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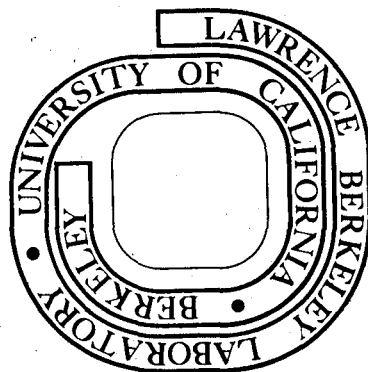
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Energy Separation Between the Open (C_{2v}) and Closed
(D_{3h}) Forms of Ozone*

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One of the most important recent discoveries¹⁻⁸ of theoretical chemists is the existence of a bound, low-lying cyclic (D_{3h}) isomer of O_3 . The normal open (or C_{2v}) form, with equilibrium geometry $r(O-O) = 1.278\text{\AA}$, $\theta(OOO) = 116.8^\circ$, has of course been known for many years.⁹ However the energy separation between the C_{2v} and D_{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 ΔE hereafter) problem is the standard¹⁰ double zeta plus polarization set employed by Siu and Hayes.⁴ Although they did not consider the effects of electron correlation,¹¹ their self-consistent-field (SCF) ΔE value of 8.9 kcal is probably within a few kcal of the Hartree-Fock limit. In an earlier paper, Hayes and Siu¹² stated their belief that correlation effects should increase the Hartree-Fock value of ΔE , 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 O_3 , Hay, Dunning, and Goddard⁷ conclude that ΔE is > 32 kcal. However it appears that the methods used to calculate ΔE were considerably less reliable than employed in the rest of this important paper. The cyclic isomer of O_3 was discovered by Peyerimhoff and Buenker¹ and their more recent study⁶ 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 ΔE to be 16.1 kcal. The most recent theoretical study, by Burton and Harvey,⁸ adds $p_x, p_y,$ and p_z bond functions to the basis of SBP and used the PNO-CEPA method to predict a ΔE value of 4.6 kcal.

Since state-of-the-art 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 reliable¹¹ 0(9s5p1d/4s2p1d) double zeta plus polarization basis was used, with the set of six d-like functions having gaussian orbital exponent $\alpha = 0.8$.

Although this same basis has been used in SCF studies by Rothenberg and Schaefer,¹ Siu and Hayes,⁴ and Hay, Dunning, and Goddard,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 $\sim 1.44 \text{ \AA}$ is now generally accepted.⁴⁻⁸

CI was carried out using the recently developed BERKELEY¹⁴ system of programs. All singly excited Slater determinants relative to the Hartree-Fock reference configurations

$$\text{open } 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 3b_2^2 1b_1^2 4b_2^2 6a_1^2 1a_2^2 \quad (1)$$

$$\text{closed } 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 3b_2^2 1b_1^2 6a_1^2 1a_2^2 2b_1^2 \quad (2)$$

were included. Double excitations were selected using the cumulative perturbation theory method of Raffanetti, Hsu, and Shavitt.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 important¹⁶ 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/hour¹⁷, 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 Siu¹², that correlation is more important for the C_{2v} than the D_{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 methods¹⁸ for approximately including these effects, one of the most useful is the simple formula derived by Davidson.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 correction²⁰ 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.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.

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16. This procedure was considered desirable since the second most important configuration of open ozone ($1a_2^2 \rightarrow 2b_1^2$) has a large coefficient¹², 0.1393 here. Similarly, the third configuration ($1b_1^2 \rightarrow 2b_1^2$) occurs with coefficient

References (Cont'd)

- 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.
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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.

Isomer	SCF Orbitals Double Occupied	Cumulative Threshold ^a σ	Number of Principal Configurations ^a	Slater Determinants Tested	Slater Determinants in CI	Total Energy (hartrees)	ΔE (kcal/mole)
Open	6	0.01	1	16,739	5,641	-224.65081	} 16.2
Closed	6	0.01	1	16,331	4,750	-224.62497	
Open	3	0.09	1	39,873	5,706	-224.75948	} 18.5
Closed	3	0.09	1	38,579	4,913	-224.73000	
Open	6	0.01	3	16,739	5,372	-224.64995	} 16.4
Closed	6	0.01	3	16,331	4,668	-224.62384	
Open	3	0.09	3	39,873	5,102	-224.75202	} 15.5
Closed	3	0.09	3	38,579	4,728	-224.72735	

^a See text and reference 15.

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