

Theoretical studies of photoexcitation and ionization in H₂O

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Theoretical studies are reported of the complete dipole excitation and ionization spectrum in H₂O employing Franck-Condon and static-exchange approximations. Large Cartesian Gaussian basis sets are used to represent the required discrete and continuum electronic eigenfunctions at the ground-state equilibrium geometry, and previously devised moment-theory techniques are employed in constructing the continuum oscillator-strength densities from the calculated spectra. Detailed comparisons are made of the calculated excitation and ionization profiles with recent experimental photoabsorption studies and corresponding spectral assignments, electron impact-excitation cross sections, and dipole ($e, 2e$)/($e, e + \text{ion}$) and synchrotron-radiation studies of partial-channel photoionization cross sections. The various calculated excitation series in the outer-valence ($1b_1^{-1}$, $3a_1^{-1}$, $1b_2^{-1}$) region are found to include contributions from valence-like $2b_2$ (σ^*) and $4a_1$ (γ^*) virtual orbitals, as well as appropriate nsa_1 , npa_1 , nda_1 , npb_1 , npb_2 , ndb_1 , ndb_2 , and nda_2 Rydberg states. Transition energies and intensities in the ~ 7 to 19 eV interval obtained from the present studies are seen to be in excellent agreement with the measured photoabsorption cross section, and to provide a basis for detailed spectral assignments. The calculated ($1b_1^{-1}$) X^2B_1 , ($3a_1^{-1}$) A_1 , and ($1b_2^{-1}$) B_2 partial-channel cross sections are found to be largely atomic-like and dominated by $2p \rightarrow kd$ components, although the $2b_2$ (σ^*) orbital gives rise to resonance-like contributions just above threshold in the $3a_1 \rightarrow kb_2$ and $1b_2 \rightarrow kb_2$ channels. It is suggested that the latter transition couples with the underlying $1b_1 \rightarrow kb_1$ channel, accounting for a prominent feature in the recent high-resolution synchrotron-radiation measurements. When this feature is taken into account, the calculations of the three outer-valence channels are in excellent accord with recent synchrotron-radiation and dipole ($e, 2e$) photoionization cross-sectional measurements. The calculated inner-valence ($2a_1^{-1}$) cross section is also in excellent agreement with corresponding measured values, although proper account must be taken of the appropriate final-state configuration-mixing effects that give rise to a modest failure of the Koopmans approximation, and to the observed broad PES band, in this case. Finally, the origins of the various spectral features present in the measured $1a_1$ oxygen K -edge electron energy-loss profile in H₂O are seen to be clarified fully by the present calculations.

I. INTRODUCTION

Photoprocesses in the water molecule are relevant to aspects of the aeronautical, astrophysical, and biological sciences.¹ Recent refinements in VUV synchrotron-radiation,^{2,3} electron-impact excitation,⁴ and dipole ($e, 2e$)/($e, e + \text{ion}$)⁵ spectroscopy have provided highly reliable experimental determinations of cross sections for photoexcitation, ionization, and dissociation in this important compound.⁶⁻⁸ In the present article, correspondingly reliable theoretical studies of the complete vertical-electronic dipole excitation and ionization spectrum in H₂O are reported. The overall character of the observed spectrum and its prominent features are clarified on the basis of the present calculations

in terms of elementary molecular-orbital concepts. Particular attention is paid in this to contributions from $2b_2$ and $4a_1$ virtual valence orbitals to the spectrum, an aspect of photoprocesses in H₂O that has apparently been the subject of some controversy.⁶⁻⁸

In order to discuss and clarify both the discrete and continuous spectra in H₂O from the common perspective of molecular-orbital calculations, it is convenient to employ in the development Stieltjes-Tchebycheff techniques previously devised for this purpose.^{9,10} A significant number of applications of this approach to molecular photoexcitation and ionization studies have been reported to date, largely in the one-electron vertical-electronic (Franck-Condon), separated-channel, static-exchange approximation.^{11,12} Methods have also been formulated for cases in which the effects of configura-

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tion interaction are of paramount importance in molecular photoionization, and detailed computational applications reported.¹³ In the present study of the electronic dipole spectrum in H₂O, separated-channel static-exchange calculations are found to provide generally satisfactory results, although there is also some evidence of channel coupling present in specific cases, as indicated below.

The calculated discrete excitation series converging on the $(1b_1^{-1})^2B_1$, $(3a_1^{-1})^2A_1$, and $(1b_2^{-1})^2B_2$ ionic limits are seen to include contributions from Rydberg as well as $4a_1$ and $2a_2$ valence-like orbitals. Both the positions and intensities of the calculated series are in excellent accord with recent VUV synchrotron-radiation studies, and would seem to account satisfactorily for all of the features in the observed spectrum.² Correspondingly, the calculated partial-channel photoionization cross sections for parent-ion production are in very good accord with the results of recent dipole (e , $2e$) and synchrotron-radiation studies.^{3,5} Resonance-like $2b_2$ contributions are found in kb_2 final-state symmetry just above threshold in both $(3a_1^{-1})^2A_1$ and $(1b_2^{-1})^2B_1$ channels, the latter feature apparently autoionizing into the $(1b_1^{-1})^2B_1$ channel, and accounting for a prominent maximum appearing in recent synchrotron-radiation measurements of the corresponding partial cross section.³ When this channel coupling is taken into account, it is seen that the present calculations are in excellent accord with the measured outer-valence-shell partial-channel cross sections.^{3,5} Because the Koopmans approximation is generally valid in H₂O,¹⁴⁻¹⁶ the separated-channel, static-exchange approximation gives cross sections in good accord with the measured values in the $2a_1$ inner-valence region.^{5,17} However, the effects of final-ionic-state configuration mixing are required to account for the large width of the measured photoelectron band in this interval.¹⁴⁻¹⁷ Finally, the calculated K -edge excitation and ionization cross section accounts satisfactorily for all of the prominent features in the measured electron-impact spectrum.⁴ Comparisons are made throughout of the present comprehensive results with previously reported theoretical studies of the discrete and continuous spectra in H₂O.¹⁸⁻³⁵

TABLE I. Dipole allowed excitation spectra in H₂O.^a

Orbital (HFIP/EVIP) ^b	$^1A_1 \rightarrow ^1B_1(x)$	$^1A_1 \rightarrow ^1B_2(y)$	$^1A_1 \rightarrow ^1A_1(z)$
$1b_1$ (13.76/12.61)→	a_1	a_2	b_1
$3a_1$ (15.41/14.73)→	b_1	b_2	a_1
$1b_2$ (19.50/18.55)→	a_2	a_1	b_2
$2a_1$ (37.02/32.2)→	b_1	b_2	a_1
$1a_1$ (559.46/539.7)→	b_1	b_2	a_1

^aDipole allowed final-state symmetries in H₂O for electric-field polarizations in the body frame in the x (out of plane), y , and z directions.

^bValues in parentheses refer to Hartree-Fock ionization potentials (HFIP) in eV calculated in a $(9s, 5p; 4s)[4s, 2p; 2s]$ basis (Refs. 41 and 42) (total HF energy = -76.0076 a.u.), and the experimental vertical ionization potentials (EVIP) of Turner *et al.*, (Ref. 15) and Siegbahn *et al.* (Ref. 14).

A brief discussion of the physical basis underlying the static-exchange approximation employed in the present development is presented in Sec. II. The discrete-basis-set methodology used to solve the appropriate static-exchange equations is given in Sec. III, and the results of the calculations are reported and discussed in Sec. IV. Some concluding remarks are made in Sec. V.

II. STATIC-EXCHANGE APPROXIMATION IN H₂O

Photoelectron spectra in H₂O exhibit five distinct bands that can be associated in the first (Koopmans) approximation with the removal of electrons from individual molecular orbitals having corresponding vertical ionization potentials [$1b_1$ (12.61 eV), $3a_1$ (14.73 eV), $1b_2$ (18.55 eV), $2a_1$ (32.2 eV), and $1a_1$ (539.7 eV)].¹⁴⁻¹⁷ Appropriate theoretical studies indicate the three outermost vertical ionic states are indeed Koopmans or single-hole like with two-hole one-particle configurations accounting for less than ~5% of the total wave functions in each case.³⁶ Similarly, the K -edge ionic state can be regarded as a strongly shifted Koopmans-like state, whereas there is some evidence that the inner-valence $2a_1$ PES band at 32.2 eV includes a number of satellite states in the 30 to 35 eV interval.^{5,17,36} In all five cases, however, it is clear that single-hole or Koopmans states provide the appropriate potentials for calculations of vertical electronic excitation/ionization spectra, since the effects of relaxation and reorganization apparently play a small role in vertical ionization in H₂O.

Appropriate excitation and ionization spectra are obtained in the present development from conventional configuration-interaction or Ritz variational calculations employing singlet-coupled many-electron wave functions of proper symmetry. In the separated-channel approximation these are written in the forms³⁷⁻⁴⁰

$$k\Phi_i^{(\gamma)} = (\phi_1 \phi_2 \dots k\phi_i^{(\gamma)} \dots \phi_N), \quad (1)$$

where the ϕ_i ($i=1, N$) are the occupied canonical ground-state Fock spin orbitals, the i th orbital ϕ_i has been replaced ($\phi_i \rightarrow k\phi_i^{(\gamma)}$) by the excitation or continuum orbital $k\phi_i^{(\gamma)}$ to be determined, γ is the channel label designating the final-state symmetry of excitation or ionization, and the parentheses indicate a singlet-coupled Slater determinant. The appropriate many-electron and orbital symmetries for dipole-allowed excitations in H₂O corresponding to the three independent body-frame polarization directions are conveniently tabulated in Table I. The orbitals $k\phi_i^{(\gamma)}$ can be determined by expansion in the virtual Fock orbitals, ϕ_α ($\alpha > N$), including the continuous portion of the spectrum, in conjunction with the Ritz principle

$$\delta E[k\Phi_i^{(\gamma)}] = \delta \langle k\Phi_i^{(\gamma)} | H | k\Phi_i^{(\gamma)} \rangle = 0, \quad (2)$$

where H is the total many-electron Hamiltonian. Alternatively, carrying out the variation of Eq. (2) explicitly gives the familiar static-exchange equations^{39,40}

$$(h_i - \epsilon) k\phi_i^{(\gamma)} = 0 \quad (3)$$

for the excitation/ionization orbitals $k\phi_i^{(\gamma)}$. Here ϵ refers to negative discrete or positive continuum energies, and

$$h_i = T + V + V_i^{(N-1)} \quad (4)$$

is the one-electron static-exchange Hamiltonian, with T and V kinetic and nuclear potential-energy operators, respectively, and $V_i^{(N-1)}$ the appropriate singlet-coupled static-exchange or hole potential obtained upon removal of an electron from the i th occupied orbital. In the case of ground-state H₂O, the hole potentials take the form

$$V_i^{(N-1)} = \hat{J}_i + \hat{K}_i + \sum_j 2\hat{J}_j - \hat{K}_j, \quad (5)$$

where the sum in j is over the Coulomb (\hat{J}_j) and exchange (\hat{K}_j) operators of the doubly occupied unexcited orbitals, and \hat{J}_i and \hat{K}_i refer to the orbital of the active or excited/ionized electron.

When solutions of Eqs. (1)–(5) are obtained, the vertical-electronic transition energies and oscillator strengths or densities are given by the familiar expressions

$$\omega_i = \epsilon - \epsilon_i, \quad (6a)$$

$$df_i^{(r)}/d\epsilon = (4/3) \omega_i |\langle k\phi_i^{(r)} | \mu | \phi_i \rangle|^2, \quad (6b)$$

where ϕ_i and ϵ_i are the i th canonical occupied orbital and energy, respectively, and the additional factor of 2 in Eq. (6b) arises from the use of singlet-coupled wave functions [Eq. (1)]. Since the vertical-electronic approximation is employed in Eqs. (1)–(6), the corresponding partial-channel cross sections

$$\sigma_{r,i}(\omega)(\text{Mb}) = 109.75 (df_i^{(r)}/d\epsilon)(\text{eV}^{-1}) \quad (7)$$

implicitly invoke vibrational and rotational closure in the vertical-electronic Franck–Condon approximation. Consequently, comparisons with appropriate corresponding experimental measurements that implicitly sum over vibrational and rotational states are clearly in order.

When configuration mixing between channels is potentially important, Eqs. (6) and (7) are still appropriate, although the orbitals of Eqs. (1)–(5) are inadequate. In such cases it is necessary to include in the Ritz variational calculations [Eq. (2)] configurations in which two or more occupied orbitals are individually excited ($\phi_i \rightarrow k\phi_i^{(r)}$, $\phi_j \rightarrow k\phi_j^{(s)}$). In this way the excitation or ionization orbitals required in Eqs. (6) and (7) are determined in the presence of mixing with other singly excited configurations involving different occupied and virtual orbitals. This approach can be designated as the couple channel static-exchange or Tamm–Dancoff approximation.

III. CALCULATIONS IN H₂O

In order to obtain solutions of Eqs. (1)–(5) it is necessary to first construct a suitable Hartree–Fock ground-state wave function. This is accomplished in the present study at the experimental equilibrium geometry [$R(\text{O}–\text{H}) = 1.81a_0$, $\theta(\text{H}–\text{O}–\text{H}) = 104.5^\circ$]⁴¹ employing a (9s, 5p; 4s)/[4s, 2p; 2s] Cartesian Gaussian basis set of standard type.^{41,42} The resulting total Hartree–Fock and canonical-orbital energies are shown in Table I, the latter in comparison with corresponding experimental values.^{14,15} It is seen that the HF or Koopmans values

for the outer three valence orbitals are in general accord with measured values, whereas there are larger discrepancies in the two deeper-lying orbitals. The total Hartree–Fock energy is in accord with results obtained from comparable basis sets.⁴¹

Discrete-basis-set methodology is employed in the present development to obtain solutions of Eqs. (1)–(5) for both negative and positive energies. Large supplemental Gaussian basis sets are employed in conjunction with the valence basis used in the ground-state calculation in construction of virtual Fock states. These, in turn, are used to represent the static-exchange orbitals of Eqs. (1) and (5) employing conventional procedures.⁴³

In Table II are shown supplemental basis sets used in conjunction with the valence basis in the present calculations in H₂O. The orbital exponents are chosen as extensions of those in the valence basis in order to form an even-tempered sequence having successive exponent ratios of ~ 1.8 . It is seen that the basis sets, therefore, include very compact and very diffuse functions, approaching linear dependence in the interval. Such basis sets have been found previously to provide spectrally complete pseudostates in other molecules.^{11–13} Those static-exchange pseudostates lying below threshold provide approximations directly to the corresponding Rydberg or valence states, whereas those lying above threshold provide the information required in construction of the corresponding oscillator-strength density and

TABLE II. Supplemental Cartesian Gaussian basis sets employed in H₂O pseudospectral calculations.^a

Type	Number ^b	Exponent range ^c
<i>a</i> ₁ (46) symmetry		
<i>s</i>	8	0.158–0.001
<i>p_z</i>	8	0.119–0.001
<i>d_{x²–y²}</i> , <i>d_{xy}</i> , <i>d_{z²}</i>	12, 12, 12	0.85–0.001
<i>a</i> ₂ (12) symmetry		
<i>d_{xy}</i>	12	0.85–0.001
<i>b</i> ₁ (21) symmetry		
<i>p_x</i>	8	0.119–0.001
<i>d_{xz}</i>	12	0.85–0.001
<i>b</i> ₂ (23) symmetry		
<i>p_y</i>	8	0.119–0.001
<i>d_{yz}</i>	12	0.85–0.001

^aBasis functions employed, in addition to the target (9s, 5p; 4s)/[4s, 2p; 2s] valence basis, in the solution of Eqs. (1)–(5). All functions are located on the oxygen nucleus.

^bNumbers in parentheses give the dimensionalities of resulting virtual Fock pseudospectra. In the case of *a*₁ symmetry the 46-term virtual spectrum obtained is arbitrarily truncated by deleting the six highest-lying virtual Fock orbitals obtained. Consequently, the separated-channel static-exchange pseudospectra obtained in this case are comprised of 40 terms each.

^cAn exponent ratio of 1.8 for successive values is employed in the indicated ranges.

photo cross section [Eq. (7)] following the previously described moment methods.^{9,10}

The computational methodology employed in the present development is the same for each particular excitation/ionization channel considered (Table I). A large one- and two-electron integral tape is first written over the entire list of valence and supplemental (Table II) basis orbitals. Smaller tapes are then constructed from this master upon which are written the integrals required in the construction of the pseudospectra for the individual channels of Table II. These smaller tapes are then transformed in the construction of virtual Fock symmetry orbitals appropriate for the final-state symmetry of interest. Single-excitation CI calculations are then performed and all roots and vectors are obtained, from which the transition frequencies and strengths of Eqs. (6) are constructed. Note that the development is the same in the cases of uncoupled and coupled-channel calculations, although the integral tapes and CI matrices are, of course, larger in the latter case.

IV. PHOTOEXCITATION AND IONIZATION IN H₂O

In order to interpret the origins of the various features in the calculated and measured photo cross sections reported below, it is helpful to first recall the general natures of the occupied and virtual canonical orbitals in H₂O.⁴⁴ The outer-valence region is comprised of $1b_1(\pi)$, $3a_1(\gamma)$, and $1b_2(\sigma)$ orbitals which are largely of nonbonding π_x type, angular or torsional γ -bonding type, and O-H σ -bonding type, respectively, whereas the inner valence $2a_1(2s)$ and K -edge $1a_1(1s)$ orbitals are largely $2s$ and $1s$ oxygen-like, respectively. There is also some evidence, however, of O-H bonding character present in the $2a_1$ orbital. The virtual spectrum will be comprised of $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ antibonding valence-like orbitals, as well as more diffuse molecular orbitals of good symmetry type made up of s , p , d , and higher angular momentum atomic Rydberg orbitals. The continuous region of the orbital spectrum will include Coulombic type functions that are natural continuations of the Rydberg series, as well as possible contributions from the valence $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ orbitals indicated above.

In the following subsections the calculated photoexcitation and ionization spectra in H₂O in the outer-valence ($1b_1$, $3a_1$, $1b_2$), inner-valence ($2a_1$), and K -edge ($1a_1$) regions are described and discussed, and comparisons are made with corresponding experimental and previously reported theoretical studies.

A. Valence region in H₂O

In Fig. 1 is given a semiquantitative overview of the calculated separated-channel series associated with excitation of electrons from the three outermost orbitals in H₂O. Also shown in the figure is the total photo cross section obtained from synchrotron-radiation measurements that achieve ~ 0.03 Å spectral resolution.² More detailed quantitative descriptions of the calculated excitation series and photoionization cross sections in the separated-channel approximation are given in Tables III

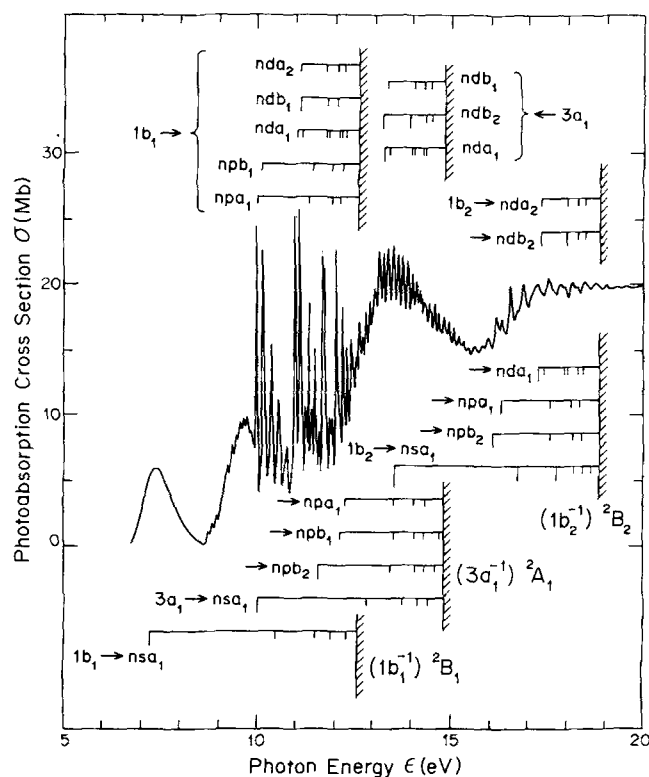


FIG. 1. Outer-valence-shell photoabsorption cross section in H₂O; experimental values from the synchrotron radiation measurements of P. Gürtler, V. Saile, and E. E. Koch (Ref. 2); theoretical values and assignments from separated-channel static-exchange (IVO) calculations employing the basis sets of Table II as described in the text; intensity scale: strong, $f > 0.1$; medium, $0.1 > f > 0.01$; weak, $f < 0.01$.

to VI and Figs. 2 to 4, respectively. As in previous studies,^{11,12} the calculated discrete excitation series are made to converge on the experimentally observed,^{14,15} rather than Hartree-Fock, vertical-ionization potentials (Table I).

1. $1b_1$ (I.P. = 12.61 eV) spectrum

It is seen from Table III that well-defined $1b_1 \rightarrow nsq_1$, npa_1 , nda_1 ; npb_1 , ndb_1 ; and nda_2 series are obtained from the calculations, in very good accord with the assignments based on measured values also shown in the table. Note that the calculations include mixing among the various Rydberg states of given molecular orbital symmetry, but that the series nevertheless separate into s , p , and d components having approximate quantum defects of 1.4, 0.7, and 0, respectively. Quantum-defect and Coulomb estimates of transition energies and f numbers, respectively, obtained using these values are also shown in Table III to aid in the series identification.^{8,45} The various calculated $1b_1$ excitations are in accord with some of the previously reported theoretical studies,¹⁸⁻³⁰ although in many cases these do not employ sufficient numbers of the compact and diffuse basis functions (Table II) required to satisfactorily describe the relevant states (see Table VI).

TABLE III. $1b_1$ (I. P. = 12.61 eV) excitation spectra in H₂O.

Present results ^a [energy (eV)/f number]	Experimental values ^b [energy (eV)/intensity]	Defect estimates ^c [energy (eV)/f number]
$1b_1 \rightarrow nsa_1/4a_1$		
7.24/0.020 79	7.44/strong	7.30/0.000 60
10.53/0.000 14	10.64/weak	10.60/0.000 14
11.53/...	...	11.56/0.000 05
11.95/...	...	11.97/0.000 03
12.37/...	...	12.18/0.000 01
$1b_1 \rightarrow npa_1$		
9.98/0.006 48	9.998/sharp	10.04/0.005 08
11.35/0.002 49	11.374/	11.36/0.002 78
11.87/0.001 04	11.890/	11.87/0.001 26
12.20/...	12.120/	12.13/0.000 67
...	12.288/	12.27/0.004 40
...	12.361/	12.35/0.000 26
...	12.411/	12.41/0.000 18
$1b_1 \rightarrow nda_1$		
11.05/0.006 40	10.990/sharp	11.10/0.019 3
11.15/0.002 78	11.122/	...
11.76/0.003 23	11.729/	11.76/0.008 1
11.81/0.002 35
12.09/0.001 15	...	12.07/0.004 2
12.12/...
12.25/...	...	12.23/0.002 4
...
$1b_1 \rightarrow npb_1$		
10.10/0.001 76	10.171/sharp	10.04/0.001 23
11.37/0.000 33	11.432/	11.36/0.000 42
11.86/0.000 21	...	11.87/0.000 19
12.21/0.000 11	...	12.13/0.000 10
$1b_1 \rightarrow ndb_1$		
11.11/0.015 5	11.057/sharp	11.10/0.010 3
11.74/0.005 3	11.770/	11.76/0.004 4
12.04/0.004 0	12.061/	12.07/0.002 2
...	12.235/	12.23/0.001 3
...	12.337/	12.27/0.000 8
...	12.399/	12.36/0.000 6
...	12.448/	12.41/0.000 4
$1b_1 \rightarrow nda_2$		
11.09/0.005 16	11.055/sharp	11.10/0.011 5
11.75/0.002 95	...	11.76/0.004 8
12.06/0.001 69	...	12.07/0.002 5
12.24/0.001 35	...	12.23/0.001 4
12.57/...	...	12.36/0.000 9

^aVertical excitation energies obtained from the separated-channel static-exchange development of Eqs. (1)–(7) employing the basis sets of Table II. The values shown are made to converge on the experimentally observed vertical ionization potential of 12.61 eV (Ref. 15). In the case of $1b_1 \rightarrow nda_1$ excitations, two separate $nd(x^2)$ and $nd(x^2 - y^2)$ series are obtained. Previously reported calculations of the lowest few excitations in various approximations [Refs. 18–30] employing smaller basis sets than those of Table II are in general accord with the present results (see Table VI).

^bExperimental positions taken from the measurements of P. Gürtler, V. Saile, and E. E. Koch (Ref. 2). See also H.-t. Wang, W. S. Felps, and S. P. McGlynn (Ref. 6). Approximate intensity designations are made here on the basis of the measured cross section. The higher members of the measured np and nd series are here assigned as $1b_1 \rightarrow npa_1$ and ndb_1 excitations, respectively, on the basis of calculated intensities. Although the latter assignment is in accord with Wang *et al.* (Ref. 6), the former is not.

^cQuantum-defect estimates obtained for $n=3, 4, \dots$ from the Rydberg formula [$\epsilon_n = \epsilon_t - 13.6 \text{ eV}/(n - \delta)^2$] and Coulomb approximation [$f_n = g(\epsilon_t)/(n - \delta)^3$], where δ is the appropriate defect and $g(\epsilon_t)$ is the photoionization oscillator-strength density at threshold in Hartree a.u. [Fig. 2(a)]. Procedures employed in separating the total $g(\epsilon_t)$ values into the contributions from the various Rydberg series discussed in the text give $1b_1 \rightarrow ka_1$; $ks=0.0$, $kp=0.1$, $kd=0.52$; $1b_1 \rightarrow kb_1$, $kp=0.015$, $kd=0.28$; $1b_1 \rightarrow ka_2$, $kd=0.31$, all in a.u. The defects employed are $\delta=1.40$, 0.7 , and 0 for ns , np , and nd series, respectively, in general accord with the corresponding oxygen-atom values of $\delta=1.20$, 0.76 , and 0.03 (Ref. 8). In the case of the nda_1 excitations, the indicated quantum-defect values are appropriate for both $nd(x^2)$ and $nd(x^2 - y^2)$ series.

The (1.40) defect of the $1b_1 - ns a_1$ series is somewhat larger than the corresponding free oxygen-atom value of 1.2,⁸ and the f number of the resonance ($n=3$) transition is significantly larger than that obtained from the Coulomb approximation, suggesting that the $4a_1(\gamma^*)$ valence orbital perturbs the entire series. This observation is verified by examination of the calculated static-exchange orbitals, which are seen to include admixtures of the $4a_1(\gamma^*)$ orbital. Note, however, that only the lowest ($n=3$) member of the $1b_1 - ns a_1/4a_1(\gamma^*)$ series has a substantial f number, a situation clarified by the significantly larger $4a_1(\gamma^*)$ contribution to the former than to the higher-lying members of the series. The resonance transition is known to photodissociate into $\text{OH}(X^2\Pi) + \text{H}(^2S)$ radical fragments,⁸ accounting for the broad, diffuse nature of the band (Fig. 1). Presumably, a diabatic dissociative surface associated with the $1b_1^{-1}4a_1(\gamma^*)$ configuration crosses the $1b_1 - ns a_1$ Rydberg series in the immediate vicinity of the ground-state vertical Franck-Condon region. It is perhaps remarkable that there has been little discussion of the intravalence nature of this strong dissociative transition in H₂O.⁶⁻⁸

The $1b_1 - np a_1$ and $np b_1$ series of Fig. 1 and Table III are seen to be largely Rydberg in character, with defects of ~ 0.7 , in good accord with the corresponding free oxygen-atom value of 0.76.⁸ Moreover, the calculations are in good agreement with the measured positions and intensities, confirming the spectral assignments in these cases. The higher members of the measured np series are given the assignment $1b_1 - np a_1$ on the basis of the larger calculated f numbers relative to the $1b_1 - np b_1$ series.

Evidently, four distinct $1b_1 - nd$ series, i.e., $1b_1 - nd(x^2 - y^2)a_1$, $nd(x^2 - y^2)a_1$, $nd b_1$, and nda_2 , all having quantum defects of ~ 0 , are obtained from the calculations. These are seen to be largely Rydberg in character, and are in generally good agreement with the positions and intensities of the four assigned nd series.^{2,45} Note that, as might be expected, the f numbers of the nd series are uniformly larger than those of the corresponding $np a_1$ and $np b_1$ series.

With the exception of strong broad structures at ~ 9.7 and 11.5 eV, which are discussed separately further below, the calculated discrete series of Table III are seen to account for all of the spectral features below the $(1b_1^{-1})^2B_1$ threshold (12.61 eV) in the measured photoabsorption cross section (Fig. 1).

In Fig. 2(a) are shown the $1b_1 - ka_1$, ka_2 , and kb_1 contributions to the $(1b_1^{-1})^2B_1$ partial-channel photoionization cross section in H₂O, as well as the sum of these in comparison with measured values.^{3,5} It is seen that the $1b_1 - kb_1$ and ka_2 contributions are indistinguishable from one another, and that the $1b_1 - ka_1$ component is approximately twice these values. The former observation is understood by noting that the $1b_1(\pi)$ orbital is purely atomic oxygen $2p_x$ in character, and that the $kp_x b_1$ orbital contributions (Table II) to $1b_1 - kb_1$ ionization are expected to be negligible, with the threshold cross section for $1b_1 - kp_x b_1$ ionization estimated (Table III) to be an order of magnitude smaller than $1b_1 - kdb_1$.

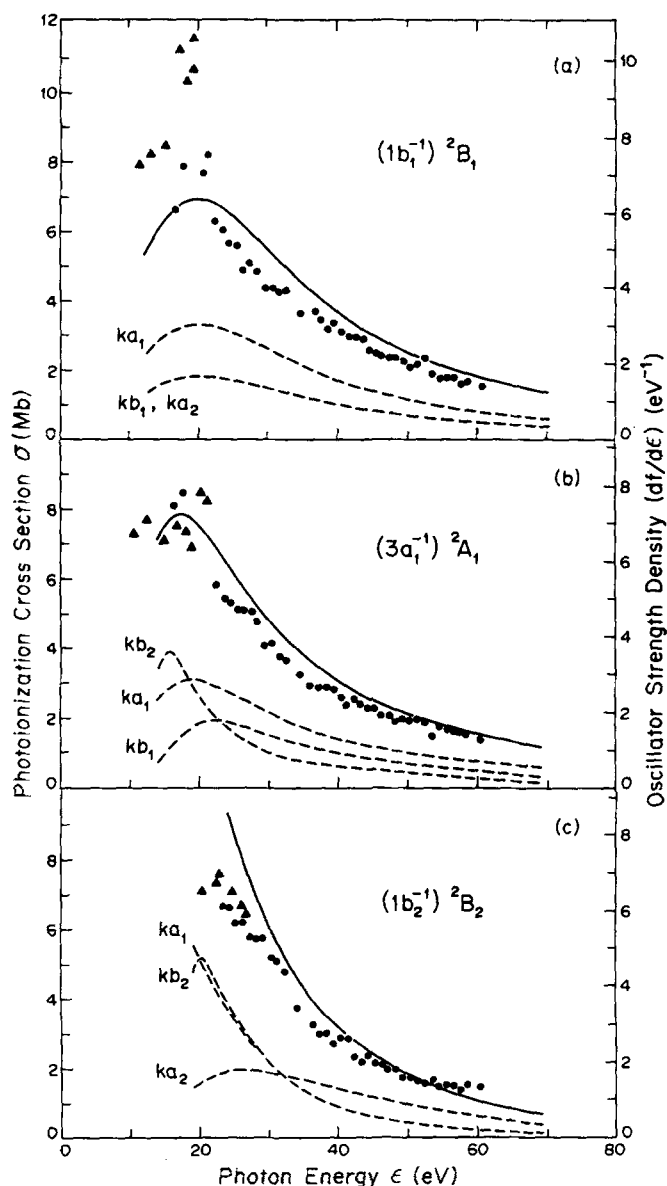


FIG. 2. Outer-valence-shell partial-channel photoionization cross sections in H₂O. (a) $(1b_1^{-1})^2B_1$ cross section; (—) vertical-electronic static-exchange calculations; (---) static-exchange polarization components as indicated; (●) dipole (e , $2e$) measurements of K. H. Tan, C. E. Brion, Ph. E. Van der Leeuw, and M. J. Van der Wiel (Ref. 5); (▲) synchrotron-radiation measurements of O. Dutuit, K. Ito, A. Tabche-Fouhaile, P. Morin, T. Baer, P. M. Guyon, and I. Nenner (Ref. 3); (b) As in (a) for $(3a_1^{-1})^2A_1$ ionization, (c) as in (a) for $(1b_2^{-1})^2B_2$ ionization.

Consequently, both $1b_1 - kb_1$ and ka_2 cross sections are purely $2p_x - kd_{xz}$ and kd_{xy} atomic-like, respectively, in nature, and therefore can be expected to be identical. Similarly, the $1b_1 - kda_1$ component is seen from Table III to dominate the ka_1 contribution. In this case, however, both $kdz^2 a_1$ and $kd(x^2 - y^2)a_1$ contributions are present, giving rise to a cross section approximately twice those for the two other (x and y) polarization components.

The calculated $(1b_1^{-1})^2B_1$ separated-channel static-ex-

change cross section is evidently in good agreement with the dipole (*e*, 2*e*) measurements, whereas there is a prominent feature at ~18 to 20 eV in the synchrotron-radiation measurements not present in the calculated profile. It is unlikely that a feature of this nature can arise as a consequence of static-potential shape-resonance effects. Rather, as is discussed further below, autoionization of states converging upon higher limits are more likely candidates, with $1b_2 \rightarrow 3s a_1 / 4a_1$ and $2b_2$ excitations favored, in particular. When this feature is accounted for in such a manner, as is discussed further below, it is seen that the measured values for the $(1b_1^{-1})^2 B_1$ partial cross section are in good agreement with the present calculations. The corresponding (*e*, *e* + ion) measurements,⁵ as well as PES band shapes,^{15,16} suggest the $(1b_1^{-1})^2 B_1$ cross section results in the production of H₂O⁺ parent ions only,⁵ with no evidence of radical fragments, in general accord with the largely non-bonding character of the $1b_1(\pi)$ orbital.

2. $3a_1$ (I.P. = 14.73 eV) spectrum

In Table IV are shown the calculated $3a_1 \rightarrow n a_1$, $n b_2$, and $n b_1$ excitations, which are seen to separate into well-defined $n s a_1$, $n p a_1$, $n d a_1$; $n p b_2$, $n d b_2$; and $n p b_1$, $n d b_1$ series, respectively. The $3a_1 \rightarrow n s a_1$ series contains a $3s a_1 / 4a_1$ partially intravalence resonance member at ~9.9 eV that is seen to be stronger than the defect estimate, whereas the higher members of the series are weak with defect-like *f* numbers ($\delta = 1.4$), a behavior in accord with the $1b_1 \rightarrow n s a_1$ series discussed above. The position and intensity of the resonance in this case, which is known to dissociate into OH($A^2\Sigma^+$) + H(2S) radical fragments,⁶ is in excellent agreement with measured values,^{2,7} whereas the higher members of the series are apparently too weak to be observed.

Of the three calculated *np* series ($3a_1 \rightarrow n p a_1$, $n p b_1$, and $n p b_2$), the first two are seen to be purely Rydberg in character ($\delta = 0.7$), whereas the resonance *f* number in the $3a_1 \rightarrow n p b_2$ series is significantly larger than the corresponding defect estimate. Examination of the appropriate orbitals reveals the presence of contributions from the $2b_2(\sigma^*)$ valence orbital, accounting for the large *f* number and the significantly lower position in the spectrum of this transition. Careful examination of the measured photo-cross section of Fig. 1 suggests the presence of a broad feature at ~11.5 eV underlying the Rydberg series converging on the $(1b_1^{-1})^2 B_1$ limit which can be given the designation $3a_1 \rightarrow 3p b_2 / 2b_2(\sigma^*)$ on the basis of the present calculations. This feature has apparently not been previously assigned in the discrete spectrum of H₂O.⁶⁻⁸ Because the weaker higher members of the $3a_1 \rightarrow n p b_2$ series, and of the $n p a_1$ and $n p b_1$ series, overlap with other strong transitions (Fig. 1), detailed spectral assignments are not possible in these cases. However, the positions of the experimentally assigned $3a_1 \rightarrow 4p$ (13.5 eV), $5p$ (14.1 eV) excitations are in general accord with the calculated values. The presence of vibrational structure in the strong feature in the ~13 to 14 eV interval of the photo cross section similar to that observed in the $3a_1^{-1}$ PES band¹⁵ can be attributed to intensity borrowing of the weak $3a_1 \rightarrow n p$ series from the strong $1b_2 \rightarrow 3s a_1 / 4a_1$ intravalence transition (see below).

Of the four calculated $3a_1 \rightarrow n d$ series [$3a_1 \rightarrow n d(x^2) a_1$, $n d(x^2 - y^2) a_1$, $n d b_2$, and $n d b_1$], the $n d(x^2) a_1$ and $n d b_2$ transitions are seen to be relatively strong and to overlap to a considerable degree. The two resonance transitions in these series account for a portion of the strong feature centered at ~13.5 eV in the photo cross section (Fig. 1), which is seen to exhibit a vibrational structure similar to that of the measured $(3a_1^{-1})^2 A_1$ PES band.^{15,16} The higher members of these two series, as well as the members of the weaker $3a_1 \rightarrow n d(x^2 - y^2) a_1$ and $n d b_1$ Rydberg series, are presently unassigned.

In Fig. 2(b) are shown the calculated $3a_1 \rightarrow k a_1$, $k b_1$, and $k b_2$ photoionization components and the total $(3a_1^{-1})^2 A_1$ partial cross section in comparison with measured values.^{3,5} It is seen that the $3a_1 \rightarrow k a_1$ and $k b_1$ components are somewhat similar to the $1b_1 \rightarrow k a_1$ and $k b_1$ profiles of Fig. 2(a). This is a consequence of the similarity of $2p$ orbital natures of the $3a_1$ and $1b_1$ molecular orbitals. However, the presence of $2s$ hybridization and $1s$ H-atom contributions in the $3a_1$ orbital expand it somewhat spatially, resulting in ionization profiles that are peaked at lower energies than in the corresponding $1b_1$ ($\rightarrow k a_1$ and $k b_1$) cases. In contrast to these, the $3a_1 \rightarrow k b_2$ profile of Fig. 2(b) is seen to contain a prominent feature just above threshold that can be attributed to contributions from the $2b_2(\sigma^*)$ valence orbital. This orbital also contributes to the resonance transition in the $3a_1 \rightarrow n p b_2$ series (Table IV), suggesting the presence of a diabatic $(3a_1^{-1} 2b_2)$ surface that cuts rather sharply through the Franck-Condon region in this case, resulting in a splitting of intensity between the discrete and continuous regions of the spectrum. A similar situation is observed in the $1\pi_g \rightarrow n \sigma_u / k \sigma_u$ cross section in O₂.⁴⁷ Evidently, the calculated $(3a_1^{-1})^2 A_1$ cross section is in very good agreement with the measured (*e*, 2*e*) and synchrotron-radiation values.^{3,5} Corresponding (*e*, *e* + ion) measurements, as well as the PES band shapes,^{15,16} suggest that the $(3a_1^{-1})^2 A_1$ channel results in production of H₂O⁺ parent ions only, in accordance with the largely angular bonding nature of the $3a_1(\gamma)$ orbital.

3. $1b_2$ (I.P. = 18.55 eV) spectrum

The calculated $1b_2 \rightarrow n a_1$, $n b_2$, and $n a_2$ excitations of Table IV are seen to separate into well-defined $n s a_1$, $n p a_1$, $n d a_1$; $n p b_2$, $n d b_2$; and $n d a_2$ series. The resonance in the $n s a_1$ series is the strongest feature in the entire spectrum, and apparently accounts for much of the broad strong band centered at ~13.5 eV in the measured cross section.² This assignment is in general accord with Gürtler *et al.*,² who place the resonance at ~13.8 eV, apparently on basis of quantum-defect estimates. As indicated above, the near degeneracy of the strong $1b_2 \rightarrow 3s a_1 / 4a_1$ resonance with weaker $3a_1 \rightarrow n p$ and *nd* excitations suggests configuration mixing in the ~13 to 14 eV interval, presumably accounting for the $3a_1^{-1}$ PES band vibrational structure in the measured photoabsorption cross section. The measured ionization curve suggests formation of neutral fragments in this interval,⁷ in accord with the dissociative character of the diabatic $1b_2^{-1} 4a_1$ configuration. The calculated positions of the higher members of the series are also in general agreement with the experimental assignments. The second

TABLE IV. $3a_1$ (I. P. = 14.73 eV) and $1b_2$ (I. P. = 18.55 eV) excitation spectra in H₂O.

Present results ^{a,b} [energy (eV)/f number]	Defect estimates ^c [energy (eV)/f number]	Present results ^{a,b} [energy (eV)/f number]	Defect estimates ^c [energy (eV)/f number]
$3a_1 \rightarrow nsa_1/4a_1$		$1b_2 \rightarrow nsa_1/4a_1$	
9.88/0.0670	9.42/0.0381	13.23/0.1755	13.24/0.1956
12.77/0.0069	12.72/0.0089	16.47/0.0436	16.54/0.0579
13.67/0.0032	13.68/0.0033	17.44/0.0165	17.50/0.0172
14.07/0.0014	14.09/0.0016	17.86/0.0083	17.91/0.0082
14.33/...	14.30/0.0009	18.10/...	18.12/0.0046
		18.28/...	18.24/0.0028
$3a_1 \rightarrow npa_1$		$1b_2 \rightarrow npa_1$	
12.24/0.000185	12.16/0.000369	15.97/0.0142	15.98/0.0127
13.51/0.000091	13.48/0.000091	17.28/0.0044	17.30/0.0043
13.99/...	13.99/0.000041	17.79/0.0014	17.81/0.0020
14.30/...	14.25/0.000022	18.05/...	18.07/0.0010
$3a_1 \rightarrow nda_1$		$1b_2 \rightarrow nda_1$	
13.14/0.0133	13.22/0.0181	16.95/0.01200	17.04/0.0147
13.23/0.0094	...	17.10/0.00019	...
13.85/0.0045	13.88/0.0076	17.67/0.00870	17.70/0.0062
13.90/0.0030	...	17.73/0.00013	...
14.19/0.0035	14.19/0.0039	18.00/...	18.01/0.0032
14.24/0.0001	...	18.19/...	...
$3a_1 \rightarrow npb_2/2b_2$		$1b_2 \rightarrow npb_2/2b_2$	
11.53/0.03763	12.16/0.00518	15.77/0.0187	15.98/0.0143
13.35/0.00266	13.48/0.00175	17.27/0.0046	17.30/0.0048
13.97/0.00090	13.99/0.00079	17.81/0.0023	17.81/0.0022
14.25/0.00039	14.25/0.00042	18.07/0.0011	18.07/0.0012
14.54/...	14.39/0.00025		
$3a_1 \rightarrow ndb_2$		$1b_2 \rightarrow ndb_2$	
13.13/0.0315	13.22/0.0266	17.04/0.0271	17.04/0.0344
13.86/0.0157	13.88/0.0112	17.70/0.0132	17.70/0.0145
14.19/0.0080	14.19/0.0057	18.01/0.0080	18.01/0.0074
14.39/0.0043	14.35/0.0033	18.19/0.0043	18.17/0.0043
14.76/...	14.45/0.0021		
$3a_1 \rightarrow npb_1$		$1b_2 \rightarrow nda_2$	
12.08/0.00194	12.16/0.00214	17.03/0.0066	17.04/0.0139
13.45/0.00067	13.48/0.00072	17.70/0.0037	17.70/0.0059
13.97/0.00031	13.99/0.00033	18.01/0.0021	18.01/0.0030
14.23/0.00018	14.25/0.00018	18.18/0.0017	18.17/0.0017
14.67/...	14.39/0.00010		
$3a_1 \rightarrow ndb_1$			
13.25/0.00400	13.22/0.00769		
13.88/0.00235	13.88/0.00325		
14.18/0.00137	14.19/0.00166		
14.35/0.00107	14.35/0.00096		
14.75/...	14.45/0.00061		

^aAs in Table III, footnote a, employing the indicated experimentally observed vertical ionization potentials (Ref. 15).

^bExperimental values for $3a_1 \rightarrow 3s$ (9.85 eV), $\rightarrow 4s$ (12.9 eV), $\rightarrow 4p$ (13.5 eV), $\rightarrow 5p$ (14.1 eV), $1b_2 \rightarrow 3s$ (13.8 eV), and $\rightarrow 4s$ (16.9 eV) excitations are reported by P. Gürtler, V. Saille, and E. E. Koch (Ref. 2), in general accord with the calculated values.

^cAs in Table III, footnote c, employing the threshold oscillator-strength densities of Figs. 2(b) and 2(c). The estimated threshold contributions from the various Rydberg symmetry contributions are $3a_1 \rightarrow ka_1$; $ks=0.16$, $kp=0.0033$, $kd=0.49$; $3a_1 \rightarrow kb_2$, $kp=0.063$, $kd=0.72$; $3a_1 \rightarrow kb_1$, $kp=0.026$, $kd=0.22$; $1b_2 \rightarrow ka_1$; $ks=0.80$, $kp=0.16$, $kd=0.40$; $1b_2 \rightarrow kb_2$, $kp=0.17$, $kd=0.93$, $1b_2 \rightarrow ka_2$, $kd=0.37$, all in a.u.

and third members of the series, in particular, carry relatively large f numbers, giving rise to vibrational structures in the measured photoabsorption cross section similar to that observed in the $1b_2^{-1}$ PES band.^{15,16}

The calculated $1b_2 \rightarrow npa_1$ and npb_2 series are seen to be largely Rydberg in character ($\delta=0.7$), although the resonance $1b_2 \rightarrow 3pb_2$ transition is evidently lowered somewhat by a contribution from the $2b_2(\sigma^*)$ valence orbital. Because these series are weak, they are apparently obscured in the measured cross section by other stronger series (Fig. 1), accounting for the lack of assignments in these cases.

The four calculated $1b_2 \rightarrow nd$ series when taken together are relatively strong, but overlap with the nsa_1 series, making spectral assignment difficult in this case. However, the calculated positions and intensities are evidently in very good agreement with the quantum-defect estimates employing the value $\delta=0$, verifying the Rydberg character of the nd series.

The three calculated partial-channel photoionization components $1b_2 \rightarrow ka_1$, kb_2 , and ka_2 are shown in Fig. 2(c), together with the $(1b_2^{-1})^2B_2$ sum in comparison with measured values.^{3,5} Of these, the $1b_2 \rightarrow ka_2$ profile exhibits the familiar $2p \rightarrow kd$ behavior, whereas the $1b_2 \rightarrow kb_2$ profile apparently contains a $2b_2(\sigma^*)$ or $\sigma \rightarrow \sigma^*$ contribution just above threshold, similar to the $3a_1 \rightarrow kb_2$ component of Fig. 2(b). However, the $1b_2 \rightarrow ka_1$ profile differs considerably from the $2p \rightarrow kd$ like profiles of Figs. 2(a) and 2(b) in that there is evidently a very large $1b_2 \rightarrow ksa_1$ threshold contribution (see also Table IV). Because of this large $1b_2 \rightarrow ka_1$ threshold value, as well as that of the $1b_2 \rightarrow kb_2$ contribution, there is a noticeable discrepancy between theory and experiment in the $(1b_2^{-1})^2B_2$ cross section in the ≈ 20 to 30 eV interval. Comparisons of Figs. 2(a) and 2(c) suggest that the prominent feature at ~ 18 to 20 eV in the measured $(1b_1^{-1})^2B_1$ channel can be attributed to possible autoionization of the $1b_2 \rightarrow 2b_2(\sigma^*)$ contribution in the $1b_2 \rightarrow kb_2$ cross section into the $1b_1 \rightarrow kb_1$ continuum background. In addition, configuration mixing of the $1b_2 \rightarrow 4a_1$ intravalence excitation with $3a_1 \rightarrow np$ and nd series can reduce the threshold value of the corresponding $1b_2 \rightarrow ka_1$ photoionization cross section. This process can presumably produce neutral fragments in excited electronic states, resulting in a competition between fluorescence and autoionization, in accord with recent observations of Balmer β emission from H₂O with a threshold at 17.87 eV.³ Additional evidence for the production of neutral excited species in the ~ 18 to 20 eV interval in H₂O is provided by a prominent feature in the difference of the measured absorption and ionization cross sections.⁷ Finally, the situation is further complicated by the dissociative nature of the $(1b_2^{-1})^2B_2$ ionic state, which leads to production of OH⁺ and H⁺ fragments, as well as H₂O⁺ parent ions.⁵

The foregoing remarks suggest that a complete quantitative understanding of photoionization in the $(1b_1^{-1})^2B_1$ and $(1b_2^{-1})^2B_2$ channels of H₂O requires that the effects of configuration mixing be incorporated into the development. By contrast, the $(3a_1^{-1})^2A_1$ continuum is apparently largely one electron in nature, and is described satis-

factorily by the separated-channel static-exchange approximation.

4. $2a_1$ (I.P. = 32.3 eV) spectrum

The calculated inner-valence $2a_1 \rightarrow na_1$, nb_2 , and nb_1 excitations of Table V are seen to be generally weak,

TABLE V. $2a_1$ (I. P. = 32.2 eV) excitation spectra in H₂O.

Present results ^a energy (eV)/ f number]	Defect estimates ^b [energy (eV)/ f number]
$2a_1 \rightarrow nsa_1/4a_1$	
27.31/0.00935	26.89/0.00854
30.23/0.00149	30.19/0.00199
31.15/0.00089	31.15/0.00075
31.55/0.00025	31.56/0.00036
31.85/0.00021	31.77/0.00020
$2a_1 \rightarrow npa_1$	
29.62/0.00805	29.63/0.00230
30.95/0.00030	30.95/0.00078
31.46/0.00051	31.46/0.00035
31.79/0.00018	31.72/0.00019
$2a_1 \rightarrow nda_1$	
30.61/0.000233	30.69/0.000370
30.76/0.000017	...
31.33/0.000155	31.35/0.000156
31.40/0.000043	...
31.66/0.000066	31.66/0.000080
31.71/...	...
31.98/...	31.82/
$2a_1 \rightarrow npb_1$	
29.47/0.00217	29.63/0.00222
30.91/0.00084	30.95/0.00075
31.45/0.00043	31.46/0.00034
31.72/0.00025	31.72/0.00018
$2a_1 \rightarrow ndb_1$	
30.78/0.00024	30.69/0.00081
31.39/0.00014	31.35/0.00035
31.68/0.00008	31.66/0.00018
31.85/0.00001	31.82/0.00010
$2a_1 \rightarrow npb_2/2b_2$	
28.77/0.00753	29.63/0.00205
30.78/0.00095	30.95/0.00070
31.40/0.00047	31.46/0.00031
31.68/0.00025	31.72/0.00017
$2a_1 \rightarrow ndb_2$	
30.51/0.00253	31.82/0.00030
31.26/0.00102	30.69/0.00241
31.61/0.00045	31.35/0.00102
31.82/0.00011	31.66/0.00052

^aAs in Table III, footnote a, employing the indicated experimentally determined vertical ionization potential (Refs. 16 and 17). Additional series similar to those given here are expected to appear converging on the higher-lying ionization potentials (Ref. 36).

^bAs in Table III, footnote c, employing the threshold oscillator-strength densities of Fig. 3(a). The estimated Rydberg-symmetry threshold contributions are $2a_1 \rightarrow ka_1$, $ks=0.035$, $kp=0.028$, $kd=0.010$; $3a_1 \rightarrow kb_1$, $kp=0.027$, $kd=0.022$; $2a_1 \rightarrow kb_2$, $kp=0.025$, $kd=0.065$, all in a.u.

with little evidence present of significant contributions to the nsa_1 and npb_2 series from $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ valence orbitals, respectively. In this respect the inner-valence $2a_1$ series differ from the corresponding outer-valence series described above (Tables III and IV), to which the virtual valence orbitals make noticeable contributions. Although experimental studies of excitation series in the inner-valence region of H₂O are apparently unavailable at present, the calculated transition energies and f numbers can be compared with quantum-defect estimates. With the exceptions of some irregularities in the npa_1 , and nda_1 series, which may indicate mixing among the various contributing l waves, the calculated static-exchange excitation series are seen to be in general agreement with the corresponding defect estimates.

In Fig. 3(a) are shown the calculated $2a_1 \rightarrow ka_1$, kb_1 , and kb_2 contributions to the $(2a_1^{-1})^2A_1$ cross section, as well as the vertical electronic result in comparison with measured $(e, 2e)$ values.⁵ The three polarization components are seen to be broad and unstructured, presumably as a consequence of the spatially compact, largely oxygen $2s$ character of the $2a_1$ orbital. Consequently,

although the (out-of-plane) $2a_1 \rightarrow kb_1$ component exhibits a broad, weak maximum, the ka_1 and kb_2 profiles are generally $2s \rightarrow kp$ like in energy dependence. The calculated $(2a_1^{-1})^2A_1$ vertical electronic cross section obtained from summation of the three polarization components is evidently in generally good agreement with the experimental values.⁵

In spite of the good agreement obtained between theory and experiment for the $2a_1$ cross section shown in Fig. 3(a), there is a modest failure of Koopmans theorem in the inner-valence region in H₂O, i.e., the measured $2a_1$ PES band in H₂O is comprised of two or more ionic states.^{5,36} This point is illustrated by Fig. 3(b), in which the measured valence-shell ($e, 2e$) photoelectron spectrum for 41 eV incident photons is compared with theoretical values in the intensity-borrowing approximation.¹³ The latter spectrum is obtained from the expression¹³

$$p_{hv}(\omega) = \sum_{\alpha} \sigma_{\alpha}(h\nu) / (\omega_{\alpha} \sqrt{\pi}) \exp[-(\omega - \epsilon_{\alpha})^2 / \omega_{\alpha}^2], \quad (8a)$$

where

$$\sigma_{\alpha}(h\nu) = \sum_i |a_i^{(\alpha)}|^2 \sigma_i(h\nu). \quad (8b)$$

Here, ϵ_{α} are the energies of the ionic states, ω_{α} the corresponding widths, $\sigma_i(h\nu)$ the static-exchange orbital cross sections, and $|a_i^{(\alpha)}|^2$ the so-called spectroscopic factors.¹³ It is seen from Fig. 3(b) that the three outer-valence ($1b_1$, $3a_1$, $1b_2$) PES bands in H₂O are each comprised of single ionic states, in accordance with Koopmans theorem, for which the spectroscopic factors are unity. By contrast, a number of ionic states having nonnegligible spectroscopic factors contribute to the $2a_1$ inner-valence band, accounting for its substantially greater width relative to the outer-valence bands.³⁶ In each case the individual linewidths ω_{α} (≈ 1 eV) can be estimated from the envelopes of vibrational excitation in the Franck-Condon energy-gradient approximation,⁴⁸⁻⁵⁰ although in the present work these are simply chosen to provide a reasonable fit to the measured profile. It is seen that the measured spectrum, which includes the appropriate electron analyzer transmission-efficiency corrections,⁵¹ is in generally good agreement with the theoretical results of Eqs. (8) obtained following this procedure, although there is a modest misalignment of the peak positions.

5. Total valence-shell cross section

In Fig. 4 are shown the four calculated valence-shell partial-channel photoionization cross sections in H₂O, the corresponding total cross section, and measured total photoionization values obtained from synchrotron-radiation and $(e, e + \text{ion})$ electron-impact studies.^{3,5} The two measured photoionization cross sections of Fig. 4 include contributions from all ionic fragments produced, and, consequently, are appropriate for comparison with the calculated values for parent-ion production. Evidently, the measured cross sections exhibit appropriate increases at the three outer-valence thresholds, and there is even a small discernible feature present near the $2a_1$ threshold in the $(e, e + \text{ion})$ data. Although the ex-

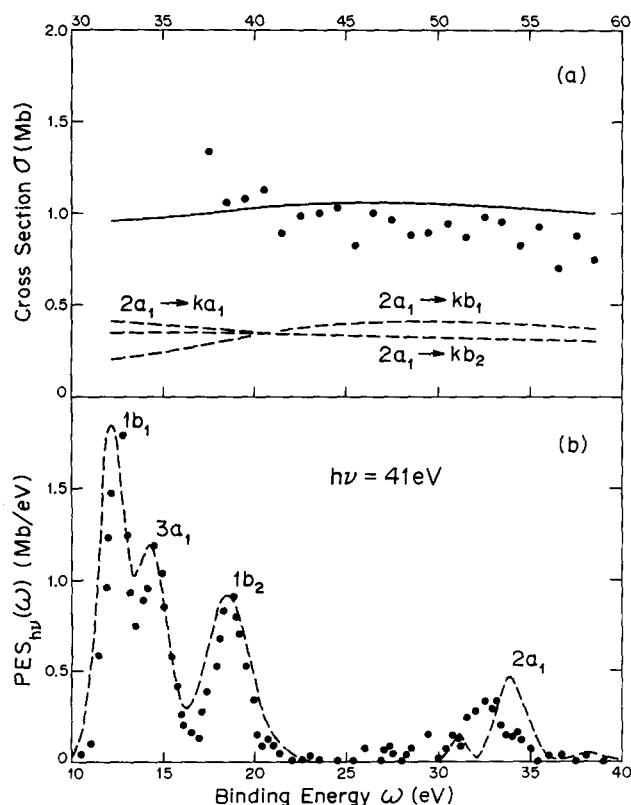


FIG. 3. (a) Inner-valence-shell $(2a_1^{-1})^2A_1$ partial-channel photoionization cross section in H₂O; (—) vertical-electronic static-exchange orbital cross section; (---) calculated polarization components as indicated; (●) dipole $(e, 2e)$ measurements (Ref. 5). (b) Valence-shell photoelectron spectrum in H₂O for 41 eV incident photon energy; (---) theoretical values in the intensity-borrowing approximation of Eqs. (8), obtained as discussed in the text; (●) dipole $(e, 2e)$ measurements (Ref. 5), corrected for electron-analyzer transmission efficiency (Ref. 51) and normalized to the theoretical values at the peak of the $3a_1^{-1}$ band.

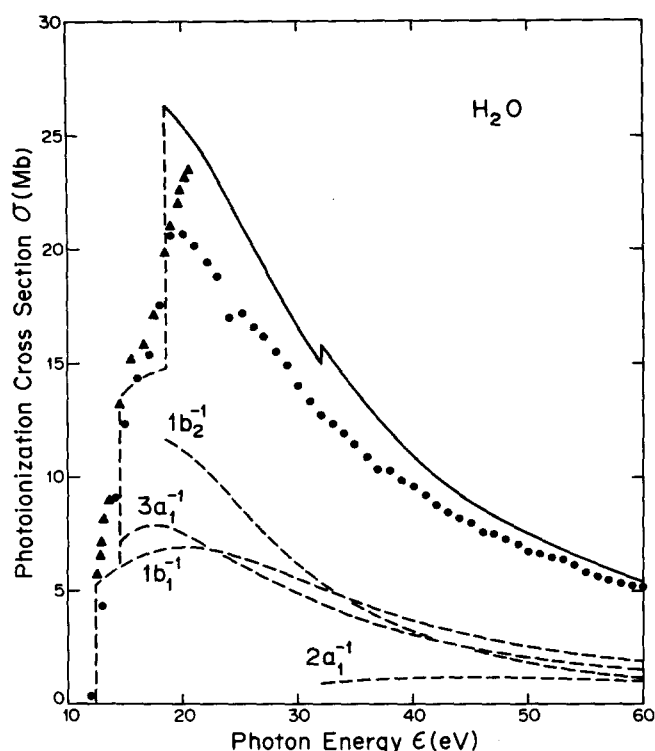


FIG. 4. Valence-shell total photoionization cross section in H₂O; experimental, (●) (*e*, *e*+ion) measurements (Ref. 5); (▲) synchrotron-radiation measurements (Ref. 3); (---) calculated partial-channel ionization cross sections as indicated; (—) total calculated vertical-electronic ionization cross section.

perimental and theoretical values are in general agreement, the calculated $1b_2^{-1}$ channel cross section is seen to provide an overestimate in the ~20 to 25 eV energy interval. The effects of channel coupling and autoionization can be expected to diminish the $1b_2^{-1}$ value in this energy interval, however, presumably also accounting for the structure in the synchrotron-radiation measurements of the $(1b_1^{-1})^2B_1$ profile of Fig. 2(a), as indicated above. In spite of the neglect of channel coupling in the present calculations, the total cross section obtained is seen to be in generally good agreement with the measured values, suggesting the separated-channel results provide a useful first approximation to the valence dipole spectrum in H₂O.

6. Comparisons with previous calculations

In Table VI is shown a summary of experimental outer-valence-shell assignments and excitation energies in H₂O in comparison with the present calculations and with previously reported theoretical values. With the possible exception of the early estimates of Yeager *et al.*,²⁷ the previously reported studies, particularly those in the IVO approximation,^{29,30} are generally in accord with the present more comprehensive larger-basis-set calculations. The latter are also seen here, as in Tables III and IV, to be in excellent accord with the experimental values.² The largest discrepancy between measurement and the present calculations is apparently for the $1b_1 \rightarrow 3s$ excitation, in which case the RPAE cal-

TABLE VI. Comparisons of theoretical and experimental excitation energies in H₂O.

Experimental assignments ^a and energies— ϵ_i (eV)		Present results ^b ϵ_i (eV)/ f_i	Previous calculations ϵ_i (eV) ^c				
			Refs. 27	28	29	30	33
$1b_1 \rightarrow 3s$	7.44	7.24/0.0208	7.22	7.30	7.30	7.61	7.43
$3pa_1$	9.998	9.98/0.0065	9.02	9.90	10.04	10.06	
$3pb_1$	10.171	10.10/0.0018	9.48	10.32	10.16	10.16	
$3da_1$	10.990	11.05/0.0064	9.61		11.07		
$3da_2$	11.041	11.09/0.0052			...		
$3db_1$	11.057	11.11/0.0155			11.17		
$3da_1$	11.122	11.15/0.0028			11.17		
$1b_1 \rightarrow 4s$	10.64	10.53/0.0001			10.64		10.80
$4pa_1$	11.374	11.35/0.0025			11.42		
$4pb_2$	11.432	11.37/0.0003			11.48		
$4da_1$	11.729	11.76/0.0032					
$4db_1$	11.770	11.74/0.0053					
$3a_1 \rightarrow 3s$	9.85	9.88/0.0670	9.54	9.80	...	9.82	9.55
$3pa_1$		12.24/0.0002					...
$3pb_2$		11.53/0.0376					11.30
$3pb_1$		12.08/0.0019					
$3da_1$		13.14/0.0133					
$3db_2$		13.13/0.0315					
$3da_1$		13.23/0.0094					
$3db_1$		13.25/0.0040					

^aValues taken from the measurements and assignments of P. Gürtler, V. Saile, and E. E. Koch (Ref. 2). See also Ref. 6.

^bPresent values of Tables III and IV.

^cReferences to previous calculations as indicated. See also Ref. 1 for citations of earlier theoretical results. The RPAE calculations of Ref. 33 have been adjusted to account for the 1.15 eV difference between experimental and HF ionization potentials (see Table I).

culations³³ are seen to be in somewhat better accord with experiment. The latter calculations also suggest relatively strong configuration mixing between the $1b_2 \rightarrow 3sa_1/4a_1$ excitation and other hole-particle combinations (not shown), in support of related comments made in Secs. IV A.2 and IV A.3. In spite of its general interest and importance, it is seen from Table VI that relatively few theoretical studies have been reported to date of the discrete dipole excitation spectrum in H₂O.⁵⁻⁸

Previously reported studies of valence-shell photoionization cross sections in H₂O include those in plane-wave,³¹ one-center Coulomb,³² RPAE,³³ one-center inversion potential,³⁴ and X_α ³⁵ approximations. Although the plane-wave results are not in accord with experimental values or with the present calculations, the one-center Coulomb and inversion-potential calculations give cross sections in generally good agreement with measured values, confirming the dominance of the oxygen atom orbitals in the photoionization of H₂O. Similarly, the X_α studies indicate good agreement between oxygen atom and H₂O orbital cross sections, although no comparisons with the available experimental values are reported.³⁵ There is no evidence in any of the three one-center calculations of contributions from $2b_2(\sigma^*)$ or $4a_1(\gamma^*)$ orbitals in the cross sections or in the discrete spectral regions, however. By contrast, the present calculations suggest that single-channel results should overestimate the $(1b_2^{-1})^2B_2$ cross section at threshold [Fig. 2(c)], allowing for the possibility of autoionization into the $(1b_1^{-1})^2B_1$ channel to account for the presence of a strong feature in the ~18 to 20 eV interval [Fig. 2(a)]. Of the previously reported theoretical studies, only the RPAE results exhibit a similar feature. Consequently, it is clear that more detailed coupled-channel calculations are in order to clarify this point, and that apparent agreement between single-channel calculations and experimental values can possibly mask important and interesting features in molecular photoionization cross sections.

B. *K*-edge (I.P.=539.7 eV) region in H₂O

The calculated $1a_1 \rightarrow na_1$, nb_1 , and nb_2 excitation series are shown in Table VII in comparison with corresponding quantum-defect estimates obtained employing defects of $\delta = 1.40$, 0.7, and 0 for *s*, *p*, and *d* series, respectively. As in the case of outer- and inner-valence excitations, the $1a_1 \rightarrow na_1$ series is evidently comprised of individual interlaced $nsa_1/4a_1$, npa_1 , $nd(z^2)a_1$, and $nd(x^2 - y^2)a_1$ series, and the $1a_1 \rightarrow nb_1$ and nb_2 excitations include npb_1 , ndb_1 and npb_2 , ndb_2 Rydberg series, respectively. In addition, the nb_2 excitations include the now familiar $2b_2(\sigma^*)$ contribution. Because of the well-known sensitivity of *K*-edge 1s-to-valence-orbital excitations to electronic relaxation and reorganization effects neglected in the present studies, the calculated $1a_1 \rightarrow 3sa_1/4a_1$ and $2b_2$ transitions at 530.9 and 531.7 eV, respectively, fall somewhat below the observed strong features at 534.0 and 535.9 eV in the measured electron impact-excitation spectrum [Fig. 5(b)].⁴ The relative intensities of the measured peaks are in general agreement with the calculated values, however. More-

TABLE VII. $1a_1$ (I.P. = 539.7 eV) excitation spectra in H₂O.

Present results ^{a,b} [energy (eV)/f number]	Defect estimates ^c [energy (eV)/f number]
$1a_1 \rightarrow nsa_1/4a_1$	
530.91/0.03985	534.39/0.00269
537.17/0.00114	537.69/0.00063
538.45/0.00029	538.65/0.00024
538.95/0.00011	539.06/0.00011
539.28/...	539.27/0.00006
$1a_1 \rightarrow npa_1$	
536.43/0.00861	537.13/0.00019
538.06/0.00009	538.45/0.00006
538.79/0.00005	538.96/0.00003
539.23/0.00001	539.22/0.00002
$1a_1 \rightarrow nda_1$	
538.20/0.00011	538.19/0.00167
538.23/0.00200	...
538.85/0.00065	538.85/0.00070
538.87/0.00018	...
539.12/0.00007	539.16/0.00036
539.14/...	...
$1a_1 \rightarrow npb_1$	
536.13/0.01763	537.13/0.00021
538.23/0.00009	538.45/0.00007
538.89/0.00003	538.96/0.00003
540.30/...	539.22/0.00002
$1a_1 \rightarrow ndb_1$	
538.17/0.00357	538.19/0.00223
538.85/0.00139	538.85/0.00094
540.15/0.00060	539.16/0.00048
$1a_1 \rightarrow npb_2/2b_2$	
531.69/0.07252	...
537.51/0.00214	537.13/0.00205
538.59/0.00058	538.45/0.00070
539.03/0.00024	538.96/0.00031
539.34/...	539.22/0.00017
$1a_1 \rightarrow ndb_2$	
538.17/0.00037	538.19/0.00029
538.87/0.00018	538.85/0.00012
539.22/0.00002	539.16/0.00006

^aAs in Table III, footnote a, employing the indicated experimentally determined vertical ionization potential.¹⁴

^bThe measure *K*-edge electron energy-loss spectrum [Fig. 5(b)] is seen to include strong features at 534.0, 535.9, and 537.1 eV that are in accord with the relative positions and strengths of the calculated $1a_1 \rightarrow 3sa_1/4a_1$, $2b_2$, and $3pb_1$ excitations. A fourth peak in the measured spectrum falls in the region (538.5 eV) of many individual Rydberg transitions making specific assignment impossible.

^cAs in Table III, footnote c, employing the threshold oscillator-strength densities of Fig. 5(a). The estimated Rydberg symmetry contributions are $1a_1 \rightarrow ka_1$, $ks=0.011$, $kp=0.0023$, $kd=0.045$; $1a_1 \rightarrow kb_1$, $kp=0.0025$, $kd=0.060$; $1a_1 \rightarrow kb_2$, $kp=0.025$, $kd=0.0078$, all in a.u.

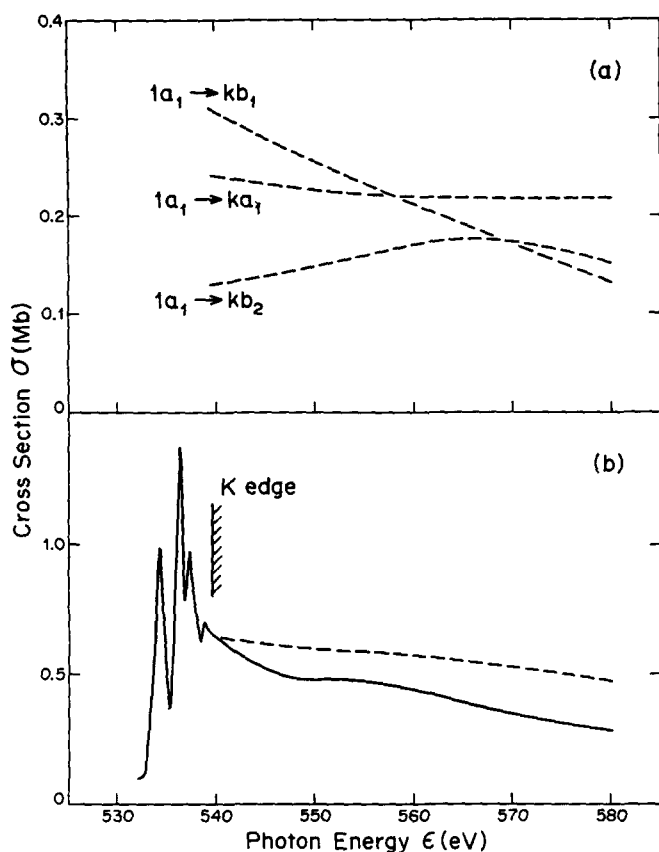


FIG. 5. (a) Calculated static-exchange *K*-edge photoionization cross sections in H₂O as indicated. (b) Total *K*-edge photoionization cross section in H₂O; (---) calculated static-exchange results obtained from (a) above; (—) measured electron energy-loss spectrum (Ref. 4) multiplied by the factor $(\epsilon/\epsilon_i)^3$ and normalized to the calculated value at threshold.

over, the calculated $1a_1 \rightarrow 3pb_1$ Rydberg transition, which is significantly and inexplicably stronger than the corresponding quantum-defect estimate, is seen to be in good agreement with the third strong feature at 537.1 eV in the electron impact-excitation spectrum. An additional excitation peak identified in the experimental profile falls in the region of many individual Rydberg excitations (538.5 eV), so a specific assignment is not possible in this case. Evidently, the calculated excitation series of Table VII account for the strong features observed below threshold in the electron impact-excitation measurements.⁵

Because the $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ valence orbitals contribute primarily to the discrete excitations of Table VII, presumably as a consequence of the very attractive nature of the $1a_1^{-1}$ hole-state potential, the $1a_1 \rightarrow ka_1$, kb_1 , and kb_2 photoionization cross sections are expected to be largely unstructured. This expectation is verified by the calculated profiles shown in Fig. 5(a), which are seen to be generally unstructured, although there is a weak, broad maximum in the $1a_1 \rightarrow kb_2$ channel. The total *K*-edge photoionization cross section obtained from the calculations is compared with measured values in Fig. 5(b). The measured energy-loss spectrum⁵ has been converted to cross-sectional values by multiplying with

the factor $(\epsilon/\epsilon_i)^3$ and normalizing to the calculated value at threshold. Evidently, the two results are in general but not precise agreement, with the weak maximum at ~555 eV in the measured values attributable to the corresponding broad feature in the calculated $1a_1 \rightarrow kb_2$ contribution.

V. CONCLUDING REMARKS

A great many experimental studies of photoprocesses in the water molecule have been reported to date, including recent detailed measurements of total photoabsorption and ionization cross sections, and of the partial-channel branching ratios for production of specific parent-ionic states and of dissociative ionic fragments. In view of the importance of this familiar compound in many connections, and in the absence of completely satisfactory earlier theoretical studies, a comprehensive theoretical account of the general features of the complete dipole excitation spectrum in H₂O is given here.

As in previously reported studies in this series, which now includes investigations of H₂, N₂, O₂, F₂, CO, CO₂, H₂CO, C₂H₂, and O₃ molecules, it is found helpful to clarify the calculated discrete excitation series and photoionization cross sections in H₂O in terms of contributions from valence $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ virtual orbitals, and from the more diffuse orbitals that give rise to Rydberg series and corresponding hydrogen-like photoionization continua. The discrete-basis-set methodology employed is particularly well suited for this purpose, allowing for the discussion of both discrete and continuum portions of the spectrum on a common basis.

Use of very large basis sets in the present study results in highly satisfactory descriptions of intravalence and Rydberg transitions in the static-exchange or improved-virtual-orbital approximation. Specifically, the calculated na_1 series are seen to separate into well defined nsa_1 , npa_1 , and nda_1 Rydberg series. The $4a_1(\gamma^*)$ virtual valence orbital is found to contribute strongly to the nsa_1 series, particularly to the $1b_1 \rightarrow$, $3a_1 \rightarrow$, and $1b_2 \rightarrow 3sa_1/4a_1$ resonance members, which lead to broad photodissociation bands, and which are given a mixed Rydberg/valence designation. This is in marked contrast to most earlier theoretical studies, which suggest the excited states in H₂O include only Rydberg transitions. The nb_2 series are found to include npb_2 and ndb_2 Rydberg series, as well as perturbing contributions from the $2b_2(\sigma^*)$ virtual valence orbitals, whereas the nb_1 excitations are entirely npb_1 and ndb_1 Rydberg-like in nature. Of particular interest in the calculations is the appearance of four *d*-type [$nd(z^2)a_1$, $nd(x^2 - y^2)a_1$, ndb_1 , and ndb_2] Rydberg series, in excellent accord with recent detailed assignments of the $1b_1$ excitations. Although the separated-channel static-exchange calculations are seen to provide a useful first approximation to the important discrete spectral features in the ~7 to 20 eV energy interval in H₂O, there is evidence of configuration mixing in some cases, which require subsequent additional study.

The calculated outer-valence-shell ($1b_1^{-1}$) X^2B_1 , ($3a_1^{-1}$) 2A_1 , and ($1b_2^{-1}$) 2B_2 partial-channel photoionization cross sections are found to be in generally good agreement with corresponding synchrotron-radiation and dipole (e , $2e$) measurements. In particular, the measured values for the ($3a_1^{-1}$) 2A_1 channel are in very good agreement with the calculations, suggesting that the separated-channel approximation is a good one in this case. There is evidence, however, of coupling between the ($1b_1^{-1}$) 2B_1 and ($1b_2^{-1}$) 2B_2 channels, in which case a strong feature in the measured $1b_1^{-1}$ profile not present in the separated-channel calculations can be attributed to autoionization of $1b_2 \rightarrow 2b_2$ contributions in the $1b_2 \rightarrow kb_2$ continuum. Similarly, the calculated separated-channel ($1b_2^{-1}$) 2B_2 cross section provides an overestimate in the ~ 20 eV threshold region, suggesting that this absorption strength should properly appear in the ($1b_1^{-1}$) X^2B_1 channel when the appropriate coupling is included in the development. When these features are accounted for, it is seen that the calculated and measured values are in good accord.

Because of a modest failure of Koopmans' theorem in the inner-valence $2a_1$ region in H₂O, a number of final ionic states contribute to photoelectron spectra in the ~ 30 to 40 eV binding-energy region, giving rise to a very broad effective $2a_1^{-1}$ band. Calculations in the intensity-borrowing sudden approximation, employing separately reported spectroscopic factors and the static-exchange $2a_1$ orbital cross section, are seen to be in good agreement with measured PES and corresponding cross sections obtained from dipole (e , $2e$) studies.

The total valence-shell photoabsorption and ionization cross sections obtained from the separated-channel static-exchange calculations are seen to account quantitatively for all of the important features present in the corresponding measured profiles. Specifically, the $1b_1$ -, $3a_1$ -, and $1b_2 \rightarrow 3sa_1/4a_1$ intravalence transitions are seen to dominate the discrete spectral interval, and increases at the various thresholds in the measured ionization cross section are attributed to corresponding features in the $1b_1^{-1}$, $3a_1^{-1}$, and $1b_2^{-1}$ ionization continua. Moreover, the weak ($2a_1^{-1}$) 2A_1 contribution is seen to account for a broad structure in the measured cross section at the appropriate threshold.

Finally, the calculated $1a_1^{-1}$ K -edge excitation spectra are seen to clarify the origins of three strong features observed below threshold in the measured electron energy-loss spectrum. In contrast to the valence-shell spectra, the $1a_1^{-1}$ hole-state potential supports low-lying $4a_1(\gamma^*)$ and $2b_2(\sigma^*)$ orbitals that contribute entirely to the discrete spectral region, accounting for two of the measured features, with the third peak attributed to a strong $1a_1 \rightarrow 3pb_1$ Rydberg transition. The photoionization continua are correspondingly unstructured and largely monotonic, although a very weak broad feature in the measured ionization profile is clarified by the calculated cross section.

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