

**GENERAL-MODEL-SPACE STATE-UNIVERSAL COUPLED-CLUSTER METHOD: EXCITED STATES OF OZONE**

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*Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.*

The low-lying excited states of ozone are investigated using the recently developed general-model-space state-universal coupled-cluster methods and the results are compared with other multireference coupled-cluster and spin-adapted unitary-group coupled-cluster approaches. The role played by the choice of different molecular orbitals in coupled-cluster calculations is also explored. It is found that the low-lying  $1,3B_2$  states are particularly sensitive to the choice of the molecular orbitals. This observation explains some significant differences between the results obtained with spin-adapted and spin-non-adapted multireference coupled-cluster approaches, as documented by earlier studies. The use of appropriate orbitals brings the effect of spin-adaptation to its normal range.

**Keywords:** Multireference methods; Coupled cluster; Ozone; Excited states; CCSD.

An *ab initio* computation of potential energy surfaces (PESs) for a multitude of low-lying electronic states with a sufficiently high accuracy and a minimal cost has always represented a very challenging problem. Essentially, we can employ either variational approaches, such as the configuration interaction (CI) method, or perturbative type approaches, such as the coupled-cluster (CC) methods. Both may be of either a single reference (SR) or a multireference (MR) type.

Generally, the CI methods are well established. Their formulation is straightforward and they can be easily generalized to their MR version. However, they lack size-extensivity and are not efficient in describing the dynamic correlation. To compensate the latter deficiency, the MR CI often employs an unnecessarily large reference space, resulting in an increased computational cost. The CC methods, on the other hand, are size-extensive and very effective in handling dynamic correlation. Yet, while their SR version is again well defined, its extension to a MR variety is not without prob-

lems. Essentially, there are two types of MR CC methods, namely the so-called valence-universal<sup>1,2</sup> (VU) and state-universal<sup>3</sup> (SU) ones. They are also referred to, respectively, as Fock-space and Hilbert-space theories. Besides these true MR CC approaches, several state-specific type approaches were developed. They usually employ the basic MR concepts, while relying on the SR formalism, or at least treating one-state at a time. All these possibilities, as well as their advantages and disadvantages, have been extensively reviewed<sup>4-6</sup>.

The method that will be used in this paper belongs to the SU category<sup>3</sup>. Due to a number of obstacles, very few actual applications of the MR CC methods have been carried out since their inception more than two decades ago. One common obstacle is the intruder state problem. The MR theories generally assume that several low-lying states are fully dominated by an equal number of reference configurations that span the model space. In practical applications, however, this assumption is not easy to fulfil for all the states considered in the entire range of geometries that one wishes to explore. When this assumption no longer holds, the intruder state problem might arise. In an often-occurring situation, beside a leading configuration, some other configurations have large weights in the ground state yet do not dominate the excited states, so that it is difficult to include these configurations in the model space. We also often encounter the case that a model space, which is suitable for some geometries, is inappropriate for others. Another complication arises due to a presumed need of the complete model space (CMS) in order to achieve the exact size-extensivity. The CMS, spanned by configurations corresponding to all possible occupations of valence orbitals, often involves highly-excited configurations and makes the intruder state problem more likely to occur.

To tackle these problems, we have recently formulated a SU CCSD formalism that can employ a general model space<sup>7</sup> (GMS), spanned by an arbitrarily selected set of configurations. With such a GMS, we can at least reduce the probability of the occurrence of the intruder states. The key idea that enabled us to use a GMS, while retaining the size-consistency<sup>8</sup>, are the constraining conditions (C-conditions) for the internal excitations. Furthermore, in order to address the situation in which some configurations have heavy weights in the states of interest, yet cannot be included in the model space, we have introduced what can be characterized as a “more-references fewer-states”-type approach<sup>9</sup>, namely a  $N$ -reference  $M$ -state method ( $N, M$ )-CCSD with  $N \geq M$ . The latter is a general MR SU extension of the reduced multireference (RMR) CCSD method<sup>10</sup>, which in turn is a special case of the externally corrected (ec) SR CCSD methods<sup>11</sup>. The ( $N, M$ )-CCSD method ex-

exploits an  $N$ -reference ( $NR$ ) CISD wave functions as a source of higher-than-pair clusters in an  $M$ -reference SU CCSD method. In this way, we can employ more references while computing fewer states. Thus, those configurations that have heavy weights in the state of interest can always be included in the larger reference space of the MR CISD that supplies the amplitudes for external corrections, regardless of whether they are suitable references for other states or not.

The above mentioned methods<sup>7,9</sup> have been applied to a number of molecular systems and some of these results have been published<sup>12</sup>. In this report, we consider several excited states of the ozone molecule. Within the framework of the MR CC theory, ozone has been treated with the two-determinant SU CCSD method<sup>13</sup> and with the two-electron/two-orbital active space VU CCSD method<sup>14,15</sup>. The equation-of-motion (EOM) CC methods have also been applied<sup>16,17</sup>. We have considered this system using our state-specific, unitary-group-approach (UGA)-based CCSD<sup>18</sup>. Some significant differences between these various approaches were found. In this study, we thus revisit the ozone molecule using GMS CCSD and extend these calculations via  $(N,M)$ -CCSD.

Following a brief exposition of the necessary formalism, terminology, and notation, we present the results for the ground and excited states of the ozone molecule as obtained with a DZP and an aug-ccpVTZ basis sets. The role played by the molecular orbitals employed will be considered in detail.

## METHOD

Physical situation that requires a MR description of wave functions arises when a set of states of interest is dominated by several configurations. In other words, we require a number of configurations in order to provide a good zero-order description of the states of interest. In such situations we employ the MR CC methods that are based on an effective Hamiltonian formalism. We thus consider a model space  $\mathcal{M}_0$ , spanned by a set of chosen orthonormal configurations  $|\Phi_i\rangle$ ,  $\mathcal{M}_0 = \text{span}\{|\Phi_i\rangle\}$ , and a corresponding target space  $\mathcal{M}$  that is spanned by a set of orthonormal state wave functions  $|\Psi_i\rangle$ ,  $\mathcal{M} = \text{span}\{|\Psi_i\rangle\}$ . Both spaces  $\mathcal{M}_0$  and  $\mathcal{M}$  have the same dimension  $M$ .

The model and target spaces are interrelated in the following way. The wave operator  $U$  transforms each reference  $|\Phi_i\rangle$  into some linear combinations of target states  $|\Psi_i\rangle$ , i.e.,

$$U|\Phi_i\rangle = |\tilde{\Psi}_i\rangle \quad (1)$$

$$|\Psi_i\rangle = \sum_j c_{ij} |\tilde{\Psi}_j\rangle. \quad (2)$$

Note that while  $|\Psi_i\rangle$ 's are mutually orthonormal,  $|\tilde{\Psi}_j\rangle$ 's are not. The projection operator  $P$

$$P = \sum_i |\Phi_i\rangle\langle\Phi_i| \quad (3)$$

projects vectors in the target space back to the model space, namely

$$P|\tilde{\Psi}_i\rangle = |\Phi_i\rangle. \quad (4)$$

Similarly as for the wave operator  $U$ , when  $P$  acts on a pure state, we obtain a linear combination of the reference configurations

$$P|\Psi_i\rangle = |\tilde{\Phi}_i\rangle = \sum_j c_{ij} |\Phi_j\rangle \quad (5)$$

so that the mixed reference set  $\{|\tilde{\Phi}_i\rangle\}$ , which also spans  $\mathcal{M}_0$ , is not orthonormal. Hence, to obtain a pure target state, the wave operator  $U$  must act on the mixed reference, namely

$$U|\tilde{\Phi}_i\rangle = |\Psi_i\rangle. \quad (6)$$

The construction of the wave operator  $U$  and the determination of the  $c_{ij}$  coefficients represent the central task of the MR CC theory. When we apply the above formalism to a SR CC theory, the wave operator is given via the exponential Ansatz

$$|\Psi\rangle = \exp[T(\mathbf{1})]|\Phi_1\rangle, \quad T(\mathbf{1}) = \sum_{k=1}^N T_k(\mathbf{1}), \quad T_k(\mathbf{1}) = \sum_j t_j^{(k)}(\mathbf{1}) G_j^{(k)}(\mathbf{1}) \quad (7)$$

where  $G_j^{(k)}(\mathbf{1})$  designates a  $k$ -fold excitation operator relative to the reference  $|\Phi_1\rangle$ , leading to the  $k$ -fold excited configuration. However, when more than one reference configuration is required, there is no unique prescription how to define  $U$ . In the SU MR CC theory, one associates a unique cluster operator  $T(j)$  with each reference  $|\Phi_j\rangle$ , so that

$$U = \sum_j \exp[T(j)]P_j \quad (8)$$

and

$$|\Psi_i\rangle = \sum_j c_{ij} \exp[T(\hat{j})]|\Phi_j\rangle. \quad (9)$$

The target wave function can thus be expanded as follows,

$$|\Psi_i\rangle = \sum_{|\Phi_j\rangle \in \mathcal{M}_0} c_{ij}|\Phi_j\rangle + \sum_{|\Xi_j\rangle \in \mathcal{M}_0^\perp} d_{ij}|\Xi_j\rangle \quad (10)$$

where the last term represents a linear combination of all the configurations spanning the orthogonal complement  $\mathcal{M}_0^\perp$  of the model space  $\mathcal{M}_0$ .

When applied to a CMS  $\mathcal{M}_0$ , only excitations out of  $\mathcal{M}_0$  (external excitations) are allowed, and the unknown cluster amplitudes are given by the SU CC equations<sup>3</sup>,

$$\langle G_i^{(k)}(\hat{i})\Phi_i | \bar{H} | \Phi_i \rangle = \sum_{j(\neq i)} \Gamma^{ij}(\hat{l}) H_{ji}^{(\text{eff})}, \quad \bar{H} = \exp[-T(\hat{i})]H \exp[T(\hat{i})] \quad (11)$$

where  $H_{ji}^{(\text{eff})}$  designates the matrix element of the effective Hamiltonian,

$$H_{ji}^{(\text{eff})} = \langle \Phi_j | H \exp[T(\hat{i})] | \Phi_i \rangle \quad (12)$$

and  $\Gamma^{ij}(\hat{l})$  is the coupling coefficient

$$\Gamma^{ij}(\hat{l}) = \langle G_i^{(k)}(\hat{i})\Phi_i | \exp[-T(\hat{i})] \exp[T(\hat{j})] | \Phi_j \rangle. \quad (13)$$

The diagonalization of the effective Hamiltonian gives then the desired energies and the  $c_{ij}$  coefficients. When the cluster expansion is limited to single and double excitations, we have the SU CCSD method.

When we wish to employ a GMS, we must address the role of the external and internal excitations, the latter interconnecting reference configurations. Since the product of internal excitations could again be a valid internal excitation, their treatment requires a special attention. We found out<sup>7</sup> that a simple, yet proper way is to apply the above mentioned C-conditions. These conditions simply require that the amplitude of a higher-order connected internal excitation be fixed to cancel out all possible products of its disconnected counterparts. For example, the two-body internal amplitudes are given by the negative of the products of one-body internal amplitudes. These C-conditions ascertain the validity of the intermediate normalization, are easy to implement, and the resulting formalism remains size-consistent<sup>8</sup> and can be applied to other types of MR CC methods that employ the SU Ansatz (9) (see, for example, its use in the Brillouin-Wigner MR

CC method<sup>19</sup>). The external excitations, on the other hand, satisfy the standard SU CC equations (11).

While the above described GMS SU CCSD method is generally applicable, its actual exploitation can be further improved. One option is to proceed beyond the SD excitation level, since the role of higher excitations is more important in MR CC methods than in SR CC. In the SR case, the standard energy expression involves only one- and two-body amplitudes. In the MR case, however, the higher-than-pair clusters already enter the effective Hamiltonian and thus the final energy. Hence, we cannot obtain exact energies via the effective Hamiltonian even when we are given the exact one- and two-body amplitudes (obtained, for example, by the cluster analysis of the FCI target wave functions).

In practice, it is impossible and uneconomical to explore the full sets of  $T_3$ ,  $T_4$ , etc., cluster amplitudes. Yet, it is highly desirable to consider an important subset of such amplitudes. A general implementation of CC methods that exploit an arbitrary subsets of  $T_3$ ,  $T_4$ , etc., amplitudes is not without problems. Thus, a much simpler approach is to obtain such amplitudes from some external source and use them in the amplitude-corrected CCSD equations, which are no more difficult than the standard CCSD equations. This is the basic idea of externally corrected CCSD methods<sup>11</sup>. From the viewpoint of MR approaches, a suitable set of zero-order wave functions for several states of interest can be constructed by relying on a reference space spanned by a sufficiently larger yet minimal set of configurations. The SD excited state manifold from these references forms the first-order interacting space. Such a manifold will contain the most important configurations, and thus cluster amplitudes, including higher-than-pair ones. It should be noted that SD excitations with respect to one reference can be higher-than-double excitations (or, more precisely, replacements) with respect to other references. This also implies that MR CISD wave functions represent a suitable external source from which we can extract the corresponding cluster amplitudes. Such a source exploits precisely the MR SD excited state manifold.

These observations point to a natural extension of the RMR CCSD method<sup>10</sup> to the GMS SU CC formalism, resulting in the  $(N,M)$ -CCSD method<sup>9</sup>. In the latter approach, we solve corrected  $M$ -reference GMS SU CCSD equations, while the approximate  $T_3$ ,  $T_4$ , etc., clusters that are considered in the corrected equations are obtained from the  $N$ -reference MR CISD. In the  $(N,M)$ -CCSD hierarchy, the standard SR CCSD method corresponds to  $(0,1)$ -CCSD. Also  $(N,1)$ -CCSD is a RMR CCSD corrected by  $N$ -reference MR CISD (i.e.  $NR$ -RMR CCSD). We also have that  $(0,M)$ -CCSD  $\equiv$  MR SU CCSD.

Finally, if  $N$  is so large that the resulting  $N$ -reference MR CISD becomes FCI, we recover the exact FCI energies for  $M$  states.

The  $(N,M)$ -CCSD calculations are generally carried out in the following way: (i) We first determine (e.g., via a small CI) which configurations are important for the  $M$  states considered. Quite likely, we obtain  $N$  configurations with  $N \geq M$ . (ii) We choose the  $M$  most important configurations as references for GMS SU CCSD. (iii) We use all  $N$  configurations as references for the MR CISD wave functions. Of these we choose  $M$  wave functions that correspond to the  $M$  states of interest. For this purpose, we sometimes have to compute more than  $M$  MR CISD wave functions, since the  $M$  lowest energy ones are not necessarily the desirable ones, particularly when the MR CISD code is not fully symmetry-adapted. (iv) We then cluster-analyze the  $M$  chosen MR CISD wave functions using the SU CCSD Ansatz with  $M$  references that were chosen in step (ii) and, finally, we extract higher-than-pair cluster amplitudes. (v) We employ these higher-than-pair cluster amplitudes in the corrected GMS SU CCSD equations and solve them to obtain the final results.

## COMPUTATIONS

For the sake of easier comparison, we consider the singlet and triplet  $B_2$ ,  $B_1$ , and  $A_2$  excited states of ozone using the same DZP basis set as in refs<sup>13,14,16,18</sup> and the aug-ccpVTZ basis set. We employ the theoretical ground state geometry optimized at the CCSD/DZP level, namely  $r_{O-O} = 1.263$  Å and  $\theta(OOO) = 117.4^\circ$ , as well as the experimental equilibrium geometry, namely  $r_{O-O} = 1.272$  Å and  $\theta(OOO) = 116.8^\circ$ . We do not correlate the core electrons. All calculated excitation energies use the ground state geometry and thus correspond to vertical transitions.

Since our current GMS SU CCSD codes are not fully spin-adapted, while we exploit the spatial symmetry  $C_{2v}$ , we must handle simultaneously the singlet and triplet states using  $M_S = 0$  Slater determinants as references. Thus, the minimal model spaces are two-dimensional for the  $B_2$ ,  $B_1$ , and  $A_2$  symmetry species.

We employ three kinds of molecular orbitals: (i) The ground state restricted RHF orbitals, used for all states of various spatial symmetry. (ii) Triplet (restricted open-shell) ROHF orbitals determined for each symmetry. Thus, the ROHF orbitals for the lowest  ${}^3B_2$  state are used for the  $B_2$  problem (obtaining energies for both  ${}^3B_2$  and  ${}^1B_2$ ), while the ROHF orbitals for the lowest  ${}^3B_1$  state are employed for the  $B_1$  block, etc. (iii) Similarly as in case

(ii), but using the open-shell singlet (OSS) SCF orbitals optimized for each singlet.

## RESULTS

Ozone has the ground state configuration  $|(core)\dots 4b_2^2 6a_1^2 1a_2^2 2b_1^0 7a_1^0 5b_2^0|$ . The computed SR CCSD energies are given in Table I for both basis sets employed. These ground state energies are used when computing the vertical excitation energies (VEE) for the excited states when using the 2R SU CCSD method.

The intense Hartley bands at about 4.9-eV have been unambiguously assigned to the  ${}^1B_2 \leftarrow {}^1A_1$  transition. The dipole-forbidden, diffuse Wulf and Chappuis absorption bands in the visible and near-infrared regions have been associated with the  ${}^1A_2$  and  ${}^1B_1$  states, respectively, and their experimental VEEs (cf. Table II) were determined with the accuracy of 0.2 eV or better<sup>20</sup>. However, the data obtained by the anion photoelectron spectroscopy of  $O_3^-$  (ref.<sup>21</sup>), which is better suited for the characterization of low-lying electronic states of ozone than the classical absorption spectroscopy, particularly when spin-forbidden singlet-triplet transitions are involved, seem to indicate that the Wulf bands may be associated with the  ${}^3A_2$  state at 1.18 eV. The presently available assignments are summarized in the last row of Table II. For the triplets, the experimental values correspond to adiabatic 0-0 transitions. To account for the geometry changes associated with different excited states when comparing the vertical excitation energies with experimental 0-0 transition energies, we recall the CI results that were obtained with a large-scale extrapolated MRD (i.e. MR CISD) method<sup>22</sup> for both the vertical (V) and adiabatic (A) (or  $T_e$ ) transitions: For the  ${}^3B_2$  state, the MRD vertical excitation energy is 1.69 eV, while  $T_e$  is 1.1 eV. For the

TABLE I  
The ground state  $X^1A_1$  energy of  $O_3$

Basis	Method	Geometry	$E$ , a.u.
DZP	CCSD	optimized	-224.908361
DZP	CCSD	experiment	-224.908178
DZP	(2,1)-CCSD	optimized	-224.923046
aug-ccpVTZ	CCSD	optimized	-225.099262
aug-ccpVTZ	CCSD	experiment	-225.098483



$^3B_1$ , VEE is 1.85 eV, while  $T_e$  is 1.27 eV. Finally, for the  $^3A_2$ , VEE is 2.0 eV and  $T_e$  is 0.86 eV. Thus, the corresponding shifts are 0.59, 0.58, and 1.14 eV, respectively.

It is not the purpose of this work to carry out a thorough study of the potential energy surface and absorption dynamics. Rather, our main concern is to explain why the state-specific UGA CCSD results<sup>18</sup> are quite significantly better than other MR CCSD results<sup>13,14,16</sup> for the triplet and singlet  $B_2$  states (by as much as 0.3 and 0.5 eV), while for other states, both types of approaches yield comparable results. Of course, a properly spin-adapted method should give better results. However, we cannot attribute the 0.3–0.5 eV improvements to the spin adaptation alone, since they usually amount to about 0.1 eV.

TABLE II

Vertical excitation energies (in eV) obtained with various CC methods and basis sets for the lowest excited singlets and triplets of ozone. The geometry optimized at the CCSD/DZP level is used. The best 2R SU CCSD data are underlined

Method	Orbitals	$^3B_2$	$^1B_2$	$^3B_1$	$^1B_1$	$^3A_2$	$^1A_2$
DZP basis, with respect to CCSD ground state							
UGA CCSD <sup>a</sup>	ROHF, OSS	1.16	5.23	1.55	2.14	1.78	2.13
2R SU CCSD	RHF	1.38	5.71	1.66	2.26	1.89	2.24
2R SU CCSD	ROHF	<u>1.09</u>	6.08	<u>1.63</u>	2.26	<u>1.87</u>	2.22
2R SU CCSD	OSS	1.72	<u>5.19</u>	1.64	<u>2.24</u>	1.87	<u>2.21</u>
VU CCSD <sup>b</sup>	RHF	1.37	5.52	1.62	2.13	1.95	2.17
EOM CCSD <sup>c</sup>	RHF	1.42	5.71	1.70	2.33	1.97	2.37
aug-ccpVTZ basis, with respect to CCSD ground state							
2R SU CCSD	ROHF	<u>1.08</u>	5.96	<u>1.65</u>	2.27	<u>1.84</u>	2.20
2R SU CCSD	OSS	1.78	<u>5.01</u>	1.66	<u>2.25</u>	1.84	<u>2.18</u>
DZP basis, with respect to (2,1)-CCSD ground state							
(4,2) CCSD	RHF	1.51	5.75	1.67	2.15	1.86	2.09
(4,2) CCSD	ROHF	<u>1.38</u>	5.90	<u>1.67</u>	2.16	<u>1.88</u>	2.12
(4,2) CCSD	OSS	1.64	<u>5.70</u>	1.68	<u>2.16</u>	1.91	<u>2.14</u>
Experiment <sup>d</sup>		1.30 (A)	4.9 (V)	1.45 (A)	2.1 (V)	1.24 (A)	1.6 (V)

<sup>a</sup> Ref.<sup>18</sup>; The ROHF- and OSS-type HF orbitals were employed for the corresponding states.

<sup>b</sup> Ref.<sup>14</sup>; <sup>c</sup> Ref.<sup>16</sup>; <sup>d</sup> Ref.<sup>20</sup>; V, vertical excitation energy; A, adiabatic energy.

*SU CCSD Results Obtained with the Optimized Geometry*

In Table II, we compare VEEs as obtained with various MR CCSD methods. We first consider the  $^3B_2$ , the lowest triplet state, and  $^1B_2$  states. Both of these states are dominated by the singly excited  $1a_2 \rightarrow 2b_1$  configuration. This excitation can be described by a single spin-adapted configuration, but involves two  $M_S = 0$  determinants within the spin-orbital based formalism. Hence, within the spin-adapted UGA formalism, the  $^3B_2$  and  $^1B_2$  states can be handled effectively as a single-reference problem (in a spin-adapted configuration sense). We can thus employ the best SCF orbitals in the state-specific way, namely the ROHF orbitals for the  $^3B_2$  and the OSS SCF orbitals for the  $^1B_2$  state. With the DZP basis set, the UGA CCSD VEEs for  $^3B_2$  and  $^1B_2$  are 1.16 and 5.23 eV, respectively. These compare well with the experimental values of 1.3 (which is the adiabatic energy) and 4.9 eV. With the spin-orbital formalism, at least two determinants are needed, and the  $^3B_2$  and  $^1B_2$  states are computed simultaneously. When the ground state RHF orbitals are used, the computed VEEs using 2R SU CCSD are 1.38 eV for  $^3B_2$  and 5.71 eV for  $^1B_2$ . These are identical with the earlier results obtained by Balková and Bartlett<sup>13</sup> and are considerably larger than the UGA CCSD VEEs – in the case of  $^1B_2$  by as much as 0.5 eV, and thus significantly worse when compared with the experiment.

The VU CCSD and EOM CCSD yield similar results. These relatively large differences are very surprising, since in all cases the same level of the CC theory is employed, except for the handling of the spin symmetry. Further calculations indicate that these differences can be attributed to the fact that different orbitals are employed in UGA CCSD and MR CC calculations.

We thus repeated the 2R SU CCSD calculations, employing the triplet ROHF orbitals as well as the OSS orbitals. When the ROHF molecular orbitals are used, the computed 2R SU CCSD VEE for the  $^3B_2$  state is 1.09 eV, which is close to the UGA CCSDs VEE (1.16 eV). At the same time, we obtain the VEE for the  $^1B_2$  state of 6.08 eV. This latter result is even worse than that obtained with the RHF orbitals. When the OSS orbitals are used, the 2R SU CCSD VEE for the  $^1B_2$  state is 5.19 eV, close to the UGA CCSD value of 5.23 eV, while the VEE for the  $^3B_2$  state, obtained at the same time, is 1.72 eV, which is worse than when using the RHF orbitals.

We have also carried out the 2R SU CCSD calculations with the aug-ccpVTZ basis. With the ROHF orbitals, we obtain 1.08 eV for the  $^3B_2$  transition. Using the OSS orbitals, the  $^1B_2$  VEE is 5.01 eV. The latter result is very close to the experimental one of 4.9 eV. Here we see again that the result for the complementary state that is obtained at the same time is inferior to

those that employ the orbitals optimized for the state considered. In brief summary, the best 2R SU CCSD data, which we have underlined in Table II, are those for  $^3B_2$  obtained with the ROHF molecular orbitals and, for  $^1B_2$  when we use the OSS orbitals.

A close comparison of the RHF, ROHF, and OSS orbitals reveals that while the  $^3B_2$  ROHF orbitals are somewhat different from the ground state RHF orbitals, the  $^1B_2$  OSS orbitals significantly differ from the RHF ones.

We consider, next, the singlet and triplet  $B_1$  and  $A_2$  states as obtained with the DZP basis. The leading configurations for the  $B_1$  and  $A_2$  states are represented by the  $6a_1 \rightarrow 2b_1$  and  $4b_2 \rightarrow 2b_1$  excitations, respectively. For the  $^3B_1$  and  $^1B_1$  states, the UGA CCSD VEEs are 1.55 and 2.14 eV, respectively. The latter result agrees well with the experimental VEE of 2.1 eV. For the  $^3A_2$  and  $^1A_2$  states, the UGA CCSD gives 1.78 and 2.13 eV, respectively. Concerning the 2R SU CCSD results, there is no big difference when using the RHF, ROHF or OSS orbitals. For the  $^3B_1$  state, the computed VEEs are around 1.65 eV, and the ROHF molecular orbitals improve the results by about 0.03 eV. For the  $^1B_1$  state, all VEEs are around 2.25 eV, while the OSS orbital results are better than the RHF ones by 0.02 eV. Similar performance is observed in the  $^3A_2$  and  $^1A_2$  cases and the use of an alternative set of SCF molecular orbitals usually gives an improvement of only 0.02–0.03 eV. This indicates that little orbital relaxation occurs in the corresponding excitation process. The spin-adapted UGA CCSD method, which always uses the appropriate SCF orbitals for each state considered, yields better results than does the 2R SU CCSD method using the same orbitals. The differences amount to about 0.1 eV, which represents the standard improvement achieved via spin-adaptation. When a much larger aug-ccpVTZ basis is employed, the 2R SU CCSD method with the ROHF or OSS orbitals gives roughly the same result as that obtained with the DZP basis. The differences are less than 0.03 eV.

### *(N,M)-CCSD Results Obtained with the Optimized Geometry*

We then consider the results obtained with the  $(N,M)$ -CCSD method and a DZP basis set. For the ground state, the second important configuration is associated with a doubly excited  $1a_2^2 \rightarrow 2b_1^2$  transition. This configuration plays a significant role in the ground state, leading to the improved ground state energy as obtained with the  $(2,1)$ -CCSD method. Here the two-reference determinants for the 2R CISD are the ground and doubly excited configurations. The  $(2,1)$ -CCSD ground energy is lower than the SR CCSD one by 15 mhartree (millihartree) (see Table I).

In order to achieve a balanced description of all states, the excited states can be computed using an additional reference. For the excited states considered here, the leading single excitations, and the second important configurations which are doubles, are

$$B_2: 1a_2 \rightarrow 2b_1, \quad 1b_1 1a_2 \rightarrow 2b_1^2 \quad (14)$$

$$B_1: 6a_2 \rightarrow 2b_1, \quad 4b_2 1a_2 \rightarrow 2b_1^2 \quad (15)$$

$$A_2: 4b_2 \rightarrow 2b_1, \quad 6a_1 1a_2 \rightarrow 2b_1^2. \quad (16)$$

The two configurations for each symmetry species form four  $M_S = 0$  determinants. These can in turn be used as references for 4R CISD calculations, which are subsequently employed in the (4,2)-CCSD method. Together with the 2R SU CCSD data, the resulting (4,2)-CCSD total energies, computed with the RHF, ROHF, and OSS molecular orbitals, are given in Table III. These results lead to the (4,2)-CCSD excitation energies given in Table II, computed relative to the (2,1)-CCSD ground state energy (Table I).

For the  ${}^3,1B_1$  and  ${}^3,1A_2$  states, the (4,2)-CCSD method gives lower energies than does the 2R SU CCSD approach by roughly a constant shift for all three types of molecular orbitals employed. For the  ${}^3B_1$  and  ${}^1B_1$ , (4,2)-CCSD

TABLE III

Total energies (in a.u.), presented as  $(E + 224)$ , for  $O_3$ , obtained with the 2R SU CCSD and (4,2)-CCSD method and a DZP basis. The geometry optimized at the CCSD/DZP level is used

Orbitals	${}^3B_2$	${}^1B_2$	${}^3B_1$	${}^1B_1$	${}^3A_2$	${}^1A_2$
2R SU CCSD						
RHF	-0.85772	-0.69850	-0.84736	-0.82525	-0.83883	-0.82594
ROHF	-0.86834	-0.68507	-0.84837	-0.82537	-0.83964	-0.82672
OSS	-0.84534	-0.71771	-0.84812	-0.82598	-0.83960	-0.82715
(4,2)-CCSD						
RHF	-0.86769	-0.71175	-0.86167	-0.84411	-0.85456	-0.84636
ROHF	-0.87236	-0.70636	-0.86186	-0.84361	-0.85400	-0.84519
OSS	-0.86266	-0.71348	-0.86134	-0.84355	-0.85303	-0.84426

reduces the energies by 13–14 and 18–19 mhartree, respectively. In the case of the  $^3A_2$  and  $^1A_2$  states, the energies drop by 13–16 and 17–20 mhartree, respectively, when we use (4,2)-CCSD. These energy lowerings are close to 15 mhartree, which is the difference between the (2,1)-CCSD and SR CCSD ground state. Hence, for the  $^3,^1B_1$  and  $^3,^1A_2$  states, the (4,2)-CCSD VEEs are very similar to the 2R SU CCSD ones.

In contrast, the results for the  $^3,^1B_2$  state are not so uniform. For the  $^3B_2$  state, the (4,2)-CCSD approach using the RHF, ROHF, and OSS orbitals lowers the energy by 10, 4, and 17 mhartree, respectively. For the  $^1B_2$  state, the corresponding numbers are 13, 21, and –4 mhartree. The reason for the above behavior is the fact that when we use the ROHF orbitals, the  $^3B_2$  wave function has a single configuration character, while its singlet  $^1B_2$  counterpart requires two configurations. The situation reverses when we use the OSS orbitals. In this case, the  $^1B_2$  function is strongly of a single-configuration type, while the  $^3B_2$  one is of a two-configuration type. Consequently, for the  $^3B_2$  state, the (4,2)-CCSD/ROHF lowers the 2R SU CCSD/

TABLE IV

Vertical excitation energies (in eV) obtained with various CC methods and basis sets for the lowest excited singlets and triplets of ozone. The experimental equilibrium geometry is used. The best 2R SU CCSD data are underlined

Method	Orbitals	$^3B_2$	$^1B_2$	$^3B_1$	$^1B_1$	$^3A_2$	$^1A_2$
DZP basis							
2R SU CCSD	RHF	1.28	5.59	1.63	2.22	1.79	2.14
2R SU CCSD	ROHF	<u>0.98</u>	5.97	<u>1.61</u>	2.22	<u>1.78</u>	2.12
2R SU CCSD	OSS	1.63	<u>5.05</u>	1.61	<u>2.20</u>	1.77	<u>2.11</u>
VU CCSD <sup>a</sup>	RHF	1.18	5.32	1.63	2.22	1.79	2.14
POL1 basis							
EOM CCSD <sup>b</sup>	RHF	1.39	5.39	1.74	2.36	1.88	2.30
EOM CCSDT-3 <sup>b</sup>	RHF	1.64	5.21	1.79	2.29	1.94	2.23
aug-ccpVTZ basis							
2R SU CCSD	ROHF	<u>0.96</u>	5.86	<u>1.62</u>	2.23	<u>1.74</u>	2.09
2R SU CCSD	OSS	1.75	<u>4.94</u>	1.69	<u>2.27</u>	1.79	<u>2.13</u>
Experiment		1.30 (A)	4.9 (V)	1.45 (A)	2.1 (V)	1.24 (A)	1.6 (V)

<sup>a</sup> Ref.<sup>15</sup>; <sup>b</sup> Ref.<sup>17</sup>

ROHF energy by about 4 mhartree, while for  ${}^1B_2$ , the (4,2)-CCSD/OSS is above the 2R SU CCSD/OSS energy by about 4 mhartree.

### *SU CCSD Results Obtained with the Experimental Geometry*

The experimental equilibrium bond length is longer than the theoretically optimized value by 0.009 Å, while the bond angle is smaller by 0.6°. The VEEs obtained using the experimental geometry for the ground state are given in Table IV, and, comparing with the results in Table II, they are often smaller than those obtained with the theoretical geometry.

In the case of the DZP basis, the VEEs obtained with SU CCSD are smaller by 0.09–0.14 eV for the  ${}^{1,3}B_2$  states, 0.02–0.04 eV for the  ${}^{1,3}B_1$  states, and 0.09–0.1 eV for the  ${}^{1,3}A_2$  states. The largest difference (0.14 eV) is found for the  ${}^1B_2$  state when the OSS orbitals are used. Interestingly, the differences are larger (often about 0.2 eV) in the VU CCSD calculations<sup>14,15</sup>. Since the ground state energies calculated using the two geometries differ by only 0.005 eV, the larger differences in the computed VEEs mean that the excited state energies are more sensitive to the geometry change.

Comparing to the DZP results, the VEEs computed with the aug-ccpVTZ differ less than or around 0.1 eV. The differences among the VEEs obtained using two geometries are also smaller, often less than 0.1 eV. The aug-ccpVTZ results are also closer to the experimental excitation energies. The results of EOM CCSD and CCSDT-3 calculations<sup>17</sup> provide some estimate of the effects of triple excitations. For the  ${}^{1,3}B_2$  states, the orbitals effects are more significant than the effects of triple excitations in EOM.

### CONCLUSIONS

In this report, the low-lying excited states of the ozone molecule are examined using the recently developed GMS SU CCSD and (*N,M*)-CCSD methods. These results are compared with those obtained by other MR CC and EOM CC methods. The  ${}^{1,3}B_2$  states are very sensitive to the choice of the molecular orbitals. In the case of the  ${}^3B_2$  state, the 2R SU CCSD with the ROHF orbitals can lower the excitation energy by 0.3 eV relative to the same method using the RHF orbitals. The difference is even more remarkable in the case of the  ${}^1B_2$  state, for which the 2R SU CCSD with the OSS molecular orbitals lowers the excitation energy by 0.5 eV relative to that using the RHF orbitals. On the other hand, the excitation energies for the  ${}^{1,3}B_1$  and  ${}^{1,3}A_2$  states are not sensitive to the use of different molecular orbitals.

The above orbital sensitivity for the description of the  $1^3B_2$  states also makes it harder to decide whether these states have a SR or a MR character. When the ROHF orbitals are used, the  $^3B_2$  state has a SR character, while its counterpart,  $^1B_2$ , is of a two-configuration type. The opposite situation occurs when we use the OSS orbitals: the  $^1B_2$  is of a SR type, while the  $^3B_2$  becomes two-configurational. This complication affects the quality of the  $(N,M)$ -CCSD calculations for the  $1^3B_2$  states.

The calculations of the excited states of ozone is a challenge problem. The fact that some excited states are unusually sensitive to the choice of the molecular orbitals certainly contributes to the difficulty. Methods that employ the ground state orbitals for the whole problem of electronic spectrum will likely show larger deficiency for some states. In this regard, state-specific approaches using different orbitals for different states should be more suitable<sup>23</sup>.

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## REFERENCES

1. Lindgren I.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, 12, 33.
2. Lindgren I., Mukherjee D.: *Phys. Rep.* **1987**, 151, 93.
3. Jezowski B., Monkhorst H. J.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1981**, 24, 1668.
4. Paldus J. in: *Relativistic and Correlation Effects in Molecules and Solids* (G. L. Malli, Ed.), Vol. 318, p. 207–282. NATO ASI Series, Series B: Physics. Plenum, New York 1994.
5. Paldus J., Li X.: *Adv. Chem. Phys.* **1999**, 110, 1.
6. Bartlett R. J.: *Int. J. Mol. Sci.* **2002**, 3, 579.
7. Li X., Paldus J.: *J. Chem. Phys.* **2003**, 119, 5320.
8. Li X., Paldus J.: *Int. J. Quantum Chem.* **2004**, 99, 914.
9. Li X., Paldus J.: *J. Chem. Phys.* **2003**, 119, 5334.
10. Li X., Paldus J.: *J. Chem. Phys.* **1997**, 107, 6257.
11. a) Paldus J., Planelles J.: *Theor. Chim. Acta* **1994**, 89, 13; b) Li X., Peris G., Planelles J., Rajadell F., Paldus J.: *J. Chem. Phys.* **1997**, 107, 90; c) Stolarczyk L.: *Chem. Phys. Lett.* **1994**, 217, 1.
12. a) Li X., Paldus J.: *J. Chem. Phys.* **2004**, 120, 5890; b) Li X., Paldus J.: *J. Chem. Phys.* **2003**, 119, 5346.
13. Balková A., Bartlett R. J.: *Chem. Phys. Lett.* **1992**, 193, 364.
14. Barysz M., Rittby M., Bartlett R. J.: *Chem. Phys. Lett.* **1992**, 193, 373.
15. Vaval N., Pal S.: *J. Chem. Phys.* **1999**, 111, 4051.
16. Comeau D. C., Bartlett R. J.: *Chem. Phys. Lett.* **1993**, 207, 414.
17. Watts J. D., Bartlett R. J.: *Spectrochim. Acta, Part A* **1999**, 55, 495.
18. Li X., Paldus J.: *J. Chem. Phys.* **1995**, 102, 8095.
19. Pittner J., Li X., Paldus J.: *Mol. Phys.* **2005**, 103, 2239.

20. Steinfeld J. I., Adler-Golden S. M., Gallagher J. W.: *J. Phys. Chem. Ref. Data* **1987**, *16*, 911; and references therein.
21. Arnold D. W., Xu C., Kim E. H., Neumark D. M.: *J. Chem. Phys.* **1994**, *101*, 912.
22. a) Banichevich A., Peyerimhoff S. D., Beswick J. A., Atabek O.: *J. Chem. Phys.* **1992**, *96*, 6580; b) Banichevich A., Peyerimhoff S. D.: *Chem. Phys.* **1993**, *174*, 93; c) Banichevich A., Peyerimhoff S. D., Grein F.: *Chem. Phys.* **1993**, *178*, 155.
23. Li X., Paldus J.: *J. Chem. Phys.* **1999**, *110*, 2844.