

Connected quadruples for the frequencies of O₃

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Coupled cluster methods with full inclusion of quadruples (T_4) are not yet applicable to O₃ frequencies, but a recently proposed noniterative quadruples method [CCSDT(Q_f)] offers an $\sim n^7$ evaluation. We report large basis set results for O₃'s structure and harmonic vibrational frequencies, improving agreement with experiment over CCSDT. © 1999 American Institute of Physics. [S0021-9606(99)31717-7]

INTRODUCTION

The electronic structure of the ozone molecule, and particularly its vibrational frequencies have been a focus of intense research for sometime.¹⁻¹² The multiconfigurational nature of the ground state makes it a demanding test for widely applicable, single reference based, correlated quantum chemical methods. In addition the size of the system precludes having benchmark full CI results even for small basis sets. Consequently, we are forced to refer the computed quantities to experiment, and this raises the specter of basis set inadequacies. This situation is especially true for frequency calculations.¹⁻¹² Assuming the experimentally determined "harmonic" frequencies are reliable, several of the earlier works, based mostly on the CI approach, failed to give a correct ordering of the stretching modes.^{1,2} In subsequent papers it was found^{3-9,12} that coupled cluster approaches offered much better solutions and provided correct ordering even at the CCSD (Refs. 3, 4) level, for some (but not all) approximations to the CCSDT model,⁵⁻⁸ and for the full CCSDT approach.^{9,12} In Ref. 9 Watts *et al.* reported excellent agreement with experiment for the frequencies computed with the CCSDT method for a DZP basis set. Lee and Scuseria⁸ used the CCSD(T) approximation and expanded basis sets, and for the largest set the results differed by 37 cm⁻¹ for the asymmetric mode. Later, Borowski *et al.*¹⁰ obtained good frequencies for larger basis sets when their MRCI data were corrected for its size extensivity failing (see also the CI results of Leininger and Schaefer).¹¹ Recently Watts and Bartlett¹² reported a thorough study of ozone's structure and frequencies with full CCSDT in large basis sets up to cc-pVTZ and up to a cc-pV5Z basis set with CCSD(T). Their results suggest that the basis set limit for the CCSDT method will overestimate the two stretching mode frequencies by 40 to 50 cm⁻¹ and by about 15 cm⁻¹ for the bending mode. They conclude that an essential factor in getting more accurate values would be the inclusion of connected quadruples (i.e., T_4). This might be expected since the zeroth-order description of O₃ would appear to require at least two determinants differing by a double excitation. Thus, the balanced treatment of higher order correlation effects would

suggest taking at least double excitations from each determinant, which partly corresponds to introducing T_4 in a single reference theory.

The aim of this paper is to report the initial assessment of the T_4 effect in the coupled-cluster theory on the structure and vibrational frequencies of the ozone molecule. Since the complete inclusion of the T_4 cluster in CCSDTQ (Ref. 13) (an $\sim n^{10}$ method), or even in the more approximate iterative CCSDTQ-1 method¹⁴ (an $\sim n^9$ method), is very demanding computationally, we apply a computationally efficient method¹⁵ that can be applied to larger basis sets. The method, termed CCSDT(Q_f), is a T_4 analogue of the well known CCSD(T) scheme. The main advantage of the method is that it offers practically the same quality of results as the iterative CCSDTQ-1 approach while the basis set scaling of the T_4 part of the calculation is no worse than $\sim n^7$. In this way we can assess the role of T_4 on the O₃ vibrational frequencies.

SYNOPSIS OF THE THEORETICAL APPROACH

As presented elsewhere,¹⁵ a T_4 correction can be developed by using the converged CCSDT amplitudes ($\bar{T}_1, \bar{T}_2, \bar{T}_3$). We have

$$E_Q^5 = \langle 0 | \bar{T}_2^\dagger [W_N T_4] | 0 \rangle, \quad (1)$$

and the lowest order T_4 is expressed as

$$T_4 = R_4 [W_N (\bar{T}_2^2/2 + \bar{T}_3)]_c. \quad (2)$$

We introduce here the resolvent operator R_n ensuring the appropriate excitation subspace and the required denominator, which in general can be defined as $R_n[X] = (n!)^{-2} \sum [\langle \Phi_{ij\dots}^{ab\dots} | X | 0 \rangle / (e_i + e_j + \dots - e_b - e_a)] \times \{a^\dagger b^\dagger \dots ji\}$.

The main point in the evaluation of the T_4 contribution is a *forced factorization*, i.e., we compute $E_{Q_f}^5$ instead of E_Q^5 which provides the simpler expression:

$$E_{Q_f}^5 = \frac{1}{2} \langle 0 | \bar{T}_2^\dagger T_2^{(1)\dagger} [W_N (\bar{T}_2^2/2 + \bar{T}_3)]_c | 0 \rangle, \quad (3)$$

where $T_2^{(1)}$ is the first order T_2 operator defined as

$$T_2^{(1)} = \frac{1}{4} \sum \frac{\langle ab || ij \rangle}{e_i + e_j - e_a - e_b} \{a^\dagger b^\dagger ji\}. \quad (4)$$

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TABLE I. Geometry and harmonic frequencies for the ozone molecule with a DZP basis set. Bond lengths in Å, angles in degrees, and frequencies in cm^{-1} .

| Method | R_e | Θ | ω_1 | ω_2 | ω_3 |
|--------------------------|-------|----------|------------|------------|------------|
| CCSD ^a | 1.263 | 117.4 | 1256 | 748 | 1240 |
| CCSD(T) ^b | 1.287 | 116.8 | 1129 | 703 | 976 |
| CCSD(TQ _f) | 1.290 | 116.6 | 1114 | 699 | 1019 |
| ΔT_4 | 0.003 | -0.2 | -15 | -4 | 43 |
| CCSDT-3 ^b | 1.285 | 116.9 | 1150 | 707 | 1117 |
| CCSDT-3(Q _f) | 1.290 | 116.6 | 1121 | 700 | 1111 |
| ΔT_4 | 0.005 | -0.3 | -29 | -7 | -6 |
| CCSDT ^b | 1.286 | 116.7 | 1141 | 705 | 1077 |
| CCSDT(Q _f) | 1.292 | 116.4 | 1101 | 695 | 1061 |
| CCSDT(Q) | 1.292 | 116.4 | 1103 | 694 | 1062 |
| ΔT_4 | 0.004 | -0.3 | -40 | -10 | -16 |
| Exp. ^c | 1.272 | 116.8 | 1135 | 716 | 1089 |

^aReference 3.^bReference 9.^cReference 22.

Such a formulation of the T_4 correction allows us to avoid the explicit introduction of the T_4 operator and, consequently, consideration of the T_4 equation. The total correlation energy of the system is then,

$$E_{\text{tot}} = E(\text{CCSDT}) + E_{Q_f}^5. \quad (5)$$

There are several important characteristics of the above approach:

- the method is (size-)extensive as it includes only connected diagrams;
- the expression is correct through fifth-order in the MBPT energy;
- the T_4 part scales only as $\sim n^7$;
- the correlation corrections to the energy and properties are quite close to those obtained with the standard ($\sim n^9$) CCSDTQ-1 method.¹⁵

RESULTS AND DISCUSSION

All calculations are performed with the ACES II program system.¹⁶ To generate the set of \bar{T}_2 and \bar{T}_3 amplitudes required for the evaluation of the $E_{Q_f}^5$ contribution, Eq. (3), we use three standard coupled cluster approaches which include the T_3 operator: CCSD(T),⁶ CCSDT-3,¹⁷ and full CCSDT.¹⁸ The first requires only a single $\sim n^7$ step, the second an iterative $\sim n^7$ step, and the full CCSDT an iterative $\sim n^8$ step. Table I contains the calculated geometry and harmonic frequencies obtained with the standard DZP basis set.¹⁹ Table II reports results for the cc-pVTZ basis set.²⁰

We observe that the effect of the connected quadruples on the geometry is quite regular. At the DZP level the bond length increases due to the T_4 operator by 0.003, 0.005, and 0.004 Å for the CCSD(T), CCSDT-3, and CCSDT methods, respectively. The changes in angle are small: -0.3° for the iterative methods and -0.2° for CCSD(T). Very similar behavior occurs for the cc-pVTZ basis. The changes in bond lengths are 0.002, 0.004, and 0.005 Å for the three ap-

TABLE II. Geometry and harmonic frequencies for the ozone molecule with a cc-pVTZ basis set. Bond lengths in Å, angles in degrees, and frequencies in cm^{-1} .

| Method | R_e | Θ | ω_1 | ω_2 | ω_3 |
|--------------------------|-------|----------|------------|------------|------------|
| CCSD ^a | 1.250 | 117.6 | 1278 | 763 | 1266 |
| CCSD(T) ^a | 1.275 | 116.9 | 1153 | 716 | 1054 |
| CCSD(TQ _f) | 1.277 | 116.8 | 1144 | 714 | 1094 |
| ΔT_4 | 0.002 | -0.1 | -9 | -2 | 40 |
| CCSDT-3 ^a | 1.274 | 117.0 | 1165 | 717 | 1142 |
| CCSDT-3(Q _f) | 1.278 | 116.7 | 1143 | 713 | 1150 |
| ΔT_4 | 0.004 | -0.3 | -22 | -4 | 8 |
| CCSDT ^a | 1.274 | 116.8 | 1163 | 717 | 1117 |
| CCSDT(Q _f) | 1.279 | 116.6 | 1133 | 709 | 1112 |
| ΔT_4 | 0.005 | -0.2 | -30 | -8 | -5 |
| Exp. ^b | 1.272 | 116.8 | 1135 | 716 | 1089 |

^aReference 12.^bReference 22.

proaches considered, whereas the angle is nearly the same as for the DZP basis set. We note that as far as bond length is concerned the quadruple contribution increases the deviation from experiment: the CCSDT/cc-pVTZ bond length is already 0.002 Å too large, so now the discrepancy amounts to 0.007 Å. This inconsistency is due to basis set inadequacies. It was estimated in Refs. 10, 12 that the basis set limit CCSDT value would be close to 1.266 Å. Assuming that the T_4 effect would remain about the same for larger basis sets we might expect excellent agreement with experiment. The same refers to the bond angle, whose estimated basis set limit for the CCSDT method is 117° ,¹² while T_4 reduces it by 0.2° which would suggest the value of 116.8° .

The modifications in the harmonic frequency values due to connected quadruple excitations collected in Tables I and II are in accord with the changes in geometry, as an increase in bond length lowers the values of the frequencies. The symmetric stretching frequency is reduced by 40 cm^{-1} by T_4 at the CCSDT level in the DZP basis set and by 30 cm^{-1} for the larger basis set, a remarkably large effect. For the other two estimates of triples, CCSDT-3 and CCSD(T), respectively, the changes are 9(15) and 22(29) cm^{-1} for the cc-pVTZ (DZP) basis set. In the case of CCSD(TQ_f), which contains the (T) triples effect with Eq. (3), the T_3 amplitudes are obtained from the initial approximation [$T_3 = R_3(W_N \bar{T}_2)$].²¹ For CCSDT-3 and CCSDT, the \bar{T}_1 , \bar{T}_2 , and \bar{T}_3 amplitudes reflect their coupled solution, but, of course, not coupled to T_4 . The effect of T_4 coupling to T_1 , T_2 , and T_3 amplitudes would first appear in the sixth-order energy. The symmetric bending frequency is much less sensitive to the presence of the T_4 operator, with the maximum change observed for the CCSDT/cc-pVTZ calculations being -10 cm^{-1} . Since CCSDT/DZP frequencies are in nearly perfect agreement with experiment, the large reduction in ω_1 moves away from the experimental value as the error grows from 6 to 34 cm^{-1} . On the other hand the ω_1 frequency for CCSDT/cc-pVTZ is too high by 28 cm^{-1} and the reduction by 30 cm^{-1} provides a result quite close to the experimental value. We believe that for both basis sets the T_4 effect is

consistent and works in the proper direction. The CCSDT/DZP frequency is too low due to basis set limitations. The same applies to the ω_2 frequency. The T_4 effect is negative and the CCSDT(Q_f) agreement with experiment is slightly worse. However, the CCSDT basis set limit¹² for both symmetric frequencies is above experiment by 40 and 15 cm^{-1} which enables the T_4 correction to cause the calculated values to be close to experiment.

The ω_3 frequency behaves in a less consistent way. We observe that for CCSD(T) the T_4 correction is large and positive, for both basis sets. For the methods which include T_3 more rigorously, it becomes more negative being -16 and -5 cm^{-1} for the CCSDT method for the two basis sets, respectively. Since at the DZP level the CCSDT method underestimates the ω_3 frequency, the T_4 correction hurts the agreement, an improper behavior due to an insufficient basis. For the estimated basis set limit, all three CCSDT frequencies are overestimated, and we expect the T_4 correction to lower the values. Looking at the bottom rows in Tables I and II, we see that this is really so: all ΔT_4 are negative. However, the magnitudes of the corrections seem to correspond to the CCSDT discrepancies in all but the ω_3 case. The estimates place the CCSDT ω_3 frequency much higher than the experimental value even with the T_4 correction. There are various possible interpretations of this fact. Since the ω_3 frequency is much more sensitive to the theoretical approach, primarily because of the additional role played by configurations that are of different symmetry than those contributing to the symmetric mode,³ it may happen that the additional approximations introduced in the CCSDT(Q_f) are the culprit. As a test of our forced factorization procedure, we also report calculations using E_Q^5 [Eq. (1)], instead of $E_{Q_f}^5$. Since this is $\sim n^9$ computational procedure, we were only able to do calculations for the DZP basis set. These results are listed in the row with header CCSDT(Q) in Table I. We see that the results for the two approaches, i.e., CCSDT(Q) and CCSDT(Q_f) are virtually identical. Another approximation introduced in the CCSDT(Q_f) method is the noniterative nature of the T_4 operator which precludes any change in T_1 , T_2 , and T_3 due to T_4 . Finally, we neglect the higher-order terms in the T_4 equation. Of course, it is also possible that higher rank clusters (T_5, \dots) can play some role here and even at the full CCSDTQ level we might not be able to

accurately obtain the experimental data. Further study in that direction is being pursued in our laboratory.

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