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Molecular geometry and vibrational frequencies of ozone from compact variational wave functions explicitly including triple and quadruple substitutions

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The performance of a multireference CISD method, CISD[TQ], is compared to that of other approaches which include a large degree of electron correlation, including Brueckner methods. The CISD[TQ] method selects as references all single and double substitutions within an active orbital space. Certain triple and quadruple substitutions from the Hartree–Fock reference are included in the CISD[TQ] wave function as singles and doubles from the selected reference set. This wave function has previously been shown in simpler cases to provide results near to those predicted by the configuration interaction wave function, including all single, double, triple, and quadruple substitutions (CISDTQ). For the challenging multireference case of ozone, the CISD[TQ] wave function yields geometries and harmonic vibrational frequencies with an accuracy similar to the full CCSDT method. These promising results suggest that for difficult multireference problems the CISD[TQ] wave function provides an efficient and accurate approach for approximating the complete CISDTQ. © *1997 American Institute of Physics.* [S0021-9606(97)02745-1]

I. INTRODUCTION

The potential energy surface and harmonic force field of the ozone molecule has received a great deal of attention in recent years,[1–19] due to its central role in atmospheric chemistry. The electronic structure of ozone can be viewed as two single O–O bonds plus two singlet-coupled π electrons, one on each terminal oxygen atom. This leads to an electronic ground state dominated by two configurations; namely, [core ...]$4b_2^2 6a_1^2 1a_2^2$ and a low-lying doubly excited configuration, [core ...]$4b_2^2 6a_1^2 2b_1^2$. The important role of higher-order excitations (i.e., triples, quadruples, etc.) and nondynamical correlation is manifested in the first- and second-order molecular properties. To elucidate the multireference character of ozone, quantum chemists have applied several theoretical methods to obtain equilibrium geometries, dipole moments, and harmonic vibrational frequencies.

In a previous theoretical study, Yamaguchi *et al.*[20] found that the two-configuration self-consistent-field (TCSCF) description of O_3 yields an equilibrium structure in closer agreement with experiment than that given by the single-determinant spin-restricted Hartree–Fock (RHF) method. However, the TCSCF approach incorrectly predicts the antisymmetric (b_2) stretching frequency to be larger than the symmetric (a_1) stretching vibrational frequency. An earlier complete-active-space self-consistent-field (CASSCF) study by Adler-Golden *et al.*[21] obtained harmonic vibrational frequencies lower than the experimentally determined harmonic frequencies, but with the correct ordering of the stretching frequencies.

The performance of many-body perturbation theory (MBPT) and coupled-cluster (CC) methods, as applied to ground state O_3, was investigated by Stanton *et al.*[22] Several forms of MBPT were found to be inadequate in their description of ozone. The worst case example is the 117% error in the b_2 stretching frequency predicted by MBPT(2). The CC methods, on the other hand, performed very well. Stanton *et al.*[22] determined that the coupled-cluster singles and doubles (CCSD) method correctly predicts the ordering of the ozone stretching vibrational frequencies.[2,22] The symmetric force field of ozone can be brought into relatively good agreement with the experimental frequencies by using MBPT(4), CCSD, or CC methods which include the effects of triple excitations. However, the antisymmetric stretching frequency fluctuates very widely depending on the various approaches for including triples excitations in the CCSD wave function.

Lee, Allen, and Schaefer[23] employed the TCSCF-based configuration interaction singles and doubles (TCSCF-CISD) wave function, and obtained improved results relative to the SCF, TCSCF, and single-reference CISD methods. However, the incorrect ordering of the stretching vibrational frequencies remained even at this level of correlation. Lee *et al.*[23] considered the effects of larger basis sets on the TCSCF-CISD method and found the ordering of frequencies remained in error. Therefore, it was determined that an inadequate treatment of electron correlation was the major cause of the discrepancies in the computed O_3 frequencies relative to experiment. This conclusion was reinforced by the study of Scuseria *et al.*[24] on the comparison of the two-reference CISD method to the single-reference CCSD method. Scuseria *et al.*,[24] using a TZ2P basis, found that the CCSD method outperformed TCSCF-CISD with respect to the predicted O_3 vibrational frequencies. This was an unexpected result at the time since the single-determinant reference used with the CCSD wave function does not contain a complete description of the biradical character of ozone. The failure of the TCSCF-CISD method in even the qualitative prediction of

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the vibrational frequencies of this system points toward the need for the inclusion of triple and quadruple substitutions, which are partially treated in the CCSD wave function.

In this study the performance of the CISD[TQ] method on the ground state of ozone is compared to previous studies including a large degree of electron correlation. The CISD[TQ] wave function was introduced by Saxe *et al.* in 1982.[25] This method is a multireference CISD (MR-CISD) defined by partitioning the orbitals into inactive, active, and external subspaces. An inactive orbital remains doubly occupied in all references, an active orbital may change occupancy within the set of references, and an external orbital remains unoccupied in all references. The CISD[TQ] method selects the references in an *a priori* fashion as all single and double substitutions within the active subspace. All single and double substitutions from this selected set of references are included in the CISD[TQ] wave function. Equivalently, all single and double substitutions from the Hartree–Fock reference are allowed, as well as selected triple and quadruple substitutions in which at most two electrons are allowed in the external subspace. This method has previously been shown by Grev and Schaefer[26] to greatly reduce the size of the CI space while retaining the accuracy of the complete CISDTQ and second-order CI (SOCI) wave functions for molecular systems dominated by a single-reference configuration. A follow-up study of six-electron model systems, as well as H_2O, by Fermann *et al.*[27] reinforced these conclusions. The CISD[TQ] and SOCI methods can be expressed as a restrictive active space CI (RASCI), and therefore benefit from the developments of Olsen *et al.*[28]

The special treatment of the active subspace warrants the use of good correlating orbitals. Grev and Schaefer[26] have shown that the SOCI energies based on CISD natural orbitals (NO's) are in excellent agreement with the CASSCF-SOCI energies. The CISD NO's represent an effective way of obtaining good correlating orbitals. Since the orbitals computed from a CISD NO procedure are ordered according to populations, substitutions which include an electron in a low occupancy orbital will not contribute significantly to the energy. Thus, the natural orbitals are well suited for truncation of the one-particle basis set. An additional advantage is that the CISD NO's are less expensive to compute than CASSCF orbitals.

Recently, our group reported the excellent performance of the CISD[TQ] wave function for the equilibrium geometry and harmonic vibrational frequencies of H_2O[29] and H_2S.[30] We find that for a multireference case such as ozone, the CISD[TQ] wave function yields geometries and harmonic vibrational frequencies with the accuracy approaching that of very high level coupled-cluster methods which fully include triple substitutions (i.e., full CCSDT).

II. THEORETICAL METHODS

A CISD[TQ] wave function was employed with the active space chosen to include all occupied valence orbitals and the valence virtual orbitals (i.e., $7a_1$, $2b_1$, and $5b_2$), while

the external subspace was chosen to be all nonvalence virtual orbitals. The three oxygen $1s$-like occupied HF orbitals were frozen for all computations. Therefore, all single and double substitutions from the Hartree–Fock reference as well as a limited number of triple and quadruple substitutions, in which at most two electrons are allowed in the external subspace, were included in the CI space. The resulting configuration space included 117 references and yields 2 086 312 configuration state functions in C_{2v} symmetry and 219 references and 4 170 855 configuration state functions in C_s symmetry. This represents a drastic reduction from the 53 167 048 (C_{2v}) or 106 323 719 (C_s) configuration state functions in the complete CISDTQ wave function. The orbitals used are the natural orbitals from a TCSCF-CISD procedure in which the two dominant configurations are chosen as references.

Geometries and harmonic vibrational frequencies were determined via single point energy computations by the PSI[31] program package using the shape-driven graphical unitary group approach[25] for the CISD[TQ] wave function, and by the ACES II program system[32] for the Brueckner-based CC results. Geometries were optimized within C_{2v} symmetry with numerical gradients computed from five energy points along each internal coordinate for the CISD[TQ] wave function and three energy points along each internal coordinate for the Brueckner-based CC wave functions. Residual internal coordinate gradients were less than 10^{-6} in atomic units. For the antisymmetric displacements using the CISD[TQ] wave function, the two active orbitals in the TCSCF become the same symmetry. Hence, it was necessary to utilize the SCFX method[33,34] to carry out the TCSCF optimization of the molecular orbitals.

The double-ζ plus polarization (DZP) basis set is the standard Huzinaga–Dunning[35,36] double-ζ ($9s5p$) augmented with a set of six Cartesian d-type polarization functions on each oxygen atom [$\alpha_d(O) = 1.211$] for a total of 48 basis functions. The exponent for the d-type polarization functions was chosen to enable a direct comparison with the work of Watts *et al.*[37]

III. RESULTS AND DISCUSSION

The performance of selected reference MR-CISD and CASPT2 on the equilibrium structure of ozone was explored by Borowski *et al.*[38] Their results indicate that any multireference approach needs a large reference space in order to accurately compute the molecular properties of O_3. The reference space used in the present study is over four times the largest reference space utilized in the study of Borowski *et al.*[38] However, the number of substitutions included in the CISD[TQ] is still only 4% of the substitutions necessary for the complete CISDTQ.

Even with its modest size the CISD[TQ] wave function has been shown to predict energy differences, geometries, and harmonic vibrational frequencies in excellent agreement with the complete CISDTQ wave function.[26,27,29,39] The CISD[TQ] predictions for the equilibrium geometry and harmonic vibrational frequencies of ozone are given in Table I.

TABLE I. Equilibrium geometry and harmonic vibrational frequencies[a] of the $\widetilde{X}\ ^1A_1$ state of ozone with a DZP basis.

Method	Reference	r_e(Å)	θ_e(deg)	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
1R CISD[b]	23	1.247	117.7	1389	783	1565
2R CISD[b]	23	1.271	116.2	1234	745	1352
CASSCF[b]	21	1.296	116.5	1098	689	989
CCSD	2	1.263	117.4	1256	748	1240
B-CCD	This work	1.260	117.3	1264	756	1302
CCSD(T)	37	1.287	116.8	1129	703	976
B-CCD(T)	This work	1.288	116.8	1127	703	1097
CCSDT	37	1.286	116.7	1141	705	1077
CISD[TQ]	This work	1.281	116.7	1166	716	1138
Experiment[c]	43, 44	1.272	116.8	1135	716	1089

[a]Frequencies in cm^{-1}.
[b]Exponent of polarization functions differs from present study.
[c]Experimentally determined harmonic vibrational frequencies.

The predicted equilibrium bond length is within 0.009 Å of the experimentally determined value, while the bond angle is accurate to 0.1°. The harmonic vibrational frequencies are predicted to an average accuracy of 27 cm^{-1} (2.4%), with the difficult b_2 stretching frequency predicted to an accuracy of 49 cm^{-1} (4.5%). This is a sizeable improvement over the 113 cm^{-1} (10.4%) error in the CCSD(T) predicted b_2 stretching frequency. The remaining errors in the theoretical predictions are due in part to incompleteness in the basis set.

As reported by Kobayashi, Amos, and Handy,[40,41] the Brueckner-based CC methods yield promising results if the wave function includes an approximation for connected triple excitations. The DZP basis set utilized by Kobayashi, Amos, and Handy,[40,41] and that used in the current study, differ in the choice of orbital exponent for the polarization functions. In order to make direct comparisons, the DZP basis set described herein was used in conjunction with the Brueckner-based CC methods and the results reported in Table I. The B-CCD(T) approach predicts an equilibrium bond length which deviates from the experimental value by 0.016 Å, while the bond angle matches the experimentally determined value of 116.8°. The harmonic vibrational frequencies are predicted to within 10 cm^{-1} (1.1%) of the experimental harmonics, with the antisymmetric stretch only 8 cm^{-1} (<1%) from the experimental value of 1089 cm^{-1}. Since the B-CCD method is outperformed by CCSD(T), it appears that for the coupled-cluster methods the inclusion of the connected triple terms is more important than the choice of molecular orbitals for the reference determinant.

The highest level theoretical results to date are those of Watts, Stanton, and Bartlett.[37] The full CCSDT method, with a DZP basis, predicts the harmonic vibrational frequencies of O_3 to within 1% of the experimental harmonic values. This result is somewhat fortuitous since there are significant discrepancies between the CCSDT predicted and experimentally determined bond lengths due to the relatively small size of the DZP basis set.

Considering the absence of full CI results and higher angular momentum functions in the basis set, it is difficult to compare the various correlated methods and conclude with any certainty which approach is producing the most accurate results. For a series of diatomic molecules, Scuseria, Hamilton, and Schaefer[42] found the full CCSDT method to give good agreement with the complete CISDTQ method. Hence, for the purpose of this study, we will assume the CCSDT predictions represent the most accurate results within a DZP basis set and compare the other methods accordingly.

The CISD[TQ] wave function predicts equilibrium geometries to within 0.005 Å in the bond length and matches the CCSDT bond angle. The predicted harmonic vibrational frequencies are in agreement between the two methods to an average of 32 cm^{-1} (3.2%). The difficult antisymmetric stretching frequency is predicted by CISD[TQ] to differ by 61 cm^{-1} (5.7%) from the CCSDT result. As previously reported in the literature,[37,40,41] the coupled-cluster based methods, which include a perturbative correction for triples, yield an accurate prediction for the difficult harmonic force field of ozone. A comparison of the CCSD(T) and B-CCD(T) approaches reveals that the inclusion of orbital relaxation effects leads to a significant improvement in the predicted antisymmetric stretching frequency of O_3.

The results of this study suggest that the CISD[TQ] wave function is capable of obtaining accurate potential energy surfaces while drastically reducing the size of the CI (CISDTQ) space. The computational cost of the CISD[TQ] method has been discussed previously,[29] and is approximately O^4V^4, where O and V are the number of occupied and virtual orbitals, respectively. This estimate agrees with the $N_rO^2V^4$ scaling for a multireference CISD, where N_r is the number of references.

Recent research has explored a more cost efficient way of treating this MR-CISD method.[26,39] If CISD NO's are used, the triple and quadruple substitutions which include an electron in a low occupancy orbital may be neglected from the CISD[TQ] wave function. The resulting wave function, labeled split-virtual (SV) CISD[TQ], has been shown to reduce the number of configurations in a CISD[TQ] wave function with little loss in accuracy.[39] Because the SV-CISD[TQ] method is no longer a MR-CISD, the number of triple and quadruple substitutions becomes less than the number of singles and doubles in the limit of large basis sets. Hence, the computational cost of the SV-CISD[TQ] is not

much greater than that of a CISD. This is because the scaling in the external space, V^4, is the same for CISD and SV-CISD[TQ]. In the limit of basis set completeness, the external space (V) becomes large, while the occupied space (O) remains constant. The current results suggest that more affordable approximations to the CISD[TQ] method, such as the split-virtual CISD[TQ] approach recently reported by our group,[39] may perform well when applied to challenging molecular systems.

IV. CONCLUSIONS

With a DZP basis set, the CISD[TQ] wave function predicts an equilibrium geometry which differs from experiment by 0.009 Å in the bond length and 0.1° in the bond angle. The harmonic vibrational frequency predictions for ozone differ from those of experiment by an average of only 27 cm^{-1} (2.4%), while the difficult b_2 stretching frequency is placed within 49 cm^{-1} (4.5%) of the experimentally determined value. These results are comparable to those achieved with high level coupled-cluster methods, such as B-CCD(T) and CCSDT. We expect the CISD[TQ] wave function to be capable of providing highly accurate results over a wide range of geometries and electronic states. Our laboratory anticipates continued progress in the development and application of the CISD[TQ] and SV-CISD[TQ] methods.

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