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Energy Separation Between the Open \((C_{2v})\) and Closed \((D_{3h})\) Forms of Ozone* 

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One of the most important recent discoveries\textsuperscript{1-8} of theoretical chemists is the existence of a bound, low-lying cyclic (D\textsubscript{3h}) isomer of \( \text{O}_3 \). The normal open (or C\textsubscript{2v}) form, with equilibrium geometry \( r(0-0) = 1.278\text{Å}, \theta(000) = 116.8° \), has of course been known for many years.\textsuperscript{9} However the energy separation between the C\textsubscript{2v} and D\textsubscript{3h} isomers continues to be a rather volatile quantity.

For reasons of brevity we cite here only the more recent and reliable results. To date, the largest basis set used to probe the open-closed energy separation (called \( \Delta E \) hereafter) problem is the standard\textsuperscript{10} double zeta plus polarization set employed by Siu and Hayes.\textsuperscript{4} Although they did not consider the effects of electron correlation,\textsuperscript{11} their self-consistent-field (SCF) \( \Delta E \) value of 8.9 kcal is probably within a few kcal of the Hartree-Fock limit. In an earlier paper, Hayes and Siu\textsuperscript{12} stated their belief that correlation effects should increase the Hartree-Fock value of \( \Delta E \), i.e. that there is more correlation energy associated with the open or normal form of ozone. In their excellent paper on the electronic spectrum of \( \text{O}_3 \), Hay, Dunning, and Goddard\textsuperscript{7} conclude that \( \Delta E \) is \( > 32 \) kcal. However it appears that the methods used to calculate \( \Delta E \) were considerably less reliable than employed in the rest of this important paper. The cyclic isomer of \( \text{O}_3 \) was discovered by Peyerimhoff and Buenker\textsuperscript{1} and their more recent study\textsuperscript{6} employs configuration interaction (CI) including roughly 200 configurations. Using a double zeta basis augmented by s-type bond functions between each pair of O atoms, Shih, Buenker, and Peyerimhoff (SBP) predict \( \Delta E \) to be 16.1 kcal. The most recent theoretical study, by Burton and Harvey,\textsuperscript{8} adds \( \text{p}_x,\text{p}_y, \) and \( \text{p}_z \) bond functions to the basis of SBP and used the PNO-CEPA method to predict a \( \Delta E \) value of 4.6 kcal.

Since state-of-the-art \textit{ab initio} methods should be capable of more precision than the 30 kcal range seen above, we decided to markedly
improve upon previous theoretical studies. The predictively reliable\textsuperscript{11} 0(9s5pld/4s2pld) double zeta plus polarization basis was used, with the set of six \( \alpha \)-like functions having gaussian orbital exponent \( \alpha = 0.8 \).

Although this same basis has been used in SCF studies by Rothenberg and Schaefer,\textsuperscript{1} Siu and Hayes,\textsuperscript{4} and Hay, Dunning, and Goddard,\textsuperscript{7} it has not been applied including correlation effects to the open-closed energy difference problem. For the open isomer, the experimental geometry was assumed, while for the closed form an 0-0 separation of \( \approx 1.44 \text{Å} \) is now generally accepted.\textsuperscript{4–8}

CI was carried out using the recently developed BERKELEY\textsuperscript{14} system of programs. All singly excited Slater determinants relative to the Hartree-Fock reference configurations

\begin{align*}
\text{open} & \quad 1a_1^2b_2^2a_2^23a_2^22b_2^24a_1^25a_2^23b_1^24b_2^26a_1^21a_2^2 \\
\text{closed} & \quad 1a_1b_1^22a_1^23a_2^22b_2^24a_1^25a_1^23b_2^21b_1^26a_1^21a_2^22b_2^2
\end{align*}

(1) (2)

were included. Double excitations were selected using the cumulative perturbation theory method of Raffenetti, Hsu, and Shavitt.\textsuperscript{15} Configurations \( i \) were selected in two different ways: (a) based on their matrix elements \( H_{1i} \) with the SCF configuration (1) or (2); and (b) based on their matrix elements with the wave function consisting of the three most important\textsuperscript{16} configurations for each isomer. Two series of CI calculations were performed differing in the number of "core" SCF orbitals held doubly-occupied in all Slater determinants. In the first series six molecular orbitals were frozen, and in the second only the (three oxygen \( 1s \)-like) \( 1a_1, 2a_1, \) and \( 1b_2 \) SCF orbitals were constrained to be doubly-occupied. The most time-consuming calculation was the first entry in the Table, i.e. for the open isomer with six SCF orbitals frozen. Using the Harris Corporation Slash Four minicomputer, this required somewhat less than 2 hours for the SCF stage (including all
molecular integrals) and 15 hours for the CI. Since the cost of time on this small machine is only about $8/hour\textsuperscript{17}, it may be seen that this study was carried out at a reasonably modest cost.

Our results are summarized in the Table. From the total energies given there it may be seen that the SCF energy difference is 6.8 kcal, a result which should be within ±3 kcal of the true Hartree-Fock ΔE value for the chosen geometries. All four CI treatments predict, as suggested first by Hayes and Siu\textsuperscript{12}, that correlation is more important for the C\textsubscript{2v} than the D\textsubscript{3h} isomer. The final pair of calculations should be the most reliable, since the use of a three configuration wavefunction in the perturbation selection scheme may be quite important for the open form. The latter prediction must be corrected for the effects of higher (triple, quadruple, etc.) spinorbital excitations, especially unliked clusters, which should be more important for the open form. Although there are fairly elaborate methods\textsuperscript{18} for approximately including these effects, one of the most useful is the simple formula derived by Davidson.\textsuperscript{19} Applying this to the final two calculations in the Table, the predicted open-closed separation is increased to 19.2 kcal. A final small correction\textsuperscript{20} will arise, since the closed form (with presumably a larger symmetric stretching frequency) will have somewhat more zero point vibrational energy. Thus we arrive at our final estimate for ΔE of 20±5 kcal. Hence we conclude that nearly all the observable properties of ozone may be explained without reference to the cyclic isomer.

Finally we note that our prediction is rather close to that of Shih, Buenker, and Peyerimhoff.\textsuperscript{6} However, this agreement must be considered somewhat fortuitous since their smaller basis predicts the closed form to lie 7 kcal below the open at the SCF level. Thus the contribution of correlation effects is much less than suggested by their results.
References

8. P.G. Burton and M.D. Harvey, "Theoretical Evidence for Metastable Cyclic Ozone", to be published.

This procedure was considered desirable since the second most important configuration of open ozone \((\text{1a}_2^2+2\text{b}_1^2)\) has a large coefficient \(0.1393\) here. Similarly, the third configuration \((1\text{b}_1^2+2\text{b}_1^2)\) occurs with coefficient...
0.0632. For cyclic ozone the second and third most important configurations are the degenerate pair $6a_1^2\rightarrow 4b_2^2$, $3b_2^2\rightarrow 4b_2^2$, both with coefficient 0.0725 in the last calculation reported in the Table.

20. D.P. Craig, personal communication.
Table

Summary of configuration interaction (CI) results for the open \( (C_2v) \) and closed \( (D_3h) \) isomers of ozone. The SCF total energies were -224.30971 and -224.29887 hartrees, respectively.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>SCF Orbitals Double Occupied</th>
<th>Cumulative Double Occupied Threshold ( \sigma )</th>
<th>Number of Principal Configurations ( \alpha )</th>
<th>Slater Determinants Tested</th>
<th>Slater Determinants in CI</th>
<th>Total Energy (hartrees)</th>
<th>( \Delta E ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open</td>
<td>6</td>
<td>0.01</td>
<td>1</td>
<td>16,739</td>
<td>5,641</td>
<td>-224.65081</td>
<td>16.2</td>
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<tr>
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<td>0.01</td>
<td>1</td>
<td>16,331</td>
<td>4,750</td>
<td>-224.62497</td>
<td></td>
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<tr>
<td>Open</td>
<td>3</td>
<td>0.09</td>
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<td>39,873</td>
<td>5,706</td>
<td>-224.75948</td>
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<td>1</td>
<td>38,579</td>
<td>4,913</td>
<td>-224.73000</td>
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<td>4,728</td>
<td>-224.72735</td>
<td></td>
</tr>
</tbody>
</table>

\( \alpha \) See text and reference 15.
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