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Satellite Bands and the Valence Ionic States of Ozone

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Abstract: The valence ionic states of ozone have been studied using a combination of multiconfiguration self-consistent field theory and configuration mixing techniques. It is found that the lower energy states of ozone show a significant mixing of one electron (primary) ionization and two electron simultaneous ionization-excitation processes leading to the predicted appearance of satellite bands with considerable intensity in the ultraviolet photoelectron spectrum. It is thus not possible to interpret the valence photoelectron spectrum of ozone in terms of the usual one electron orbital ionization processes. The calculations show that the same excited state configurations that are important in the neutral ozone optical absorption electronic spectrum also figure prominently as interacting excitation or "shake-up" states. The relationship between the relative degree of inadequacy of the frozen orbital approximation (Koopmans' theorem) when comparing ionic states energies and the importance of ionization-excitation processes is pointed out.

The relative energies of the valence ionic states of molecular systems are most easily determined experimentally by photoelectron spectroscopy with photon sources in either the vacuum ultraviolet[1,2] or X-ray[3] frequency regions. In experiments using a vacuum ultraviolet energy source on a diamagnetic system it is typically found that there is a one to one correspondence between the observed spectral maxima and the valence molecular orbitals of the system. This correspondence confirms in a striking manner the shell or orbital structure of atoms and molecules.[4,5] Thus each ionization process is identified with the removal of an electron from some molecular orbital of the system, with an ionization energy just equal to the Hartree-Fock self-consistent field orbital energy of that electron (Koopmans' theorem) in the neutral parent molecule.[6] The result of identifying a molecular orbital with each ionization process in a photoelectron spectroscopy experiment can be used to supply information about the nature of the orbitals themselves through band shape studies, comparative energy shifts for different compounds for a given orbital type electron, correlations in isoelectronic series, ionization cross section and angular distribution studies, etc. Of course, the correct association of orbitals and ionization processes is fundamental and essential to these analyses.

The identification of an experimental ionization energy with an orbital energy neglects the instantaneous rearrangement of the remaining electrons that will naturally accompany the ionization process and which contributes a relaxation term to the theoretical ionization energy. Although simple models which describe this change of overall charge distribution of the remaining electrons when one electron is ionized have been proposed and discussed,[7,8] the models are typically expressed in terms of the relaxed orbitals, quantities which, if available, render the theoretical models unnecessary for quantitative energy predictions. The relaxation energy can be accounted for by direct calculation of the ion (or hole) state energy and wave function within the single electronic configuration Hartree-Fock theory.

Even with relaxation energy taken into account in a theoretical calculation of ionization energies there is still a further approximation in the neglect of the inherent inaccuracy of single configuration Hartree-Fock theory, called the correlation energy error. This error is expected to be roughly proportional to the number of electrons in the system. Thus ion states are typically expected to have smaller correlation energy errors than the neutral species precursor state[9,10] and calculated ionization energies in the single electronic configuration approximation should be incorrect to the extent of this difference in correlation energy between the ground and ion states.

A method of increasing popularity for treating problems where the single configuration self-consistent field approximation is inadequate is the multiconfiguration self-consistent field (mcscf) theory.[11,12] In the latter the molecular wave function is expressed as a sum of a number of electronic configurations of the same space and spin symmetry and both the orbitals, and configuration bases expansion coefficients are optimized simultaneously in a variational calculation. Typically, the Hartree-Fock electronic configuration is the dominant one in the configuration expansion and essentially determines the nature of the orbitals occupied in this electronic configuration. The nature of the orbitals occupied only in the correlating configurations is then essentially determined by the smaller configuration expansion coefficients of the remaining configurations and are thus optimized as correlating orbitals for the strongly occupied molecular orbitals. Thus a small and compact multiconfiguration expansion using optimized molecular orbitals is comparable in accuracy to a much larger configuration mixing calculation using an arbitrary orbital basis. The correlating configurations typically differ by the electron occupancy in one or two orbitals from the primary or Hartree–Fock configuration.

The discussion so far has been limited to single electron ionization processes which give rise to the primary ion states of the system. There exists, however, the possibility of simultaneous ionization and excitation where it can be considered that one electron is ionized while a second is excited to a higher energy bound state ("shake-up" process). In X-ray photoelectron spectroscopy such multielectron processes give rise to what are called satellite lines which are found experimentally to be displaced to higher binding energy from, and of significantly lower intensity than, the primary photoline.[13,14] In vacuum ultraviolet photoelectron spectroscopy the possible appearance of shake-up bands has been suggested and discussed but only recently has there been an attempt to quantitatively predict the energies and intensities of such bands.[15-17] Since the electric dipole operator connects orthogonal state configurations differing only by at most the occupancy of one spin orbital clearly the intensity of a shake-up state configuration should be determined largely by how strongly it mixes with a primary ion state configuration.

Satellite band intensity can only come at the expense of the photoionization intensity to form the primary ion state. If satellites appear prominently in the photoelectron spectrum then there must be a corresponding diminution of intensity that would otherwise signal the presence of the primary ion. If there are several satellite states interacting with a parent ion it is possible that the intensity to reach the primary ion, which is the principle ionization process, is spread over many satellite states to the extent that ionization to the primary ion will be too weak to be observed. This phenomenon is known to sometimes occur for the lower multiplicity state in the X-ray photoelectron spectroscopy of radicals.[23] Since the intensity giving mechanism for satellite states involves configuration mixing with primary hole state configurations, it is possible to find (theoretically) electronic states of relatively low energy which because of their low content of the primary hole state configurations will be experimentally unobserved. These states then constitute a class of "forbidden" electronic states in a photoelectron spectroscopy experiment.

Under conditions where the interaction of primary ion and shake-up states is moderate the single electron ionization intensity may be spread over several primary ion-satellite states and the appearance of multiple bands in the photoelectron spectrum is the natural consequence. Thus there will no longer be a one to one correspondence between the occupied molecular orbitals of the system and bands in the valence photoelectron spectrum, as is expected, and as usually serves as the basis of interpretation of these spectra.

In order to define the nature of the shake-up bands more precisely it is convenient to describe the possible electronic configurations and the states they give rise to that can be associated with the satellite states. With regard to spin the satellite states must obviously have the same spin multiplicity as the primary ionic states. For space symmetry in cases of low geometric point group symmetry and where there is at least one primary ion state of each irreproducible representation, as for example in the ozone molecule, the satellite states can be regarded as belonging to the space symmetry of the primary ion states. With these restrictions in mind the satellite states can be classified as differing by one or two electron excitations from some reference or primary ionic state, which are precisely the type of correlating state configurations which are also needed to improve the theoretical description of the primary ion state wave function.

The question of correlating state configuration vs. spectroscopic state in cases where one is seeking higher electronic states of a given spin and space symmetry is a familiar problem for which there has not yet been found a practical solution. Ideally, it would be desirable to carry out a separate mcscf calculation for each spectroscopic state of interest. However, this procedure is not practical since the optimal correlating orbitals for one electronic state may differ considerably from those of an adjacent spectroscopic state, leading to difficulties such as the variational collapse and nonorthogonality of the higher electronic states to the lower state of the same spin and space symmetry. On the other hand, the straightforward configuration mixing technique suffers from none of these problems but the number of configurations generated using all members of an arbitrary orbital bases of at least double-ζ size (two basis functions for each occupied atomic orbital) is so large as to rule out this technique as being particularly applicable today.

The accurate calculation of ionization energies to form valence ionic states from the ground state requires either that each electronic state be calculated accurately or that each state be calculated with the same relative error so that in taking differences between the valence ionic states and the ground state energies the error subtracts out and does not contribute to the calculated ionization energies. Several methods have been proposed to implement this latter idea with regard to configuration mixing techniques,[18-22] and this general approach seems to be the most practical today.

It would be expected that ozone, with some eight electronic states reportedly lying below 7 eV above the ground state at the ground state equilibrium geometry[24,25] should be a good candidate for finding low-lying satellite states in the valence ionic state region of the photoelectron spectrum. Much effort has been expended in theoretical investigations of the low-lying electronic states of neutral ozone and a semiquantitative understanding of the electronic structure of ozone is apparently available. What is clear from much of this work is that multiconfiguration effects are important in describing all of the low-lying states accurately, even in the neighborhood of their respective equilibrium geometries.

The photoelectron spectrum of ozone has been measured and reported by several investigators[26-28] with only one attempt at a detailed theoretical assignment of the spectrum above 14 eV; and that based on semiempirical calculations.[28] The only ab initio theoretical assignments have been based on Koopmans' theorem (neglect of reorganization and correlation effects) and an LCAO-Xα calculation using the transition state method.[29] The semiempirical calculation found multiconfiguration effects to be important in interpreting the photoelectron spectrum. Given these latter results, and what is currently predicted about the optical absorption spectrum of ozone, it seems well worthwhile studying the ozone molecule both to contribute to a further clarification of its electronic structure in various ionic states and an understanding of the mutual interaction of satellite and primary ionic states in that system.

Method and Results

The electronic structure of ozone in its ground state is $1a_1{}^2 1b_2{}^2 2a_1{}^2 3a_1{}^2 2b_2{}^2 4a_1{}^2 5a_1{}^2 3b_2{}^2 1b_1{}^2 4b_2{}^2 6a_1{}^2 1a_2{}^2$ in C_{2v} symmetry with the molecule lying in the *yz* plane and the coordinate *y* transforming as b_2. The $2b_1$ molecular orbital is low lying even in the single configuration ground state self-consistent field wave function where it is unoccupied and such orbitals are determined in the field of all 24 elec-

Table I. Summary of Multiconfiguration Self-Consistent Field Results

State	Total energy[a]	No. of configurations	Fixed open shell orbital	Primary configuration energy[a,b]
$^1A_1$	−224.31074	13		−224.20282
$^2A_1$	−223.79794	10	$6a_1$	−223.68017
$^2A_2$	−223.79781	10	$1a_2$	−223.75820
$^2B_2$	−223.75828	10	$4b_2$	−223.65032
$^2B_1$	−223.65225	10	$1b_1$	−223.47635

[a] In au. [b] These are the energies of the single configuration components in the multiconfiguration wave function.

Table II. Data on the Configuration Mixing Calculations

State	No. of parent determinants	Accuracy[a]	Total no. of determinants	No. of calcd doublet states below 24 eV
$^1A_1$	2	1.0000×10^{-5}	134	
$^2A_1$	6	6.2554×10^{-4}	446	8
$^2A_2$	1	5.0000×10^{-5}	185	3
$^2B_2$	7	2.3265×10^{-4}	440	6
$^2B_1$	3	6.0000×10^{-4}	214	5
				22

[a] Accuracy criterion given by $|H_{ij}|^2/(E_i - E_j)$ where H_{ij} is the Hamiltonian matrix element between determinants i and j, and E_i and E_j are the total electronic energies of determinants i and j, respectively.

trons of the molecule. Each of the eight low-lying excited states of ozone referred to previously have been shown to involve a single or double electron excitation into the $2b_1$ orbital in their primary orbital electronic configuration. Note that $1b_1$, $1a_2$, and $2b_1$ can be considered as π-type orbitals. Goddard and coworkers[24] have in fact classified the electronic states of ozone according to the number of π orbitals in their primary orbital electronic configuration description: 4π (the ground state and $\pi \rightarrow \pi^*$ type excitations), 5π (a single or double excitation involving a $\sigma \rightarrow \pi^*$ type jump from the ground state), and 6π (double excitations into the $2b_1$ (π^*) orbital from the ground state).

Multiconfiguration self-consistent field wave functions were determined for the ground and primary ion states (i.e., ion states that differ from the ground state by just a single spin orbital occupancy) of ozone with the following details. The basis set consists of a double-ζ set of Gaussian orbitals using the contraction coefficients of Dunning.[30] All calculations here were carried out at the equilibrium geometry of ground state ozone taken from ref 31. For the ground state and each of the four possible ion states ($^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$) mcscf calculations were carried out on the lowest energy state configuration of each symmetry allowing variable occupancy only of spin-paired sets of electrons among the seven orbitals $\{1b_1, 4b_2, 6a_1, 1a_2, 2b_1, 7a_1, 5b_2\}$, with the occupancy of the singly occupied orbital (in the ion states) fixed as such. Thus in the neutral molecule ground state there are four spin-paired sets of electrons to be distributed among seven orbitals leading to 13 configurations if only spin paired double excitations from the primary ground state electronic configuration are allowed. For the ion states three pairs of electrons are distributed among six orbitals (the seventh orbital containing the odd electron) giving rise to ten configurations, again, if only spin-paired double excitations from the lowest energy primary ion configuration are considered. The results of the mcscf calculations are tabulated in Table I.

Using the calculated mcscf wave functions configuration mixing calculations were carried out as follows. To the variable occupancy orbital basis used in the mcscf calculations were added the $4a_1$, $5a_1$, and $3b_2$ molecular orbitals to make a total of ten variably occupied molecular ortibals in all. All single and double excitation configurations from each of a selected number of parent (single or multideterminant) configurations whose second order energy interaction were greater than a calculated numerical criterion for any of the parent determinants were added to the configuration list. The energy eigenvalues and configuration expansion coefficients for each state were then determined (where necessary) by successive diagonalization of matrices of order up to 240 with the lowest 30 states carried over from step to step. The number of parent configurations was chosen by a type of iterative process where to all the primary state configurations of a given spin and space symmetry are successively added configurations that were found to mix substantially with any of the primary state configurations. The energy interaction criterion used to screen configurations has the form $|H_{ij}|^2/(E_i - E_j)$, where j is a parent determinant, and its value was chosen internally separately for each state symmetry consistent with existing programming limitations, combined with an attempt to obtain a balanced description of all the electronic states. A summary of the number of parents, interaction criterion value, and final number of determinants for each state is given in Table II.

The objective of the detailed process outlined above was an attempt to obtain a balanced description of all the states of interest while circumventing some of the difficulties described in the introductory section. Thus the mcscf process is expected to produce a set of orbitals most appropriate to the lowest ion state of that symmetry while being less appropriate, and therefore less accurate, for the higher ion states of the same symmetry when only a limited orbital basis configuration mixing calculation is carried out, as was done here. We can thereby be reasonably sure that the energies of the higher ion states are true upper bounds to the experimental energies and that the true state probably lies at lower energy than calculated here. It is also to be expected, however, that the configuration mixing calculations will to a large extent mitigate the effects of the possible inappropriateness of the molecular orbital basis for the higher ion states.

In the last column of Table II are listed the number of ion states of each symmetry calculated to fall below 24 eV above the neutral ground state. Experimentally, only some nine states, at most, can be resolved in the photoelectron spectrum of ozone below 24 eV to be compared with some 22 doublet states calculated to fall in that range shown in Table II. What has not been taken into account yet is the aspect of intensity. The calculation of photoionization cross-section as a function of photon energy is a difficult problem that has not been tackled here.[32] Instead the following intuitive approach has been used. It is assumed that only primary ionization processes carry intensity and if the energy and orbital dependence of the cross-section is neglected then the square of the coefficient of the primary ion state configuration in a multiconfiguration expansion (of the sum of squares of all such primary ion state configurations of that symmetry) should be a good qualitative measure of relative intensity. In Table III are listed the calculated vertical ionization energies of the ion states with "intensity" greater than 0.05 by the above criterion, a comparison of the ion state energies with experiments, and their orbital assignments.

In Table IV are displayed the satellite configurations that

Table III. Results of Configuration Mixing Calculations and Comparison with Experiment for Ozone

	Theoretical			Experimental		
	Configuration mixing					
State	Energy[a, b]	Intensity	Koopman's theorem[e]	Brundle[a, c]	Dyke et al.[a, d]	Assignment
$^1A_1$	0					
$^2A_1$	12.53	0.764	15.28	12.75	12.75	$6a_1^{-1}$
$^2A_2$	12.81	0.889	13.43	13.03	13.02	$4b_2^{-1}$
$^2B_2$	13.09	0.772	15.75	13.57	13.57	$1a_2^{-1}$
$^2B_1$	15.91	0.444	21.52	16.0–18.5	(15.60) Peaks at 16.54 and 17.45	$1b_1^{-1}$ + shake-up
$^2A_1$	17.61	0.393	22.77			$5a_1^{-1}$ + shake-up
$^2B_2$	19.02 19.40	0.132 0.299	21.60			$3b_2^{-1}$ + shake-up
$^2A_1$	20.34 21.69	0.023 0.062	—	18.7–21.5	broad multipeaked bands centered at 20.00	$5a_1^{-1}$ + shake-up
$^2B_2$	22.08	0.332	—			$3b_2^{-1}$ + shake-up
$^2B_1$	22.95	0.332	—			$1b_1^{-1}$ + shake-up
$^2A_1$	22.58 23.12 23.84	0.144 0.229 0.053	—			$6a_1^{-1} + 5a_1^{-1} + 4a_1^{-1} +$ shake-up

[a] In eV. [b] Total (configuration mixing) energy = −224.38162 au for the neutral ground state. [c] From ref 27. [d] From ref 28. [e] From ref 31.

Table IV. Orbital Occupancies of Principal Satellite Configurations

	$^2B_1$		$^2A_1$					$^2B_2$		
$4a_1$	2	2	2	2	2	2	2	2	2	2
$5a_1$	2	2	2	2	2	2	2	2	2	2
$3b_2$	2	2	2	2	1	2	2	2	2	2
$4b_2$	2	2	1	2	2	2		1	2	1
$6a_1$	2	2	2	1	2	1	1	2	1	
$1b_1$	2	1	2	1	2	2	2	2	2	2
$1a_2$			1	2	1		2		1	2
$2b_1$	1	2	1	1	1	2	2	2	1	2
No. of π electrons	3	3	4	4	4	4	6	4	4	6

[a] The $1a_1$–$3a_1$ and $1b_2$–$2b_2$ are doubly occupied in all the configurations.

contribute to the observed ion states listed in Table III. There are, as mentioned, "forbidden" ion states with energies below 24 eV above the neutral ground state whose principal state configurations are not shown here.

Discussion

As can be seen from Table III the calculations here give a good accounting of the observed photoelectron spectrum of ozone. As expected, the lower ionization potentials are in better agreement with experiment than the higher ion state energies. Thus, for example, the three lowest ionization potentials are calculated very close to, but uniformly lower than, the observed vertical ionization energies by 0.2–0.5 eV, indicating that these ion states are being better described than the neutral ground state. The ordering of these three levels deduced experimentally[28] is $6a_1^{-1} > 4b_2^{-1} > 1a_2^{-1}$ where the −1 superscript indicates the primary ion configuration formed by the removal of that orbital from the primary ground state configuration. The Koopman's theorem results, also shown in Table III, are $1a_2^{-1} > 6a_1^{-1} > 4b_2^{-1}$ independent of Gaussian orbital basis set.[31,33] A recent LCAO-Xα calculation using the transition state procedure,[29] which is considered to be equivalent to a direct Hartree-Fock calculation on the single configuration hole state, predicts the experimental ordering $6a_1^{-1} > 4b_2^{-1} > 1a_2^{-1}$. However, the direct Hartree-Fock self-consistent field calculations on the hole state configurations themselves displayed in Table I still show the Koopmans' theorem ordering. It is therefore not clear precisely what method or orbital basis the LCAO-Xα transition state procedure for ion states corresponds to in this context. Finally, the configuration mixing results of Table III do show the deduced experimental ordering of primary ionic states.

The next reported observed feature in the valence region photoelectron spectrum is a very weak band observed only in the more intense He II spectra with a vertical ionization potential of 15.60 eV.[28] The next calculated ionic state with substantial intensity shown in Table III is the first $^2B_1$ state at 15.90 eV. However, all the other first ionic states of their respective symmetries were calculated at lower energy than observed, and the corresponding behavior would therefore also be expected of the $^2B_1$ state. Thus both energy and intensity considerations rule out the $^2B_1$ state as being the weak ionic state at 15.60 eV. A possible candidate is a $^2B_2$ state (not shown in Table III) calculated to appear at 16.45 eV with relative intensity 0.012 which is some 67 times weaker than the lowest energy $^2B_2$ state. This weak $^2B_2$ state corresponds to the simultaneous ionization-excitation configuration (in obvious notation) $6a_1^{-1}\ 1a_{-1}\ 2b_1^{+1}$ relative to the neutral ground state of ozone.

The region between 14 and 22 eV can be divided into two main groups of broad and poorly resolved bands, one between 16.0 and 18.5 eV with at least two resolvable peaks (16.5 and 17.5 eV) and a second group showing apparently three peaks.[26-28] The calculated energies and intensities shown in Table III predict the presence of three bands in the region of the first group with more or less the same intensity for each but with individually reduced intensities (by a factor of ~2) relative to the lowest energy three bands. This first group of broad bands corresponds to several one electron ionization processes; $1b_1^{-1}$, $5a_1^{-1}$, and $3b_2^{-1}$, respectively, but with considerable additional ionization-excitation character as shown by the reduced intensities. The second $^2B_2$ state assignment in this region corresponds to two electronic states calculated at 19.02 and 19.40 eV. For states of a given symmetry so close in energy the intensity distribution between them is expected to be a sensitive function of both the orbital and configurational basis sets. It is therefore not clear in such cases whether the prediction of two states with sufficient intensity to be observed is real or not and it is only natural to relate to them as a single band.

The second group of bands is assigned analogously to the first group with the addition of another $^2A_1$ state which contains a small component of the $4a_1^{-1}$ primary configuration. The calculated individual state intensities in this group are only slightly lower than the first group, but there are more states in the second group which should make it overall more intense than the first group. This is what is observed experimentally. For these positive ion states in the second group there are no corresponding primary (pure one electron) ionization processes. Thus the application of single configuration molecular orbital theory (semiempirical or ab initio) cannot be used to correctly interpret the valence photoelectron spectrum of ozone.

The two groups of broad bands in the 16-22-eV region of the photoelectron spectrum are mainly the results of the interaction of the $1b_1^{-1}$, $5a_1^{-1}$, and $3b_2^{-1}$ primary ion configurations with the simultaneous ionization–excitation configurations built on the lower energy $6a_1^{-1}$, $4b_2^{-1}$, and $1a_2^{-1}$ primary ionization processes. This relationship is clear from Table IV which shows the occupancies for the interacting satellite state configurations. Another interesting aspect of this listing of the main interacting ionization–excitation configurations is that the excitation part can, in almost every case, be identified with one of the lowest lying excited states of neutral ozone in its equilibrium geometry and sometimes with several of them depending on which orbital is considered as being ionized.

The question raised by Brundle[27] of the location of the $4a_1^{-1}$ primary ion state which using Koopman's theorem is calculated to fall at 29.9 eV[31] remains. In the configuration mixing calculations this state configuration is found to be spread or distributed over several $^2A_1$ states in the energy range 27–31 eV. It is therefore reasonable to assign the $4a_1^{-1}$ primary ion configuration to the 24.7-eV band observed by Dyke et al.[28] in the He II spectrum of ozone and not as low as in the 18.7-21.5-eV range as suggested by Brundle.[27]

It has recently been pointed out[34,35] that the Koopmans' theorem electron binding energy for inner shell ionization is equivalent to an intensity weighted average of all states associated with, or built upon, a given primary state configuration. This result is based on the "sudden" approximation which is decreasingly valid as the photon source energy approaches the resonance ionization energy. Nonetheless, a comparison of the Koopmans' theorem results, the single configuration self-consistent field energies, and the final configuration mixing results (Table I and III) shows that those primary ion states with the largest discrepancy between Koopmans' theorem and experiment are just those states for which ionization–excitation processes are most important. Thus apparently relaxation energy alone does not determine the degree of relative inadequacy of the frozen orbital approximation when comparing the energies of various adjacent valence ion states, as is commonly assumed.

The importance of ionization–excitation processes is the probable cause of the failure of simple orbital theory, in any of its many variations, to accurately predict the ionization energies of the inner valence shells of unsaturated hydrocarbons.[36] As a general rule it seems rather certain that starting at most 20 eV from the neutral ground state valence photoelectron spectra will show more bands than single configuration theory shows orbitals above that energy threshold and caution must be exercised in interpreting the observed energy values.

It also appears from the self-consistent field results on the primary ion configurations presented here (Table I) that the correlation energy of many of the positive ion states is larger than that of the neutral ground state. Thus th $6a_1^{-1}$, $1b_2^{-1}$, and $1b_1^{-1}$ ionization energies as obtaine from the self-consistent field calculations on the primar ion state configurations in the double-ζ basis are still calculated to be greater than the corresponding observed bindin energies.

In this regard, a few words would be appropriate abou the question of basis set in these calculations. It is now wel understood that a quantitative description of the electroni states of ozone requires the use of d-type orbitals on th oxygen atoms as part of the orbital expansion basis. Als missing from the valence double-zeta set of functions use here are Rydberg type orbitals which can be important i describing the excited electronic states of molecular system in the gas phase. Interestingly enough, however, it has apparently been possible to obtain a reasonably appropriate assignment of the valence region photoelectron spectrum o ozone including ionization–excitation states without either d-type or Rydberg basis functions. It now remains to be seen whether the methods used here will be equally appropriate for other systems as well.

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