Note that the $1b_2-5b_2(\sigma^*)$ resonance is degenerate with the corresponding $2a_1-5b_2(\sigma^*)$ transition discussed above. Presumably localized 1s end-oxygen-atom orbital calculations in ozone, including relaxation effects, will aid in refining the position of these features, which are expected to appear just below threshold on basis of the measurements in O$_2$. The $1b_2-7a_1$ excitations of Table V form separate $n$-s, and $n$-p Rydberg series, although the basis set is apparently insufficient to resolve them completely. Moreover, the resonance transition into the $7a_1(\sigma^*)$ valence-like orbital is degenerate with the $2a_1-7a_1(\sigma^*)$ excitation indicated above, suggesting that localized-orbital calculations including relaxation are in order. The corresponding $1b_2-ka_1$ photoionization cross section shown in Fig. 6(b) is rapidly increasing at threshold, in accord with recent measurements in O$_2$. Finally, the $1b_2-7a_1$ excitations evidently comprise a weak Rydberg series, and the associated photoionization continuum apparently exhibits an $n$-d bound resonancelike broad maximum.

3. 1a$_1$ spectra (I. P. = 546.2 eV)

The $1a_1-np_2$ series of Table V evidently contains a strong $1a_1-5b_2(\sigma^*)$ transition and a very weak $1a_1-np_2$ Rydberg series, with a correspondingly weak unstructured photoionization continuum [Fig. 6(c)]. As in the $2a_1-7a_1$ series, there is a strong $1a_1-7a_1(\sigma^*)$ resonance in the $1a_1-na_1$ series of Table V and also interacting $n$-s, and $n$-p Rydberg series, the positions of which are in general accord with defect estimates. In this case the photoionization continuum of Fig. 6(c) is slightly increasing near threshold. The $1a_1-5b_2(\sigma^*)$ spectrum of Table V and Fig. 6(c) is evidently highly similar to that of the $2a_1$ orbital. Because the $1a_1$ transitions into the valence-like $5b_2(\sigma^*)$, $7a_1(\sigma^*)$, and $2b_2(\pi^*)$ virtual orbitals are not degenerate with the corresponding $2a_1$ and $1b_2$ excitations, the K-edge spectrum in O$_2$ below threshold will be more structured than that in O$_2$.

V. CONCLUDING REMARKS

The present studies provide an overall account of the vertical dipole excitation/ionization spectrum in molecular ozone in the IVO-static-exchange approximation. Use of the Stieltjes--Tchebycheff technique and conventional bound-state computational methods allows for discussion and clarification of the resulting discrete and continuous spectra on a common basis using familiar molecular-orbital concepts. It is found that the various excitation and ionization spectra can be understood in terms of contributions from valence-like virtual $2b_1(\pi^*)$, $5b_2(\sigma^*)$, and $7a_1(\sigma^*)$ orbitals and from more diffuse Rydberg-like orbitals. In addition, there is also evidence of contributions in $ka_1$ final-state symmetry from $kd$ atomic-like orbitals. Similar interpretations have also been employed previously in studies of diatomic and other polyatomic molecules.

Certain of the partial-channel photoexcitation/ionization cross sections in ozone are qualitatively similar to previously reported results in molecular oxygen. The $1a_2(n)$ and $1b_1(n)$ cross sections, in particular, are highly similar to $1a_1$ and $1b_1$ results in molecular oxygen, respectively, apparently as a consequence of the out-of-plane $\pi$ character of the $1a_1$ and $1b_1$ molecular orbitals. There are also similarities between the $6a_2(n)$ and $4b_2(n)$ cross sections in ozone and the $1s_\pi$ and $1s_\sigma$ channels in O$_2$, respectively. The similarity is less precise in these cases than it is for the $1a_2(n)$ and $1b_1(n)$ orbitals, however, apparently as a consequence of the largely in-plane $\pi$ character of the $6a_2$ and $4b_2$ canonical orbitals. Most striking, however, is the strong $\sigma-\sigma^*$ resonance in the $3b_2-6b_2$ channel, which is in qualitative accord with a closely related $\sigma-\sigma^*$ feature in the molecular oxygen $3a_2-4a_2$ cross section. The calculated K-edge spectra in O$_2$ also show similarities to recent photoabsorption cross-section measurements in O$_2$.

Although the results reported here are in accord with electron impact--excitation spectra and with general expectations, experimental partial-channel photoionization cross sections are not available for comparison at present. Of course, it will be necessary to combine the static-exchange cross sections with the results of intensity-borrowing ionic-state and Franck-Condon calculations prior to making detailed comparison with measured partial-channel cross sections, particularly in the inner-valence-shell region of the spectrum. In order to independently assess the reliability of the outer-valence-shell cross sections, which should be largely independent of the effects of shakeup in the ionic cores, it will be desirable to make comparisons with static-exchange cross sections based on ionization of more localized GVB orbitals, which can provide an appropriate description of the biradical character of ground state ozone. Similarly, it will also be helpful to compare in the K-edge region photoionization calculations employing relaxed localized hole states, rather than the symmetry orbitals employed in the present development. Furthermore, because static-exchange calcula-
tions can give incorrect positionalings of compact intra-valence transitions in certain cases, it will also be desirable to investigate the effects of configuration mixing in this connection. These topics are investigated separately in subsequent papers.

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