

# Ab initio theoretical results on the stability of cyclic ozone<sup>a)</sup>

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In the last five years there has been a great deal of interest<sup>1-6</sup> in the possible existence of excited states of ozone, bound with respect to the O<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) plus O (<sup>3</sup>P) dissociation limit. Since the bond energy of O<sub>3</sub> is only 24.2 kcal/mole, this requires very low-lying excited states. Hay *et al.*<sup>1</sup> have provided strong theoretical evidence that the lowest triplet state (<sup>3</sup>B<sub>2</sub>) of ozone is bound by 4-10 kcal, a result that has been indirectly verified by later experimental studies.<sup>2</sup> Recent controversy<sup>5,6</sup> has focused on a second state of ozone, the ring or cyclic state, <sup>1</sup>A<sub>1</sub> (6π). So far there is no direct experimental evidence for the ring state; however, should the ring state lie less than 15 kcal above the ground state (~10 kcal below the dissociation limit), an extensive experimental search would be justified.

The problem with obtaining accurate estimates of the energy separation between ring and open ozone is that both the electronic structure and the electron-correlation energy of these states is very different. Indeed, accurate Hartree-Fock (HF) calculations predict the ground state to be neither open [<sup>1</sup>A<sub>1</sub> (4π)] nor cyclic [<sup>1</sup>A<sub>1</sub> (6π)]; instead, the <sup>3</sup>B<sub>2</sub> (4π) state is found to be the lowest HF state.<sup>1</sup> This error is a result of extremely large correlation effects in the <sup>1</sup>A<sub>1</sub> (4π) state owing to the singlet biradical character of this state. In this Communication we report the results of extensive calculations employing correlated wavefunctions for both states of ozone.

The basis used is the valence double zeta basis (contracted Gaussian functions) of Huzinaga<sup>10</sup> and Dunning<sup>11</sup> augmented with a set of *d* functions (α = 0.8853) on each oxygen. For the open state we used the experimental geometry<sup>12</sup> (R<sub>OO</sub> = 1.28 Å, ∠OOO = 116.8°) while for the cyclic state we used the geometry (R<sub>OO</sub> = 1.45 Å, ∠OOO = 60°) obtained from theoretical calculations.<sup>13</sup>

Our approach to including electron correlation is to solve self-consistently, using the generalized valence bond (GVB) method,<sup>7,8</sup> for a set of orbitals that account for the dominant correlation effects of *all* valence electron pairs. This leads to a set of 18 valence GVB orbitals of which nine can be considered as localized HF-like orbitals and nine as correlating orbitals (one associated with each valence HF orbital), all of which are solved for self-consistently.<sup>9</sup> Within this set of 18 optimized orbitals, even extensive CI (high order excitations) lead to only moderate sized calculations.

The strategy in the CI calculations is to include all configurations that could have a discriminatory effect on the two states of interest rather than trying separately to obtain the lowest possible energy for each state. To

do this we partition the GVB orbitals into the following sets:

- (A) The O<sub>i</sub>-O<sub>j</sub> bond pair (π for open, σ for ring).
- (B) The O<sub>i</sub>-O<sub>c</sub> and O<sub>j</sub>-O<sub>c</sub> bond pairs.
- (C) All lone pairs.
- (D) The O 1s pairs (the *core* orbitals).
- (E) All additional orbitals in the basis (the *virtual* orbitals).

Thus sets A, B, C, D, and E contain 2, 4, 12, 3, and 24 orbitals, respectively.

The major difference between the open and ring states is in set A, and hence the calculations include higher order correlations involving this pair. Thus the configurations for the GVB(9)-POL-CI calculations reported here are generated with respect to three dominant configurations (the three possible two-electron occupancies of set A). The calculations include single and double excitations within the set A+B+C and all single excitations within the set A+B+C+E from *each* of the three dominant configurations. The only restrictions placed on these configurations are that the total occupancies of sets A, B, and C remain between 1 and 3, 3 and 5, and 11 and 13 electrons, respectively. In all configurations the core orbitals (set D) are kept doubly occupied. No additional selection criteria are used; all such configurations allowed by symmetry are included in the CI calculations. Thus these calculations include a selected set of single, double, triple, and quadruple excitations in which higher order correlation terms involving the O<sub>i</sub>-O<sub>j</sub> bond pair (set A) are explicitly included. The resulting wavefunctions consist of 3461 and 2995 spin eigenfunctions (10878 and 9342 determinants) for the open and cyclic states, respectively. For comparison, an all singles and doubles CI calculation within the same basis would consist of ~39 000 determinants, and all quadruple excitations within just the valence space (18 orbitals) would consist of 492 950 determinants.

In order to test the effect of neglecting certain double excitations in the GVB-POL-CI (particularly those involving a double excitation to the virtual set), we carried out a calculation [referred to as HF-POL-CI(1+2)] in which the dominant GVB natural orbitals are replaced with localized HF orbitals,<sup>14</sup> and in which all configurations that differ from the dominant by more than a double excitation are excluded. The resulting energy separation of 18.5 kcal is in excellent agreement with the value of 18.5 kcal obtained from a full singles and doubles HF-CI.<sup>15</sup> This indicates that the double excitations

TABLE I. Summary of calculated ring-open energy separations (kcal/mole) of ozone (all with DZ  $d$  basis sets).

Calculation	Total energy (ground state)	Energy separation
HF	-224.30887	8.3 (6.8) <sup>a</sup>
GVB(1)	-224.40482	35.3
HF-POL-CI(1+2)	-224.62825	18.5
HF-CI(1+2)	-224.75948 <sup>a</sup>	18.5 <sup>a</sup>
GVB(9)-CI	-224.63493	24.5
GVB(9)-POL-CI	-224.65449	27.3

<sup>a</sup>Reference 15.

neglected in the GVB-POL-CI calculations lead to no significant differential effect.

The results of these calculations are given in Table I. The GVB-POL-CI calculations indicate that the ring state of ozone lies 27.3 kcal above the ground state. Including a small zero-point correction leads to the prediction of a  $v=0$  to  $v=0$  energy of 28 kcal, significantly above the ground state dissociation energy of 24.2 kcal. Similar calculations on a number of small molecules, including HO-OH, O-O, ethylene oxide, and CH<sub>3</sub>-OH lead to errors in bond energies of +4.2, +0.6, +2.0, and -0.7 kcal, respectively. Our estimate (*vide supra*) is that the error in the GVB-POL-CI ozone energy separation is at most 3 kcal. We conclude therefore that the ring state of ozone lies slightly above the ground state dissociation limit of ozone, but may well be metastable since there will be a small barrier to dissociation to O<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and O (<sup>3</sup>P).

The most extensive previous calculations on this system are those of Schaefer and Lucchese<sup>5</sup> who obtained an energy difference of 15.5-18.5 kcal from HF-CI (using a similar basis) in which all single and double excitations relative to the HF configuration were included. The difference between the GVB-POL-CI and HF-CI results is due to the higher order excitations (triples and quadruples) included in the GVB-POL-CI. Thus the effect of higher order excitations on the ring-open separation is 27.3 - 18.5 = 8.8 kcal. By using the GVB-POL-CI approach we are able to account for these high order electron-correlation effects explicitly while retaining an overall level of calculation much *smaller* than HF singles and doubles CI calculations.

A large number of other calculations on the ring-open energy difference using less extensive basis sets have been reported. The cyclic-open energy separations for HF wavefunctions are -48 kcal for minimal basis set,<sup>4</sup> 6.9<sup>3</sup> to 7.0 kcal for a double zeta (DZ) basis, and 6.8<sup>5</sup> to 8.3 kcal for DZ plus  $d$  functions. Using a DZ basis but  $s$  bond functions in place of  $d$  functions leads to -7.0 kcal,<sup>3</sup> and use of  $s$  and  $p$  bond functions leads to +2.9 kcal.<sup>6</sup> The error of -14 kcal in using  $s$  bond functions in place of  $d$  functions explains the low value (16.2 kcal) obtained in the CI calculations of Shih *et al.*<sup>3</sup>

Recently, Burton<sup>6</sup> has reported the results of PNO-CI

(3.8 kcal) and CEPA (4.6 kcal) calculations using a double zeta plus  $s, p$ -bond function basis. This basis leads to an HF ring-open separation of 2.9 kcal, indicating a bias of 5.4 kcal toward the ring state. The PNO-CI calculations are equivalent to an HF plus double excitations (no singles) CI calculation. To establish the error caused by leaving out single excitations in HF-CI, we carried out HF plus singles and doubles and HF plus doubles CI calculations in a double zeta basis. The single excitations are found to lower the open state by 7.1 kcal while lowering the ring state by only 2.6 kcal. Correcting the PNO-CI result for both effects leads to 3.8 + 5.4 + 4.5 = 13.7 kcal, in fair agreement with Schaefer's calculations (18.5 kcal).<sup>15</sup>

The CEPA method is an approximate procedure for including the effect of higher order excitations in a doubles CI wavefunction. The CEPA calculations reported by Burton predict that the effect of higher order excitations will be to increase the ring-open energy separation by 0.8 kcal. The GVB-POL-CI calculations, in which these higher order terms are included explicitly, indicate the effect to be much larger (8.8 kcal). Thus we conclude the unusually low ring-open separation reported by Burton is due to a combination of poor basis, lack of single excitations, and an inaccurate treatment of higher order correlations.

In conclusion, extensive GVB-POL-CI calculations predict the ring state of ozone to lie ~28 kcal above the ground state. We estimate (*vide supra*) a maximum error of 3 kcal in the GVB-POL-CI excitation energy and hence expect the ring state of ozone to lie slightly above the O<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and O (<sup>3</sup>P) dissociation limit (24.2 kcal).

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<sup>14</sup>Localized HF orbitals were obtained by projecting the dominant GVB natural orbitals onto the HF occupied orbitals. We also carried out a calculation in which the full list of configurations from GVB-POL-CI was used but with HF orbitals in place of the nine dominant GVB orbitals. This led to a ring-open

separation of 25.0 kcal, indicating that use of HF orbitals requires even higher order excitations.

<sup>15</sup>R. R. Lucchese and H. F. Schaefer III (personal communication). This calculation included single and double excitations out of all valence occupied orbitals to the full virtual space using a cumulative threshold of 0.09 hartree.