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G.B. Fitzgerald (Ph.D. Thesis)

August 1984

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Ab Initio STUDIES OF SOME UNIQUE
MOLECULAR SYSTEMS

George Benedict Fitzgerald
Ph.D. Thesis

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August 1984
Ab Initio Studies of Some Unique Molecular Systems

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ABSTRACT

Results of several unrelated ab initio studies are presented.

The first is a study of the ground and first excited states of the three smallest cycloalkynes: cyclopropyne, cyclobutyn e, and cyclopentyn e. The $^1A_1$ ground state of cyclopropyne is predicted to be a transition state, while the ground state of cyclobutyn e is a minimum on the potential energy hypersurface. Cyclobutyn e is therefore predicted to be the smallest observable cycloalkyne. Cyclopentyn e is not a relative minimum in $C_{2v}$ symmetry but is probably a stable species if allowed to relax to $C_8$ point group symmetry. The effects of electron correlation are required in order to make these predictions; at the single-configuration Hartree-Fock level of theory, none of these molecules is a minimum in its ground state.

Studies of the hydroperoxyl dimer, $(\text{HO}_2)_2$, indicate that the cyclic, two-hydrogen-bond form is a minimum on the energy surface and is energetically lower than two separated $\text{HO}_2$ molecules by 4.88 kcal/mole. This form of the dimer contains two long, weak hydrogen bonds, each about half as strong as that of the water dimer. Several other structures of the $\text{HO}_2$ dimer are found to be energetically unfavorable.
Finally, a method for performing variational self-consistent-field calculations on excited singlet states of the same symmetry as the ground state is presented. Extensions of this technique to evaluate the first and second energy derivatives with respect to nuclear motion are developed. Applications of this method to the $^1(\pi^*\pi^*)$ state of formaldehyde show that the method is capable of predicting reasonably accurate excitation energies. A full geometry optimization of this state reduces the excitation energy by about 2.3 eV from the vertical excitation energy. Evaluation of the harmonic vibrational frequencies demonstrates that this state is a minimum in $C_{2v}$ symmetry, while the $^3(\pi^*\pi^*)$ is a minimum only in $C_s$ symmetry.
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I. AB INITIO STUDIES OF SMALL CYCLOALKYNES

I.1 INTRODUCTION

Small ring systems are of continuing interest in chemistry, and monocyclic, otherwise saturated acetylenes (cycloalkynes) have received considerable attention in recent years, with several books\textsuperscript{1-4} being devoted in whole or in part to the subject. One question which remains of fundamental interest concerns the size of the smallest such ring which can actually exist, however transiently. Such a problem provides not only a unique challenge to the synthetic chemist, but should also yield insight into the limits of carbon-carbon bonding.

The smallest unsubstituted cycloalkyne isolable in quantity is the relatively large eight-membered ring, cyclooctyne. First synthesized by Blomquist and Liu\textsuperscript{5} in 1953, cyclooctyne contains a fairly 'normal' triple bond, despite an estimated 10 kcal/mole of ring strain.\textsuperscript{4} The C-C triple bond stretching frequency has been measured at 2210 cm\textsuperscript{-1}, as compared to 1974 cm\textsuperscript{-1} for acetylene\textsuperscript{6}, the prototype triple bond. Additionally, the triple bond length is 1.232±0.0006Å, not far removed from that of acetylene, 1.203Å. These results are, perhaps, not surprising in view of the fact that the eight-membered ring is large enough so that the bond angle containing the triple bond is only distorted to 158.5°±0.9°, not far from the linear arrangement associated with sp hybridization and triple bonds.

While the next smallest cycloalkyne, cycloheptyne, is apparently not isolable, the substituted ring, 3,3,7,7-tetramethylcycloheptyne

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]
has been synthesized by Krebs and Kimling. Though neither a complete structural determination, nor a vibrational spectrum has been obtained for this compound, the observed stretching frequency for the triple bond, 2180 cm$^{-1}$, indicates that this bond is rather strong.

Thus, one can see that under conditions which do not produce a great deal of strain, a strong carbon-carbon triple bond may be easily incorporated into a ring system. However, as the rings become smaller and the strain increases, these molecules become (not surprisingly) less stable and more difficult to observe. While there is considerable evidence$^{1-4}$ for the transient existence of the unsubstituted six- and five-membered rings, this evidence rests primarily upon analogy to isolable cycloalkynes, on expected reaction products derived from cycloalkyne intermediates, and on labeling and kinetic studies.$^2$ For example, Wittig$^8$ was among the first to deduce the transient existence of cyclopentyne; the reaction of 1,2-dibromocyclopentene with diphenylisobenzofuran evidently proceeds via a cyclopentyne intermediate.

Perhaps the most promising attempt thus far at the spectroscopic identification of cycloalkyne intermediates is provided by the results of Chapman and co-workers.$^9$ The flash photolysis of 1,6-bis(diazo)cyclohexanone in solid argon also proceed through a cyclopentyne intermediate as shown:

$$
\text{N}_2\text{N}_2\xrightarrow{hv} \text{N}_2\text{N}_2\text{C}=\text{O}\xrightarrow{hv} \text{N}_2\text{N}_2\text{C}=\text{O}\xrightarrow{hv} \xrightarrow{hv} \text{H}_2\text{C}:=\text{C}:=\text{CH}_2
$$

(1)

The last step in (1) was, unfortunately, too rapid to allow the
spectrum of cyclopentyne to be recorded.

There is at present no evidence for even the most transient existence of cyclobutylene:

\[ \text{I.2} \]

Wittig and Wilson\textsuperscript{10} explored pathways analogous to those employed in the cyclopentyne study,\textsuperscript{8} but were unable to verify the existence of the four-membered cycloalkyne. Montgomery and Roberts\textsuperscript{11} suffered a similar lack of success. Chapman has not yet attempted a spectroscopic study of this species, but the experiment should prove challenging in light of the failures of the earlier studies.

Despite the lack of experimental evidence for cyclobutylene, several theoretical studies do exist. Hehre and Pople\textsuperscript{12} did a complete geometry optimization of cyclobutylene in their exhaustive minimum-basis-set self-consistent-field (SCF) study of the \( \text{C}_4\text{H}_4 \) potential energy hypersurface. As expected, cyclobutylene was found to lie fairly high in energy, 117.5 kcal/mole above vinylacetylene,

\[ \text{I.3} \]

the global minimum on the \( \text{C}_4\text{H}_4 \) energy surface. Hehre and Pople did not address the question of whether or not cyclobutylene was a minimum on the surface, i.e., a stable molecule. A semi-empirical study by Kollmar and co-workers\textsuperscript{13} did investigate its stability in their study of all of the \( \text{C}_4\text{H}_4 \) isomers. These workers concluded that the molecule was in fact not a stable compound, but would rather spontaneously decay to a 'non-
classical' bicyclic structure, with a bond occurring between two diagonally opposite carbon atoms.

There have been no attempts by experimentalists (at the time of this writing) to identify the smallest conceivable cycloalkyne, cyclopropyne:

\[ \text{\includegraphics[width=0.1\textwidth]{cyclopropyne.png}} \]

An earlier study by Saxe and Schaefer\textsuperscript{14} demonstrated that in its \( ^1A_1 \) ground state the molecule was not a minimum on the \( C_3H_2 \) potential energy hypersurface. This prediction was based on the observation that motion of the \( CH_2 \) group in a direction parallel to the multiple bond lowered the energy. However, such a procedure does not completely characterize this stationary point. One would like to know if this structure represents a true transition state, i.e., possesses a single imaginary vibrational frequency,\textsuperscript{15} and if so what molecular normal mode corresponds to the reaction coordinate. To obtain this information, harmonic vibrational frequencies are required, which, unfortunately, were not readily determined at the time of the Saxe study.\textsuperscript{14}

The purpose of this investigation is thus several-fold. First, it is necessary to perform a more thorough study of the cyclopropyne molecule. In particular, harmonic vibrational frequencies are required, as discussed earlier. Also, the addition of higher angular momentum functions (polarization functions) to the basis set should have a significant effect upon the predicted properties, and should be investigated.

Secondly, a detailed ab initio study of cyclobutylene is needed.
Cyclobutylene occupies a key position in cycloalkyne chemistry. Since cyclopropyne is probably not stable,¹⁴ and since cyclopentyne has been observed at least tentatively,¹⁻⁴,⁸,⁹ cyclobutylene is either the largest unstable cycloalkyne or the smallest observable one. This study will address the question of whether or not cyclobutylene is a minimum on the \( \text{C}_4\text{H}_4 \) surface, and it is expected to produce more reliable results than the earlier semi-empirical study¹³ for such a highly strained system.

Finally, a study of cyclopentyne will provide theoretical predictions for a species which should be characterized (at least to some extent) by experimentalists in the near future. This should not only aid experimentalists in their identification of the molecule, but should also provide insight into why this is the smallest cycloalkyne which is relatively easy to observe by indirect means.¹⁻⁴,⁸,⁹

I.2 THEORETICAL

In the case of each singlet cycloalkyne studied, two electronic configurations are expected to play important roles, making ordinary self-consistent-field (SCF) calculations of dubious quality. Though the ground states of these molecules could be simply regarded as closed shell systems giving rise to carbon-carbon triple bonds, the highly strained nature of these rings requires one to consider the contribution to the wavefunction of antibonding electronic configurations, which allow for the delocalization of electron density. In all cases the in-plane \( \pi^2 \) and \( \pi^*2 \) configurations (which correspond to two electrons in the HOMO and LUMO orbitals, respectively) were found to contribute significantly to the ground state wavefunctions. Two-configuration (TC) SCF calculations were therefore necessary to describe correctly the
ground states. The first excited states of these cycloalkynes correspond to triplet $\pi\pi^*$ configurations and are well described by single-configuration SCF methods. Both the ground and first excited states of each molecule were studied.

Several different basis sets were used for each molecule. The smallest was the standard double-zeta (DZ) basis set of Huzinaga and Dunning, which may be designated C(9s5p/4s2p), H(4s/2s). For hydrogen, the s functions were scaled by a factor of 1.2, i.e., all gaussian orbital exponents were multiplied by a factor of $1.2^2 = 1.44$ relative to the optimum exponents for the isolated hydrogen atom. The second basis set, DZ+d, is obtained by augmenting the carbon atom DZ basis with a set of d-like cartesian gaussian orbitals ($\alpha=0.80$). These functions are expected to be necessary because of the strained nature of the rings. Finally, a set of p-like functions ($\alpha=1.0$) were added to the hydrogen atom basis set. This last set, termed DZ+P, was the largest and was used only for the first excited state of cyclobutylene (the second molecule studied) and was discontinued when it was found to have no significant effects upon the molecular geometry.

Complete geometry optimizations were performed within the confines of $C_{2v}$ symmetry, the highest point group symmetry possible for these molecules. Analytic SCF gradients or analytic TCSCF gradients were used to aid in the geometry optimizations. Quadratic force constants and the ensuing harmonic vibrational frequencies were calculated at each stationary point, either by analytic second derivative methods or by finite differences of analytic gradients, whichever was more expedient. Specific techniques will be reported along with each case.
Finally, at each stationary point, the effects of electron correlation were obtained using the method of configuration interaction\textsuperscript{23} (CI). All valence electrons were correlated. Carbon 1s-like orbitals were held doubly occupied in each configuration, while their virtual orbital counterparts were never occupied (this is understood to be the case, even when the term 'all single and double excitations' is used later in this paper). The actual sizes of the configuration spaces will be reported along with each specific case.

I.3 RESULTS

I.3.1 CYCLOPROPYLENE

The ground state of the cyclopropylene molecule is a $^1A_1$ state and is described by the two configurations

\[ 1a_1^2b_2^2a_1^3a_2^4a_1^8b_1^2b_2^5a_1^2b_1^26a_1^2 \]  \hspace{1cm} (2)

\[ 1a_1^2b_2^2a_1^3a_1^24a_1^2b_1^2b_2^5a_1^2b_1^23b_2^2 \]  \hspace{1cm} (3)

which correspond to $\pi^2$ and $\pi^*2$ configurations, respectively. The first excited state is a $^3B_2$ state, and is well described by the single $\pi\pi^*$ configuration

\[ 1a_1^2b_2^2a_1^3a_1^24a_1^2b_1^2b_2^5a_1^2b_1^26a_1^2b_2^2 \]  \hspace{1cm} (4)

Each of the states was studied using both the DZ and DZ+d basis sets.\textsuperscript{16,17} The harmonic vibrational frequencies were determined by analytic SCF\textsuperscript{21} and TCSCF\textsuperscript{22} second derivative methods. CI calculations at
each of the stationary points were performed as described earlier. For the $^1A_1$ state all single and double excitations relative to both configurations (2) and (3) were included, resulting in 5724 singlet configurations with the DZ basis set and 19331 with the DZ+d basis set. In the case of the $^3B_2$ state, all single and double excitations relative to configuration (4) were used, resulting in 3816 and 12582 triplet configurations with the DZ and DZ+d basis sets, respectively.

Energetics

The absolute energies of cyclopropyne (in hartrees/molecule) and the singlet-triplet energy splittings (in kcal/mole) are shown in Table I.I for both basis sets and all levels of theory employed. In each case the two-configuration singlet state lies below the triplet in energy. The most accurate calculation (DZ+d CI) predicts a splitting of only 10.6 kcal/mole.

The CI studies performed here quantitatively verify, a posteriori, the need for two configurations in the SCF description of the ground state. The CI coefficient of the triplet reference configuration (4) is 0.9386, corresponding to 88.1% of the wavefunction. For the singlet, the coefficients of reference configurations (2) and (3) are 0.8988 and -0.2749, respectively, corresponding to 80.8% and 7.6% of the CI wavefunction. Together, these two singlet configurations constitute about as much of the correlated singlet wavefunction as the single reference (4) does the correlated triplet wavefunction.

Molecular Structures

The predicted structures for singlet and triplet cyclopropyne are
shown in Figure 1.1. The effect of adding d functions to the carbon atom basis set is simply to shorten the carbon-carbon bonds by 0.02-0.04Å, as more electron density is allowed to situate between the atoms. This is to be expected, so the following discussion will center on the (more accurate) DZ+d structures.

For both the singlet and triplet structures, the predicted C-C single bond lengths of 1.52-1.53Å compare well with the 'standard' single bond length of 1.54Å. There is nothing particularly unusual here. It is now necessary to compare the C-C multiple bonds in each of the cyclopropyne structures to known double and triple bonds in order to ascertain the effects of ring strain on the nature of these bonds.

The multiple bond of \( ^3\text{B}_2 \) cyclopropyne has an electronic configuration corresponding to \( \pi\pi^* \), and one would expect this to resemble a double bond, because the \( \sigma \) orbital and the other \( \pi \) orbital are each still doubly occupied. The bond should thus be comparable to the double bond of cyclopropene; it is, in fact, only 0.02Å shorter than that bond length of 1.296Å. Also, the bond length is slightly closer to that of ethylene, rather than to that of acetylene. On this basis, one may classify it as a rather strong double bond.

The TCSCF wavefunction consists of 89% configuration (2) and 11% configuration (3). The substantial antibonding character introduced by (3) is expected to weaken the triple bond, possibly to the point of making it appear like a double bond. The predicted bond length is 1.241Å. This is 0.038Å longer than the triple bond of acetylene, but almost 0.1Å shorter than the double bond of ethylene. Based on length, the bond may be unambiguously classified as a triple bond.
Vibrational Frequencies

Consideration of the harmonic vibrational frequencies (Table I.II) further elucidates the nature of these C–C bonds. One should first note that the harmonic SCF frequencies are expected to be too large by about 12%.\textsuperscript{25,26} This empirical correction accounts for the effects of anharmonicity, basis set incompleteness, and electron correlation. As in the case of the geometries, one may concentrate on the DZ+d results, which should be more reliable than those obtained with the DZ basis set.

The C–C double bond stretching frequency of triplet cyclopropyne is predicted to be 1920 cm\textsuperscript{-1}, and represents a very strong double bond. Even after the empirical reduction of 12%, the resulting value of 1689 cm\textsuperscript{-1} is still stronger than the observed double bond frequency of either cyclopropene\textsuperscript{27} (1656 cm\textsuperscript{-1}) or of ethylene\textsuperscript{6} (1623 cm\textsuperscript{-1}).

The predicted C–C triple bond stretching frequency of singlet cyclopropyne is 2049 cm\textsuperscript{-1}. This compares well with the experimentally observed triple bond fundamentals of cyclooctyne\textsuperscript{5} (2210 cm\textsuperscript{-1}) and 3,3,7,7-tetramethyl-cycloheptyne\textsuperscript{7} (2180 cm\textsuperscript{-1}). The empirically reduced value of this frequency is only 1803 cm\textsuperscript{-1}. This still compares well with the observed value for acetylene\textsuperscript{6} (1974 cm\textsuperscript{-1}). Recently, Chapman\textsuperscript{9} has proposed that the fundamental observed at 1930 cm\textsuperscript{-1} in the spectrum of acenaphthyne

\begin{center}
\includegraphics{acenaphthyne.png}
\end{center}

be assigned to the triple bond stretch. If this is so, the value of 1803 cm\textsuperscript{-1} would appear to represent a triple bond, despite the tremendous amount of ring strain.
The single most notable feature of the frequencies reported in Table I.II is the presence of a single imaginary frequency for $^1A_1$ cyclopropyne, while all those for the $^3B_2$ state are real. Thus, while the triplet state is a relative minimum on the $C_2H_2$ potential energy hypersurface, the singlet is a transition state, consistent with the earlier prediction of Saxe and Schaefer$^{14}$ (which was made without vibrational frequencies). The normal mode corresponding to the imaginary frequency may be referred to as C-C single-bond asymmetric stretch or as a ring opening; motion along this normal mode apparently leads to the formation of propadienyldiene

![Diagram](image)

which is predicted to be the global minimum on the $C_2H_2$ energy surface by Dykstra and co-workers.$^{28}$

Concluding Remarks

The source of the instability of singlet cyclopropyne is most likely the acute bond angle of 65.9°, which is dictated by the relatively normal C-C bond lengths and the molecular symmetry. The expected bond angle for a triple bond is, of course, 180°, so this bond has been distorted to only one third of its preferred value. The triplet's bond angle is about the same, 65.4°, but need only distort from 120°, the prototype carbon-carbon double bond angle, and should thus be considerably less unstable. Comparison of these theoretical predictions to the results for cyclobutyne in the next section will shed further light on this subject.
I.3.2 CYCLOBUTYNE

The two electronic configurations necessary for the correct description of the ground state of cyclobutylene are

\[ \alpha_1^2 \beta_2^2 \alpha_2^2 \beta_2^2 \alpha_1^2 \beta_1^2 b_2^2 3a_1^2 \alpha_1^2 \beta_1^2 4b_1^2 5a_1^2 \alpha_1^2 \beta_1^2 7a_1^2 \]  

(5)

\[ \alpha_1^2 \beta_2^2 \alpha_2^2 \beta_2^2 \alpha_1^2 \beta_1^2 3b_1^2 4b_1^2 5a_1^2 \alpha_1^2 \beta_1^2 6a_1^2 \alpha_1^2 \beta_1^2 5b_1^2 \]  

(6)

while the excited state is described by the single \( ^3B_2 \) configuration

\[ \alpha_1^2 \beta_2^2 \alpha_2^2 \beta_2^2 \alpha_1^2 \beta_1^2 3b_1^2 4b_1^2 5a_1^2 \alpha_1^2 \beta_1^2 6a_1^2 \alpha_1^2 \beta_1^2 7a_1^2 5b_1^2 \]  

(7)

Both the DZ and the DZ+d basis sets\(^{16,17}\) employed in the cyclopropyne study were used here. In addition, the \( ^3B_2 \) state was studied with the DZ+P basis set, as well. Geometries were optimized in \( C_2v \) symmetry with the use of analytic SCF\(^{18,19}\) gradients in the case of the triplet and analytic TCSCF\(^{20}\) gradients in the case of the singlet state. Harmonic vibrational frequencies were evaluated using finite differences of analytic gradients.

At each stationary point CI calculations were performed in a manner analogous to that employed for the cyclopropyne molecule. In this case, all single and double excitations with respect to both (5) and (6) were used in the CI wave function for the ground state, and all single and double excitations relative to (7) were used in the triplet calculation. The size of each configuration space is shown in Table I.III.
Energetics

Consistent with the cyclopropyne system, $^1A_1$ cyclobutylene is predicted to lie lower in energy than $^3B_2$ cyclobutylene at all levels of theory and with all basis sets used (Table I.III). The most accurate calculation of the singlet-triplet splitting is again the DZ+d CI: 12.8 kcal/mole. This is 2.2 kcal/mole greater than the value obtained for cyclopropyne and indicates that the ground state is becoming more stabilized with respect to the triplet as the ring opens.

The CI predictions again quantitatively verify the need for two configurations in the SCF description of the ground state. In this case the two references (5) and (6) amount to 86.6\% of the correlated $^1A_1$ wavefunction, while reference (7) constitutes 86.7\% of the $^3B_2$ CI wavefunction; the two singlet configurations together are about as important as one triplet reference alone.

Finally, note that cyclobutylene does not lie especially low on the C$_4$H$_4$ potential energy hypersurface. The single-configuration calculations of Hehre and Pople\textsuperscript{12} predicted cyclobutylene would lie 117.5 kcal/mole above vinylacetylene, 1.3, the lowest isomer of C$_4$H$_4$. For comparison, the same study found that tetrahedrane, an experimentally unknown isomer, would be 93.8 kcal/mole above vinylacetylene. At the experimental geometry of vinylacetylene,\textsuperscript{29} a TCSCF calculation of its ground state was performed. This shows singlet cyclobutylene to be only about 78 kcal/mole above the C$_4$H$_4$ global minimum at the TCSCF level of theory. Though this ring remains high in energy, inclusion of the second configuration into the ground state wavefunction stabilizes it dramatically. However, this still says nothing about the absolute stability of the molecule; vibrational frequencies are still required to
determine whether the molecule is actually a local minimum on the potential energy hypersurface.

Molecular Structures

The predicted $C_{2v}$ geometries for singlet and triplet cyclobutene are shown in Figure I.2. Note first that the effect of adding d functions to the carbon atom basis set is again to shorten the carbon-carbon bond lengths; shrinkage is on the order of $0.015-0.025\text{Å}$, as compared to $0.021-0.037\text{Å}$ in the three-membered ring. This is another indication that the larger ring is less strained than the smaller. The effects of adding p functions to the hydrogen atom basis set were investigated only for the $^3B_2$ state. As can be seen in the figure, these effects are virtually insignificant: the shortening of the C-C single bonds by $0.001\text{Å}$ and the change in the H-C-H bond angle by $0.1^\circ$ are negligible. This larger basis was not employed in any subsequent calculations.

The C-C single bonds in both singlet and triplet cyclobutene appear to be normal single bonds. Focussing on the DZ+d structures, one sees bond lengths of $1.532\text{Å}$ (opposite the multiple bond) and $1.563\text{Å}$ (adjacent to the multiple bond) in the singlet structure; the triplet contains single bonds with length $1.577\text{Å}$ and $1.516\text{Å}$, opposite and adjacent to the multiple bond, respectively. All of these fall within range of the standard C-C single bond length, $1.54\text{Å}$, although $1.577\text{Å}$ might be considered a trifle long.

One interesting comparison between triplet and singlet single bond lengths is the reversal of the order of the C-C single bond distances. That is, one finds the relationships:
singlet \ r(\text{adjacent}; 1.563) > r(\text{opposite}; 1.532) \quad (8a) \\
triplet \ r(\text{opposite}; 1.577) > r(\text{adjacent}; 1.516) \quad (8b)

Since the structure of a triplet cycloalkyne has never been determined experimentally, it is not obvious whether or not the relationships in (8) are general. However, a comparison can be drawn with the structure of cyclobutene, which is 'isostuctural' with triplet cyclobutyne, in the sense of having one double and three single C-C bonds within a four-membered ring. For cyclobutene the experimental carbon-carbon distances\textsuperscript{30} are 1.517\text{Å} (adjacent to double bond) and 1.566\text{Å} (opposite double bond). It is evident that the analogy between cyclobutene and triplet cyclobutyne bond distances is extraordinarily good in this respect.

The multiple bond of triplet cyclobutyne is nearly 0.02\text{Å} shorter than the double bond of cyclobutene, yet over 0.1\text{Å} longer than the C-C bond of acetylene, clearly allowing its classification as a strong double bond. The C-C multiple bond of the singlet (1.258\text{Å}) is significantly closer to the bond length of acetylene than it is to that of ethylene, being only 0.055\text{Å} removed from the former. This allows it to be classified as a triple bond, though a weak one.

These bond lengths dictate an unusually small bond angle of 95.0° for the singlet, substantially removed from the 180° expected for a triple bond. Even so, this is significantly more relaxed than the 66° found in the unstable three-membered ring. It is illuminating to perform more structural comparisons between the three- and four-membered rings. The multiple bonds in both singlet and triplet cyclobutyne are longer...
than the corresponding bonds in cyclopropyne, the former by 0.017Å, and the latter by 0.047Å. Though the rings are under less strain, the multiple bonds actually appear weaker. The nature of these bonds will be further explored in the next section, which presents the results of harmonic vibrational frequency calculations.

Vibrational Frequencies

The predicted harmonic vibrational frequencies for singlet and triplet cyclobutyn e are given in Table I.IV. If the single most notable feature of the vibrational frequencies of cyclopropyne was the presence of a single imaginary frequency, then the most notable feature here is the lack of any imaginary modes at all: both singlet and triplet cyclobutyn e are relative minima on the C₄H₄ potential energy hypersurface. Cyclobutyn e is therefore the smallest potentially observable cycloalkyne. One should be cautious, since the fact that cyclobutyn e is a relative minimum says nothing about how deep or shallow that minimum actually is. This criterion is crucial to the issue of whether or not this molecule can actually be observed in the laboratory. Nevertheless, this ab initio study has produced results in marked contrast to the MINDO/3 prediction that cyclobutyn e is not a local minimum. More recently, Binkley and Frisch performed an exhaustive study of several C₄H₄ isomers to ascertain the effects of basis set and electron correlation on the predicted heats of formation. They noted that at the single-configuration SCF level of theory, cyclobutyn e is not a minimum on the potential energy hypersurface. Rather, the molecule is only predicted to be a minimum when the effects of electron correlation are considered. The results of the MINDO/3 study are thus consistent
with a single-configuration SCF study, which is simply inadequate for this system.

The multiple bond stretching frequencies are of interest in describing the nature of these triple bonds. The bond lengths reported in the previous section indicate that the singlet and triplet structures contain triple and double bonds, respectively. This is supported by the vibrational frequencies. The multiple bond stretching frequency in the triplet is 1779 cm\(^{-1}\), with the DZ+d basis. The empirical reduction\(^{25,26}\) of 12\% leads to a prediction of 1566 cm\(^{-1}\), a result which is fortuitously identical to the double bond stretch of cyclobutene.\(^{32a}\) There can be little doubt that this represents a double bond.

The C–C triple bond stretching frequency of singlet cyclobutyne is predicted to be 1911 cm\(^{-1}\) at the DZ+d TCSCF level of theory. The corrected value is 1682 cm\(^{-1}\), only 116 cm\(^{-1}\) greater than that observed in cyclobutene. This bond represents a fairly weak triple bond.

Comparison of the other predicted frequencies of singlet and triplet cyclobutyne with those observed for cyclobutene is also instructive. In particular the ring puckering frequencies at 276 (singlet cyclobutyne) and 371 cm\(^{-1}\) (triplet) bracket the observed fundamental (325 cm\(^{-1}\)) for cyclobutene. The cyclobutene ring deformation at 875 cm\(^{-1}\) is in very close agreement with the analogous frequency (878 cm\(^{-1}\)) for triplet cyclobutene, but much higher than the 618 cm\(^{-1}\) predicted for the singlet. The three cyclobutene C–C single-bond stretching frequencies are labeled ring expansion by Lord\(^{32a}\) and assigned as 1210 (\(b_2\)), 1182 (\(a_1\)), and 1113 cm\(^{-1}\) (\(a_1\)). However, Suzuki and Nibler\(^{32b}\) have reassigned the \(b_2\) mode (out of phase C–C stretch) to 886 cm\(^{-1}\) and the two \(a_1\) modes to 1113 and 986 cm\(^{-1}\). The latter
assignments are reasonably close to the present predictions for singlet cyclobutane ($a_1$ 1100, $b_2$ 963, and $a_1$ 916 cm$^{-1}$), although the ordering of the last two frequencies is reversed. The same theoretical order ($a_1 > b_2 > a_1$) is predicted for triplet cyclobutane, with upward shifts in the absolute values of 27 ($a_1$), 102 ($b_2$), and 6 cm$^{-1}$ ($a_1$). The most recent assignment of the C-C single-bond stretching frequencies is that of Aleksanyan and Garkusha$^{32c}$ and does agree with the theoretical ordering for cyclobutane. Aleksanyan and Garkusha assign 1112 ($a_1$), 1009 ($b_2$), and 874 cm$^{-1}$ ($a_1$) to the C-C single-bond modes.

Concluding Remarks

As was done for the geometric structures, it is profitable to compare the harmonic vibrational frequencies of the three- and four-membered cycloalkynes. Recall that the C-C double bond fundamental for cyclopropyne was 1920 cm$^{-1}$, while that for cyclobutane was 1779 cm$^{-1}$; a decrease in the stretching frequency by 7% accompanied a 4% increase in the bond length going to the larger ring. The singlet species also displays a 7% decrease in the triple bond fundamental upon going to the larger ring, while the bond length decreases by about 1%. Each multiple bond is both weaker and longer in the larger (less strained) ring. Since singlet cyclobutane is a local minimum while singlet cyclopropyne corresponds to a transition state, the decrease in ring strain energy must more than compensate for the observed weakening and stretching of the triple bond. The instability of cyclopropyne lies in its untenable bond angle of 66°. It would seem that a triple bond can distort to 95°, but not to 66°.
I.3.3 CYCLOPENTYNE

The largest cycloalkyne investigated by \textit{ab initio} quantum mechanical methods is the five-membered ring, cyclopentyn e. This is the smallest cycloalkyne whose existence has been verified experimentally.\textsuperscript{1}-\textsuperscript{4,8,9} One should be able to make several predictions about this species based on the results obtained for the other two cycloalkynes. As the ring opens, one expects the singlet-triplet splitting (between the two-configuration ground state and the first excited state) to increase over the value for cyclobutyn e. Also the multiple bonds should be shorter and stronger than in the four-membered ring, since increasing the ring size will reduce the amount of strain and allow more electron density to build up between the atoms. The same argument does not necessarily apply in going from the three- to the four-membered ring, since singlet cyclopropyne is a transition state and not a minimum.

The two $^1A_1$ configurations needed to describe the ground state are

\begin{equation}
1a_1^2b_2^22a_1^2b_2^23a_1^2a_1^24a_1^2b_2^25a_1^2b_1^24b_2^27a_1^2a_1^28a_1^25b_2^2b_1^23b_1^29a_1^2 \quad (9)
\end{equation}

\begin{equation}
1a_1^2b_2^22a_1^2b_2^23a_1^2a_1^24a_1^2b_2^25a_1^2b_1^24b_2^27a_1^2a_1^28a_1^25b_2^2b_1^23b_1^26b_2^2 \quad (10)
\end{equation}

while the first excited state results from the single $^3B_2$ configuration

\begin{equation}
\cdots \: 8a_1^25b_2^2b_1^23b_1^29a_1^26b_2 \quad . \quad (11)
\end{equation}

In addition to the TCSCF $^1A_1$ ground and single-configuration $^3B_2$ excited state studies, a single-configuration SCF study of the ground state using only (9) was performed. Since cyclopentyn e has been observed
experimentally, it is possible that the amount of diradical character introduced by the antibonding configuration is sufficiently small so that (10) is not necessary to the calculation. This would be in sharp contrast to the results for cyclobutene, in which the antibonding configuration is needed to obtain even a qualitatively correct description of the energy surface.

All geometries were initially optimized within $C_{2v}$ symmetry constraints using analytic gradients. Harmonic vibrational frequencies were determined at each stationary point; finite differences of analytic gradients were employed for the single-configuration $^1A_1$ study, while analytic second derivatives were used for the other two. At this point, results are available only with the DZ basis set.

Energetics

As was found for the smaller cycloalkynes, $^3B_2$ cyclopentene is predicted to lie higher in energy than TC $^1A_1$ cyclopentene at both levels of theory considered (Table I.V). The most accurate calculation (DZ CI) predicts a value for the singlet-triplet splitting of 22.0 kcal/mole. This is over 10 kcal/mole larger than the DZ CI singlet-triplet splitting of cyclobutene. Consistent with the predictions made earlier, the singlet-triplet energy difference increases along with increasing ring size.

Single-configuration $^1A_1$ cyclopentene is actually found to lie 19.3 kcal/mole higher in energy than the $^3B_2$ state at the SCF level and 4.5 kcal/mole lower at the CI level of theory. This shows that even for this relatively large ring, the second configuration is crucial in determining the energetics of the system.
Finally, note that reference configuration (11) accounts for 85.8% of the correlated triplet wave function, and reference configurations (9) and (10) together account for exactly the same amount of the two-reference singlet CI wave function. In the single reference treatment of $^1A_1$ cyclopentyne, reference (9) accounts for only 84.4% of its correlated wave function. While this is very close to the value found in the other two calculations, the slight difference is sufficient to alter the singlet-triplet energy difference from 22.0 to 4.6 kcal/mole. This once again demonstrates the importance of the second configuration (10) in treating the singlet state.

Molecular Structures

The predicted structures for the three states of cyclopentyne are shown in Figure 1.3. Recall that these are predicted using only the DZ basis, while all earlier discussions have included DZ+d results. Based on the results for the smaller cycloalkynes one can anticipate that addition of d functions to the carbon atoms will result in a shrinkage of the C-C bond lengths by about 0.015 to 0.020 Å.

Looking first at the $^3B_2$ structure, one observes C-C single bond lengths of 1.573 and 1.515 Å. Both are within range of the prototype single bond length. The single bonds in the TC $^1A_1$ structure are 1.589 and 1.514 Å, similar to those of the triplet. The single-configuration $^1A_1$ state contains C-C bond lengths of 1.605 and 1.518 Å, slightly longer than those found in the other two, and the former now represents a very long carbon-carbon single bond.

The multiple bonds of the triplet and singlet electronic states are significantly shorter than the corresponding bonds in the four-membered
rings: that of the singlet is 0.024Å shorter and that of the triplet 0.01Å shorter than the comparable bonds of DZ cyclobutyn. Indeed, the bond lengths predicted here using the DZ basis are comparable to the bond lengths of cyclobutyn found using the DZ+d basis. The triple bond of the TC ground state is 1.253Å long, only 0.05Å longer than that of acetylene; a DZ+d calculation should predict it to be even shorter. The double bond of the triplet is 1.333Å, almost identical to that of ethylene. These are strong triple and double bonds.

Since the single-configuration \(1^1A_1\) state has no diradical character incorporated into its wavefunction, its C-C triple bond should be significantly shorter than that found in the TC ground state. As seen in Fig. 3, this is indeed the case: the predicted bond length is 1.214Å, only 0.01Å longer than the prototype triple bond of acetylene. It was mentioned earlier that the C-C single bond lengths of this species were somewhat longer than those found in the other two. It appears that electron density has been shifted into the triple bond (at the expense of the single bonds) when the diradical (\(\pi^2\)) character was removed.

As was done for the smaller rings, triplet cyclopentyn may be profitably compared to cyclopenten, a known molecule. The C-C single bonds of cyclopenten have been measured by Davis and Muecke\(^{33}\) at 1.546±0.035Å and 1.519±0.030Å. These are in close agreement with the predicted values for triplet cyclopentyn. The double bond of the alkene is 1.342Å long, actually 0.01Å longer than that of triplet cyclopentyn. This confirms the statement that triplet cyclopentyn contains a particularly strong double bond.

Vibrational Frequencies
The predicted harmonic vibrational frequencies for each of the three planar cyclopentyne wave functions are shown in Table I.VI. Note first of all that none of these is predicted to be a minimum on the \( \text{C}_5\text{H}_6 \) potential energy hypersurface. In each case there is an imaginary frequency, corresponding to a ring folding mode, which would appear to lead to a minimum in \( \text{C}_5 \) symmetry. Considering the parallels between the smaller cycloalkynes and their cycloalkene counterparts, this is hardly surprising. Cyclopentene is known to be puckered with an out-of-plane angle of 28.8°±2.5°. In view of this, one would expect cyclopentyne to be puckered as well. In addition to this imaginary frequency the single-configuration \( ^1\text{A}_1 \) state possesses a second one (334 cm\(^{-1}\)), corresponding to a ring opening, as will be discussed shortly.

The magnitude of the imaginary frequency in each case is quite small, 79 (\( ^1\text{A}_1 \)), 51 (\( ^3\text{B}_2 \)), and 64 cm\(^{-1}\) (TC \( ^1\text{A}_1 \)). This indicates that the potential energy surface is flat with respect to motion along this mode. Consequently, little or no change in the remaining geometrical parameters is expected if the molecule were optimized in \( \text{C}_5 \) symmetry. Therefore, one may anticipate that the triplet and two-configuration singlet states of \( \text{C}_5 \) cyclopentyne are minima on the potential energy hypersurface with geometry and harmonic vibrational frequencies very close to the \( \text{C}_2\nu \) values. By the same argument, the large imaginary frequency of the single-configuration singlet is not likely to change significantly, and this state should still represent an unstable species, even in \( \text{C}_5 \) point group symmetry.

The DZ \( ^3\text{B}_2 \) frequencies corresponding to ring modes agree well with the experimentally observed frequencies of cyclopentene. Villarreal and co-workers, for example, report various \( a_1 \) ring modes of 600, 896,
and 962 cm\(^{-1}\), which correspond to triplet cyclopentylene values of 722, 933, and 1041 cm\(^{-1}\) (635, 820, and 916 cm\(^{-1}\) after 12\% reduction). The cyclopentene C-C double bond stretching frequency is observed at 1617 cm\(^{-1}\),\(^{34,35}\) while the predicted frequency for triplet cyclopentylene is 1819 cm\(^{-1}\). Reduction of this value by 12\%\(^{25,26}\) leads to a prediction of 1610 cm\(^{-1}\), very close to the cyclopentene value. This once again demonstrates the strength of the triplet cycloalkyne double bond. Note also that this stretching frequency is greater than that of DZ triplet cyclobutylene (1731 cm\(^{-1}\)) by 5\%. This bond is both shorter and stronger than that of the smaller ring.

Both the singlet wave functions (one- and two-configuration) yield ring mode frequencies in a range comparable to cyclopentene and triplet cyclopentylene. The \(a_1\) ring modes, for example, are 732, 911, and 1047 cm\(^{-1}\) (reduced values of 643, 803, and 921 cm\(^{-1}\)) in the TC \(^1\)A\(_1\), and 705, 888 and 1025 cm\(^{-1}\) (reduced values of 620, 781, and 902 cm\(^{-1}\)) in the single-configuration \(^1\)A\(_1\) treatment. These three frequencies are predicted to be lower in the single-configuration \(^1\)A\(_1\) state than in the TC singlet state. This is attributable to the localization of excessive electron density in the triple bond, caused by the lack of any electron correlation in the former state, and is exactly analogous to the effect observed for the C-C bond lengths.

Of fundamental importance here is the stretching frequency of the triple bond. This is predicted to be 1990 cm\(^{-1}\) in the TC \(^1\)A\(_1\) state and 2300 cm\(^{-1}\) in the other. The latter is, of course, substantially greater since no effects from the \(\pi^*\) orbital are considered. Even the smaller of these two values represents a substantive triple bond. After a 12\% reduction\(^{25,26}\) the resulting value, 1751 cm\(^{-1}\), is still reasonably
strong. It compares favorably with the proposed C-C triple bond stretching frequency of 1930 cm\(^{-1}\) found for acenaphthyne\(^9\), I.5.

While the triple bond of the one-configuration \(^1\)A\(_1\) state is quite strong, this value must be disregarded in favor of the more complete level of theory; the TC \(^1\)A\(_1\) takes into account a great deal of the correlation energy and therefore yields a substantially more reliable result. Indeed, the single-configuration \(^1\)A\(_1\) state does not even represent a minimum on the potential energy hypersurface (even in C\(_s\) symmetry), a result comparable to that found for cyclobutyne.\(^{31}\) There is an imaginary frequency of magnitude 334 cm\(^{-1}\) which corresponds to the opening of one of the C-C single bonds adjacent to the triple bond. Thus, at that level of theory, the molecule is unstable, and decomposes spontaneously. (After this was written, Gilbert and Blaze reported in J. Am. Chem. Soc. 106, 1885 (1984), that MINDO/3 predicts cyclopentyne is not a minimum on the energy surface, just as it did for cyclobutyne.\(^{13}\) As demonstrated here, the effects of electron correlation are absolutely necessary for a correct description of the molecule in its ground state, and hence the semi-empirical results are highly questionable.)

I.4 CONCLUDING REMARKS

The most significant result of the work presented here is the prediction that cyclobutyne is the smallest stable unsubstituted cycloalkyne. It should be emphasized again that there is not yet any information regarding 'how stable' it is, i.e., the depth of its potential well is still unknown; it could turn out that a small amount of internal energy might be sufficient to cause it to dissociate. However, this result is completely different from that obtained by other
The instability of the smaller cyclopropyne ring is a result of its acute bond angle. The angle of about 66° is a result of the C-C single and triple bond lengths (which are rather ordinary) and the $C_2v$ symmetry of the molecule. Basically, this shows that a triple bond can be bent from its preferred linear arrangement to 95° (the bond angle of cyclobutynne) but not as far as the 66° bond angle in cyclopropyne. It would be illuminating if there were a wider variety of compounds available to test the generality of such a supposition.

Naturally, as the size of the ring increases, the amount of ring strain will decrease. This should lead to shorter, stronger triple bonds as the $\pi^2$ configuration contributes less to the wavefunction. Additionally, the same effect should increase the energy splittings between the ground and first excited states in the larger rings. The data presented support these conjectures in going from the four- to the five-membered ring. In going from the three- to the four-membered cycloalkyne, $\Delta E$ does increase, but the expected trend for the bond lengths is not observed. One could reason that the above arguments do not apply in that case, since cyclopropyne is not a minimum on its potential energy hypersurface. As before, it would be enlightening if data were available for a wider range of molecules; in fact, preparations are being made to begin a study of cyclohexyne, the next largest cycloalkyne.

Finally, one should again note that the smallest cycloalkyne yet observed is cyclopentynne.\textsuperscript{1-4,8,9} Had the single-configuration $^1A_1$ state of this molecule turned out to be a relative minimum on the energy surface, it would have shown a fundamental qualitative difference
between this and the next smallest ring, cyclobutyne, i.e., the smallest observed ring would have been the smallest for which the antibonding configuration was not necessary to the correct description of the ground state. The results show instead that the difference between cyclopentyne and cyclobutyne is one of degree rather than one of kind: the second configuration of the five-membered ring accounts for about 15% of its DZ TCSCF wavefunction, while the antibonding configuration of the four-membered ring accounts for about 16% of its DZ TCSCF wavefunction. While this means that the smaller ring should be more difficult to observe, owing to the slightly larger diradical character, there are no basic differences between the two which would preclude the possibility of its observation.

It is hoped that these results will both inspire and aid experimentalists in their studies of small cycloalkynes. It is with confidence that I await the isolation and spectroscopic identification of cyclobutyne.
II. STUDIES OF THE HYDROPEROXYL DIMER, \((\text{HO}_2)_2\)

II.1 INTRODUCTION

The growing awareness of the importance of the hydroperoxyl radical, \(\text{HO}_2\), in atmospheric processes has led to a number of increasingly sophisticated studies in recent years. This radical occupies a central position in the kinetics of hydrogen-oxygen mixtures. For example, it is an important source of hydrogen peroxide in the upper atmosphere: \(^{38,39}\)

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_4 + \text{O}_2.
\]

This reaction is thought to proceed via an \(\text{H}_2\text{O}_4\) intermediate whose approximate lifetime is 1-20 ms. \(^{39}\) Despite the importance of \(\text{H}_2\text{O}_4\) in atmospheric chemistry, its structure has never been firmly established. \(^{40}\) Neither have there been any theoretical studies of this species, though \(\text{HO}_2\) itself has been thoroughly investigated. \(^{41-47}\)

Among the possible structures for \(\text{H}_2\text{O}_4\), one of the most aesthetically appealing is perhaps the chemically bound dimer

\[\text{H} - \overset{\text{O}}{\text{O}} - \overset{\text{O}}{\text{O}} - \text{H}\]

which is isoelectronic with butane. The possible hydrogen bonded structures include a cis form:

\[\text{H} - \overset{\text{O}}{\text{O}} - \overset{\text{O}}{\text{O}} - \text{H} - \overset{\text{O}}{\text{O}}\]

and a trans isomer:
Several cyclic structures are also possible:

\[ \text{II.3} \]

However, the structure II.5 has apparently been ruled out as the intermediate in reaction (1) by isotopic labeling experiments.\(^{49}\)

The most recent spectroscopic study of the \( \text{H}_2\text{O}_4 \) system is that of Diem, Tso, and Lee (DTL).\(^{50}\) In their experiment, dilute samples of formaldehyde were photolyzed in an \( \text{O}_2 \) matrix. Among the reaction products was \( \text{H}_2\text{O}_4 \). By examining the frequency shifts between the spectra of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O}_4 \), and by comparing these to the analogous shifts in water and hydrogen peroxide dimerization, DTL concluded that "the structure of \((\text{H}_2\text{O}_2)_2\) is probably a non-planar, six-membered ring" containing two hydrogen bonds.\(^{50}\) Their paper concluded with the hope that this would stimulate theoretical studies of the \( \text{H}_2\text{O}_4 \) system.

The goal of this study was to accept Lee's challenge by carrying out a full geometry optimization of the cyclic dimer, II.4. In addition to the geometry, the harmonic vibrational frequencies were also predicted to allow a comparison with the dimer-monomer frequency shifts observed by DTL. Finally, the geometry and frequencies of the chemically bound, open chain structure, II.1, were also predicted and compared to the experimental results.
II.2 THEORETICAL

All geometry optimizations were carried out at the SCF or TCSCF level of theory. The structure II.4 was optimized in $C_{2h}$ symmetry, which restricts the molecule to being planar and maintains the equivalency of the monomer units. If one assumes that the two units remain relatively unperturbed electronically, then the radical electron on each will stay relatively isolated in the out-of-plane $p$ orbital of each terminal oxygen. This leads to the $^{3}B_{u}$ electronic configuration

$$1a_g^2b_{2g}^2c_{3g}^2d_{4g}^2e_{5g}^2f_{6g}^2g_{1u}^2h_{2u}^2i_{3u}^2j_{4u}^2k_{5u}^2l_{6u}^2m_{7u}^2n_{8u}^2o_{9u}^2p_{10u}^2q_{11u}^2r_{12u}^2s_{13u}^2t_{14u}^2u_{15u}^2v_{16u}^2w_{17u}^2x_{18u}^2y_{19u}^2z_{20u}^2.$$  (2)

If, on the other hand, bonding occurs, then a good candidate for the ground state is the two-configuration $^{1}A_g$ state arising from the configurations

$$
\cdots 6a_{g}^{2}b_{u}^{2}c_{u}^{2}d_{g}^{2}e_{u}^{2}f_{u}^{2}g_{g}^{2}h_{u}^{2}i_{u}^{2}j_{u}^{2}k_{g}^{2}l_{g}^{2}m_{u}^{2}n_{u}^{2}o_{u}^{2}p_{u}^{2}q_{u}^{2}r_{u}^{2}s_{u}^{2}t_{u}^{2}u_{u}^{2}v_{u}^{2}w_{u}^{2}x_{u}^{2}y_{u}^{2}z_{u}^{2}.
$$  (3)

$$
\cdots 6a_{g}^{2}b_{u}^{2}c_{u}^{2}d_{g}^{2}e_{u}^{2}f_{u}^{2}g_{g}^{2}h_{u}^{2}i_{u}^{2}j_{u}^{2}k_{g}^{2}l_{g}^{2}m_{u}^{2}n_{u}^{2}o_{u}^{2}p_{u}^{2}q_{u}^{2}r_{u}^{2}s_{u}^{2}t_{u}^{2}u_{u}^{2}v_{u}^{2}w_{u}^{2}x_{u}^{2}y_{u}^{2}z_{u}^{2}.
$$  (4)

The $^{1}B_{u}$ state arising from (2) was not studied, since this is expected to lie energetically above the $^{3}B_{u}$ state by Hund's rules.

In addition to structure II.4, two geometries of the chain structure, II.1, were located, one in $C_{2h}$ point group symmetry and the other in $C_{i}$. In each case, the ground state is a closed shell $^{1}A_g$ state. The configurations are

$$1a_{g}^{2}b_{u}^{2}c_{u}^{2}d_{g}^{2}e_{g}^{2}f_{u}^{2}g_{u}^{2}h_{g}^{2}i_{u}^{2}j_{g}^{2}k_{u}^{2}l_{u}^{2}m_{u}^{2}n_{g}^{2}o_{g}^{2}p_{g}^{2}q_{g}^{2}r_{g}^{2}s_{g}^{2}t_{g}^{2}u_{g}^{2}v_{g}^{2}w_{g}^{2}x_{g}^{2}y_{g}^{2}z_{g}^{2}.$$  (5)
Finally, since it is necessary to compare the predicted dimer properties to those of the monomer at the same level of theory, a complete geometry optimization of the \( ^2\text{A}^- \) ground state of HO\(_2\) was also performed. Although this species has been studied quite extensively,\(^{41-47}\) none of the earlier calculations is strictly comparable to the level of theory employed here for the dimer.

Two basis sets were used in this investigation. The first is the DZ basis of Huzinaga\(^{16}\) and Dunning,\(^{17}\) designated O(9s5p/4s2p), H(4s/2s). As in the cycloalkyne study, the hydrogen s functions were scaled by a factor of 1.2. The DZ basis was extended by the addition of d functions (\( \alpha = 0.80 \)) to the oxygen and p functions (\( \alpha = 1.0 \)) to the hydrogen atom basis sets. This basis is termed double-zeta plus polarization (DZ+P) and designated O(9s5p/4s2p/ld), H(4s1p/2s1p).

Stationary points were located with the use of analytic gradient techniques.\(^{18,19,20}\) Harmonic vibrational frequencies for the DZ cyclic dimer structure (II.4) were determined by analytic second derivative methods,\(^{21}\) while finite differences of analytic gradients were employed for all other cases.

\[ \text{in } C_2^h \text{ and} \]

\[ 1a_g^2 1a_u^2 2a_g^2 2a_u^2 3a_g^2 3a_u^2 4a_g^2 4a_u^2 5a_g^2 5a_u^2 6a_g^2 6a_u^2 7a_g^2 7a_u^2 8a_g^2 8a_u^2 \text{ in } C_4 \text{ point group symmetry.} \]

\[ (6) \]
II.3.1 THE CYCLIC, TWO-HYDROGEN-BONDED ISOMER

The predicted stationary point geometries of DZ and DZ+P $^2\text{A}^\text{a}$ HO$_2$ are shown in Fig. II.1 with the experimentally obtained results given in parentheses. The $^3\text{B}_u$ dimer geometries appear in Fig. II.2. Agreement between theory and experiment is modest for the monomer, the bond lengths being correct to within 0.02Å and the bond angle to within 1.6° (DZ+P results). However, the experimentally determined results are vibrationally averaged, and can not be precisely compared with the theoretical geometry.

The monomer fragments within the cyclic dimer (Fig II.2) remain readily identifiable. The O–O bond distance is only 0.005Å shorter in the dimer, and the O–H bond is longer by just 0.003Å. Likewise, the O–O–H bond angle has undergone a very small change, 0.2°. This indicates that the HO$_2$ units are very weakly interacting in the dimer; indeed, the O•••H hydrogen bond distances (2.24Å, DZ+P) are quite long and preclude the possibility of any significant interactions. For comparison, the comparable hydrogen bond distance in the water dimer has been experimentally determined to be 2.02Å.

This unusually long hydrogen bond distance is also reflected in the dimerization energies. As seen in Table II.I, the dimer is predicted to be bound by only 4.52 kcal/mole (DZ) or by 4.88 kcal/mole (DZ+P) with respect to two HO$_2$ units. This is surprisingly low when compared to the calculated (DZ+P SCF) dimerization energy of water, 4.3 kcal/mole. Since the cyclic (HO$_2$)$_2$ structure contains two hydrogen bonds, one would anticipate the dimerization energy to be twice that value, rather than comparable to it. This shows that each of these hydrogen bonds is only about half as strong as that of the water dimer.
II.3.2 TWO-CONFIGURATION RESULTS

Because the HO$_2$ units in the cyclic dimer are so loosely coupled, one might expect that the two-configuration singlet state arising from (3) and (4) would lie nearby energetically. The equilibrium geometry of the TCSCF $^1A_g$ state was optimized with the DZ basis set in order to test this hypothesis. The predicted geometry (Fig. II.3) is virtually identical to the DZ $^3B_u$ structure: the bond lengths change by under 0.0002 Å and the angles by less than 0.02°. The two structures are very close energetically, as expected. The TC $^1A_g$ state has a total energy of -300.322241 hartrees, only 0.01 kcal/mole above the $^3B_u$ state energy, -300.322254 hartrees. This again demonstrates that the two HO$_2$ units are loosely interacting in the dimer.

II.3.3 OPEN CHAIN STRUCTURES

The structure of the open chain, II.1, was first optimized in C$_{2h}$ symmetry (Fig. II.4). As will be shown later, this structure is not a minimum on the H$_2$O$_4$ potential energy hypersurface, but possesses three imaginary frequencies. A subsequent optimization in C$_1$ symmetry also yielded a stationary point which was not a minimum. However, this C$_1$ structure contains only one imaginary frequency, and it is 10 kcal/mole lower in energy than the C$_{2h}$ structure. Hence, it is closer to the absolute energy minimum for this isomer and may be profitably compared to the monomer and to the cyclic dimer. As before, the more accurate DZ+P results will be discussed.

The O-H bond length in the C$_1$ chain structure is 0.950 Å, only 0.001 Å less than that found in the HO$_2$ monomer. The change in the O-H
distance in the cyclic dimer was 0.003Å, a comparable shift. The change in the O-O-H bond angle for this isomer is -1.9°, as compared to -0.3° in the other; these two values are still not substantially different from each other.

On the other hand, the O-O bond lengths change in a decidedly different manner than was found in the cyclic dimer. In this case, the O-O bond length is 1.358Å, or 0.044Å greater than the value for the monomer; the O-O length in the cyclic dimer was 1.309Å, or 0.005 less than that of the monomer. The O-O bridging bond (which is, of course, not found in the isomer II.4) is 1.405Å, almost 0.1Å longer than the bond in the monomer.

The reason for these differences is the variety of bonding in the different dimers. In the monomer, the O-O bond length is 1.314Å, roughly midway between the bond lengths of oxygen 54 (1.207Å) and hydrogen peroxide 55 (1.475Å). This reflects the fact that the unpaired electron on the oxygen atom participates in covalent bonding to some extent. In the cyclic dimer, this electrophilic oxygen atom participates in hydrogen bonding, and is able to use electron density from the hydrogen atom to decrease further the O-O distance. In the C_1 chain structure of II.1, quite the opposite occurs. The unpaired electron in each monomer is used to form a new covalent bond. The oxygen-oxygen bonds of the HO_2 units lose electron density and consequently lengthen. The new bond formed from these electrons is fairly long (1.405Å), almost as long as the O-O bond length of hydrogen peroxide 55.

The energetics of the C_1 structure are consistent with the earlier predictions of Benson 56, who used bond energy considerations to deduce that it would be endothermic with respect to two HO_2 molecules. This
structure was found to be endothermic with respect to two monomers: the predicted dimerization energies (Table II.I) of the \( \text{C}_2h \) structures are 44.1 (DZ) and 36.7 kcal/mole (DZ+P), while the values for the \( \text{C}_1 \) structures are 34.1 (DZ) and 24.7 kcal/mole (DZ+P). In going to lower symmetry, about 10 kcal/mole were gained in each case. Not much more than this is expected to be obtained upon finding the absolute minimum energy of II.I, and this isomer should still be found to be thermodynamically unstable.

II.4 VIBRATIONAL FREQUENCIES

Theoretical vibrational frequencies are crucial in determining whether or not DTL did indeed observe a "non-planar, six-membered ring." The results in Table II.III indicate that the cyclic dimer is a relative minimum on the \( \text{H}_2\text{O}_4 \) potential energy hypersurface; there is no evidence to support the conjecture that the six-membered ring is non-planar as suggested. While comparison of the calculated frequencies to those observed experimentally provides some verification, the theoretical frequencies apply to gas phase molecules at absolute zero, but the experimental ones were obtained in an \( \text{O}_2 \) matrix at 12°K. The comparison which was expected to be more relevant was that of the experimental to the theoretical dimer-monomer frequency shifts. This assumption was later found to be erroneous, but it is still instructive to proceed with such an analysis. Reasons for this will be given shortly.

The predicted frequencies for the monomer are shown in Table II.II, while those for the dimer appear in Tables II.III and II.IV. Since the experimental gas phase anharmonic frequencies for \( \text{HO}_2 \) are available,
some comparison is appropriate at the outset. At the DZ SCF level of theory the calculated harmonic vibrational frequencies are larger by 16.2% (O-H stretch), 0.2% (O-O stretch), and 9.6% (O-O-H bend) than the observed fundamentals. Similarly, at the DZ+P SCF level the predictions are too large by 19.5%, 15.7%, and 14.4%. Although the absolute agreement is better using the less complete DZ basis set, the DZ+P basis provides a more consistent agreement, which is important to the following discussions.

Diem, Tso and Lee, originally reported three dimer-monomer frequency shifts, one each for the O-H stretch (-91 cm$^{-1}$), the O-O stretch (+7 cm$^{-1}$), and the O-O-H bend (+27 cm$^{-1}$). However, in the highly symmetric structure II.4, one expects to observe two fundamentals for each of these modes, corresponding to the symmetric and antisymmetric linear combinations of equivalent bonds. This is also predicted by theory (Table II.III). Recently, DTL have reported a more accurate spectrum from the photolysis of formaldehyde and glyoxal in O$_2$ matrices. (Hereafter, these will be referred to as expt. A and expt. B, respectively.) These new results do include two frequencies for each mode, as expected, and these are listed in Table II.V. The following discussion will center first on the cyclic dimer and then on the open chain structure.

The experimental values for the dimer-monomer frequency shift in the O-H stretch are -71 and -80 cm$^{-1}$ from expt. A and -77 and -80 cm$^{-1}$ from expt. B. The theoretical values are only -32 and -44 cm$^{-1}$ using the more complete DZ+P basis set. Though the two experiments yield consistent results, the agreement with theory is very poor; the theoretical values are too low by about a factor of two. A reduction of
12% 25,26 in these values only makes things worse. The observed values for the O-O-H bending shift are +26 and +22 cm\(^{-1}\) (expt. A) and +25 and +24 cm\(^{-1}\) (expt. B); the theoretical DZ+P values are +61 and +34 cm\(^{-1}\). In this case, the worse of the two predicted numbers is too large by a factor of two. As seen in Table II.VI, the only value in good agreement is the O-O stretch shift, which happens to be the frequency least affected by dimerization.

These results apparently indicate that DTL did not observe the cyclic dimer, II.4. However, this is based on the assumption that the dimer-monomer shifts for theory and experiment will be comparable, despite the differences in environment. The recent work of Redington and Hamill\(^{61}\) shows that this is not necessarily the case. These authors did a study of the dimer-monomer frequency shift of the H-F molecule. Upon dimerizing, the H-F stretching fundamental was found to shift by -70 cm\(^{-1}\) in the gas phase, by -95 cm\(^{-1}\) in an N\(_2\) matrix, by -41 cm\(^{-1}\) in a CO matrix, and by -93 cm\(^{-1}\) in an Ar matrix. The frequency shift changes by as much as a factor of two depending on the environment of the molecule; this is a much larger effect than was anticipated. The situation could be even worse for (H\(_2\)O\(_2\))\(_2\) in an O\(_2\) matrix, since the dimer is not only trapped in the lattice but is actually formed by the interaction of the host lattice with the solute.\(^{50,60}\) This could lead to very strong host-solute interactions which alter the frequency shifts.

It is interesting to note the vibrational frequencies of the O•••H bonds, in light of the earlier comments made about them. As reported above (section II.3.1), these bonds are fairly long (2.19Å, DZ+P) and weak, the dimerization energy being about 2.4 kcal/mole per hydrogen bond. The frequencies are also consistent with these results; the values
of 173 (out-of-phase O•••H stretch) and 136 cm⁻¹ (in-phase stretch) indicate a very shallow or flat potential energy surface.

The frequencies and dimer-monomer frequency shifts of the C₁ chain structure also appear in Table II.VI. The absolute frequencies (Table II.IV) are, at first, unremarkable, when compared to the frequencies of the cyclic dimer. All comparable frequencies (O-H stretch, O-O stretch, and O-O-H bend) are within a few percent. However, these differences are enough to alter dramatically the dimer-monomer shifts. The comparison with experiment is even worse for this isomer than for the cyclic dimer. The O-H shifts are off by about 70 cm⁻¹ (DZ SCF), which is 30 cm⁻¹ worse than for the cyclic dimer. The O-O stretch, which was predicted rather well for the earlier structure, is actually off by a factor of two.

II.5 CONCLUDING REMARKS

The structures reported in Figs. II.2 through II.4 represent the first complete geometry optimizations of any H₂O₄ isomer. Though the chain structures (Fig. II.4) do not actually represent minima in the potential energy hypersurface, the elimination of the final imaginary frequency by completing the optimization in C₁ symmetry will be straightforward, and will yield an absolute minimum shortly. This final step is not expected to produce a significant change in the frequency shifts or energetics found for the C₁ structure. It is very unlikely that this is the isomer observed by DTL.⁵⁰

One can not say that the theoretical and experimental values of the frequency shifts for the cyclic dimer are in conflict. Rather, the two different results apply to different realms of (H₂O₂)₂ chemistry, and one should not compare the results of DTL⁵⁰,⁶⁰ to the gas phase
(theoretical) results. This also shows that these experimental results must be applied with care when using them to explain gas phase processes such as the atmospheric reaction (1).

The cyclic dimer, however, does represent a minimum on the $H_2O_4$ potential energy hypersurface, and it is thermodynamically stable with respect to two $H_2O_2$ molecules. It is not unreasonable to assume that this could be the isomer observed by Diem, Tso, and Lee.\textsuperscript{50,60}

Finally, the weakness of the hydrogen bonds in II.4 bears mentioning again. The predicted dimerization energies are 4.53 kcal/mole (DZ SCF) and 4.88 kcal/mole (DZ+P SCF). Such results indicate that each hydrogen bond is about half as strong as that found in the water dimer, about 4.3 kcal/mole.\textsuperscript{53} This is consistent with the large $O\cdot\cdot\cdotH$ distances, the low values for the $O\cdot\cdot\cdotH$ fundamentals, and the low singlet-triplet splitting. Every observable predicted is consistent with two weak hydrogen bonds, each notably weaker than that found in the water dimer, the prototype $H-O\cdot\cdot\cdotH$ hydrogen bond.
III. STUDIES OF EXCITED STATES

III.1 INTRODUCTION

Since the initial applications of the valence-bond method by Hietler and London\textsuperscript{62} in 1927 and the development of the LCAO-SCF method by Roothan\textsuperscript{63} in 1951, the calculation of molecular energies by \textit{ab initio} methods has become routine. The introduction of analytic gradients\textsuperscript{18-20} and analytic second derivatives\textsuperscript{21,22} of the SCF energy has allowed theoretical chemists to perform reliable calculations on entire potential energy hypersurfaces, while the formulation of methods such as MCSCF\textsuperscript{64}, CI\textsuperscript{23}, and Moller-Plesset perturbation theory (MPPT)\textsuperscript{65} has provided a means of predicting energies to an astonishing accuracy.\textsuperscript{66}

For the most part, however, these calculations have been limited to the electronic ground state potential energy surfaces. All the methods mentioned above (except MPPT) yield variational results,\textsuperscript{67} i.e., upper bounds to the true molecular energy. In an excited state calculation, the energy will be variational only if the excited state wave function is orthogonal to that of the ground state.\textsuperscript{68} For methods such as CI or MCSCF, one need only choose a higher root of the secular equation to obtain an upper bound to the excited state energy,\textsuperscript{69} though one might encounter convergence problems in such a case. Unfortunately, these methods are frequently too costly to allow the calculation of entire potential energy hypersurfaces. Most existing open-shell SCF methods\textsuperscript{70-75} can be applied to excited states provided that the state is of a different symmetry (either spin or spatial) from the ground state, and hence necessarily orthogonal. (Please note that the references 70-75 are by no means intended to be an exhaustive list, but rather are illustrative of the available literature.) This is because these methods
are developed specifically to obtain the lowest energy associated with a particular state. For example, the ground state of formaldehyde is a closed shell $^1A_1$ state:

$$\text{1a}_1^2\text{2a}_1^2\text{3a}_1^2\text{4a}_1^2\text{1b}_2^2\text{5a}_1^2\text{1b}_1^2\text{2b}_2^2$$  (1)

If the molecule is restricted to $C_{2v}$ point group symmetry in its excited states, then any excitation from an orbital of one symmetry type into another will result in a wavefunction necessarily orthogonal to the ground state and may be studied by these SCF methods. These include such states as the $n + \pi^*$ ($3b_2 + 2b_1$) $^3A_2$ and $^1A_2$ states, or the $n + \sigma^*$ ($3b_2 + 6a_1$) $^3B_2$ and $^1B_2$ states. Furthermore, any HOMO-LUMO triplet excitation, even within the orbitals of one symmetry type, may be studied, since it is orthogonal to the ground state by spin symmetry.

This still leaves several states which are inaccessible to study by SCF. Any HOMO-LUMO singlet excitation within the orbitals of one symmetry type, for example, will result in another $^1A_1$ state. Additionally, since many molecules change geometry upon electronic excitation, the states accessible to SCF in the ground state might not be at the new geometry. As an example, formaldehyde pyramidalizes to $C_s$ symmetry in some of its excited states, so that some of the states mentioned above will collapse to the same symmetry as that of the ground state ($^1A'$, in $C_s$). Thus while vertical excitation energies might be predicted for several states, location of the minimum energy geometries may not be possible.

An SCF method to obtain variationally correct energies, and the energy first and second derivatives, of excited states with the same
symmetry as the ground state would be of great utility. This would allow the optimization of molecular geometries and the prediction of harmonic vibrational frequencies for previously insuperable cases. Such calculations would provide reasonably accurate results for far less effort than is required by MCSCF or CI methods. One may argue that SCF is not of a reliable enough quality for many excited states. Excited singlet states into valence virtual orbitals generally have large correlation errors. In the case of ethylene, SCF even predicts the wrong order of the excited states and can lead to excessive Rydberg character. However, even for those cases in which more accurate energies are required, this method would be a valuable contribution. CI calculations of excited states using ground state SCF reference wavefunctions will give energies which are too high, since the references are biased towards the ground states; performing CI's using excited state SCF references provides more accurate results.

Davidson and Nitzsche illustrated this last point in a study of the \(^1\pi^*\) state of acrolein, in which both the ground and excited states were \(^1\text{A}'\). Using an ordinary (non-variational) SCF method, the vertical excitation energy was found to be 3.42 eV; a CI calculation employing this reference gave a result of 11.31 eV. The variational method yielded a prediction of 6.76 eV at the SCF level, and the CI performed with those orbitals gave 7.52 eV. The first method gave an SCF result which was too low, since the calculation was not performed in a variational manner. The CI calculation then gave a result which was too high, because the orbitals were a poor reference for the second root of the CI. The variational method gives more consistent and reliable results.

Several methods do, in fact, exist for performing excited state SCF
calculations.\textsuperscript{71,72,74,76} Of these, few are actually able to perform the type of calculation suggested here. The method of Morokuma and Iwata\textsuperscript{72} is capable of yielding an upper bound to the energy of an excited state singlet of the same symmetry as the ground state; unfortunately, the energy is too high because of certain limitations imposed upon the actual form of the open-shell orbitals. However, the methods developed by Davidson and Stenkamp\textsuperscript{74} for excited states specifically include treatment of such a case. The method gives reliable upper bounds to excited state singlets and good wavefunctions for references in CI calculations.\textsuperscript{78,79}

This method has been implemented. In addition, an extension to include the evaluation of the first and second derivatives of the excited state energy (with respect to nuclear motion) has been developed. In the following section, the method of Davidson and Stenkamp\textsuperscript{74} will be reviewed briefly. This procedure will be shown to be formally equivalent to converging to the second root of a multi-configuration (MC) SCF in a three orbital space. This leads to a convenient method for evaluation of the energy derivatives. Applications of this technique to excited states of formaldehyde will follow.

\section*{III.2 THEORETICAL}

Within the Hartree-Fock approximation a molecular wavefunction may be expressed as an anti-symmetrized product, or Slater determinant,\textsuperscript{80} of one-electron functions, $\chi_i$:

$$
\Psi_{HF} = \frac{1}{\sqrt{n!}} \begin{vmatrix}
1 & \chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\
\chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(n) & \chi_2(n) & \cdots & \chi_n(n)
\end{vmatrix}
$$

\textit{(1)}
The \( \chi_i \) are the product of a spin and a three-dimensional spatial function:

\[
\chi_i = \phi_i s_i
\]

where the \( \phi_i \) are generally taken to be orthonormal:

\[
< \phi_i | \phi_j > = \delta_{ij}
\]

Using the Born-Oppenheimer hamiltonian for an \( n \)-electron system with \( c \) nuclear centers,

\[
H = \sum_i -\nabla_i^2 - \sum_i \sum_a Z_a r_{ia} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_a \sum_{a>b} \frac{Z_a Z_b}{r_{ab}},
\]

the energy may be obtained by simply evaluating the hamiltonian matrix element \( < \psi | H | \psi > \). When the determinantal wavefunction (1) is employed, there are \( n! \) terms which appear in both the bra and ket of the integral. However, Slater\(^{80}\) has shown very elegantly how most of the terms will vanish, yielding a fairly simple expression:

\[
E = \sum_i h_{ii} + \sum_{i>j} (J_{ij} - K_{ij}) + \sum_{a>b} \frac{Z_a Z_b}{r_{ab}}
\]

where

\[
h_{ij} = < \chi_i(1) | -\nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}} | \chi_j(1) >
\]
\[ J_{ij} = \frac{1}{r_{12}} \langle x_i(1) x_j(2) | x_i(1) x_j(2) \rangle \]  
\[ K_{ij} = \frac{1}{r_{ij}} \langle x_i(1) x_j(2) | x_i(1) x_j(2) \rangle . \]

At this point it is convenient to define the Coulomb and exchange operators \( J_i \) and \( K_i \), as well:

\[ J_i(1) x_j(1) = \frac{1}{r_{12}} \langle x_i(2) | x_i(2) \rangle x_j(1) \]  
\[ K_i(1) x_j(1) = \frac{1}{r_{12}} \langle x_i(2) | x_i(2) \rangle x_j(1) . \]

One can now impose the restricted Hartree-Fock (RHF) condition on the \( x_i \). This requires the two \( x_i \) which represent a doubly occupied orbital to have the same spatial function \( \phi_{i} \) (but opposite spins, of course), in order to insure that the wavefunction is an eigenfunction of \( S^2 \) and \( S_z \). If the wavefunction represents a closed-shell system with \( n \) electrons in \( N = n/2 \) orbitals, then the wavefunction may be written:

\[ \psi = A \{ \phi_1 \phi_1 \phi_2 \phi_2 \cdots \phi_N \phi_N \} . \]

The energy expression (6) may be simplified by performing the spin integration in (7), (8), and (9) yielding

\[ E = \sum_{i}^{N} h_{ii} + \sum_{i>j}^{N} (2J_{ij} - K_{ij}) + \sum_{a>b}^{N} \frac{Z_a Z_b}{r_{ab}} . \]

The summation in (13) now runs over \( N \) spatial functions, instead of \( n \) spinorbitals as in (6), and the \( J_{ij} \) and \( K_{ij} \) are defined in terms of \( \phi_i \) instead of \( x_i \).
An open-shell singlet wavefunction may be written\textsuperscript{74,81} as

\begin{equation}
\psi = \frac{1}{\sqrt{2}} A \{ \text{(core)} \phi_a \phi_b \} - \frac{1}{\sqrt{2}} A \{ \text{(core)} \phi_a \beta \phi_b \} \tag{14}
\end{equation}

\begin{equation}
= \frac{1}{\sqrt{2}} \psi_1 - \frac{1}{\sqrt{2}} \psi_2 \tag{15}
\end{equation}

where 'core' represents \( N-1=M \) closed-shell orbitals. The chief feature of Davidson's method for excited singlet states is the relaxation of the orthogonality constraint between the open-shell orbitals \( a \) and \( b \), so that the orthornormality conditions (4) become:

\begin{equation}
\langle \phi_i | \phi_j \rangle = \delta_{ij} + \delta_{ia} \delta_{jb} + \delta_{ib} \delta_{ja} S. \tag{16}
\end{equation}

Substitution of (14) into the expression \( \langle \psi | H | \psi \rangle \) produces three different terms to be dealt with,

\begin{equation}
\langle \psi | H | \psi \rangle = \frac{1}{2} H_{11} - \frac{1}{2} H_{12} + \frac{1}{2} H_{22} \tag{17}
\end{equation}

each of which is a matrix element between two determinants containing \( n! \) terms. Evaluation of such expressions containing non-orthogonal orbitals has been done in the past, at least for closed-shell systems.\textsuperscript{80,82} These expressions for the open-shell singlet were evaluated by considering all \((n!)^2\) terms within each matrix element, in a procedure analagous to that used by Slater\textsuperscript{80} in obtaining expression (6). The expressions for \( H_{11} \) and \( H_{22} \) are essentially the same as for the orthogonal case, since the spin functions force \( \chi_a \) and \( \chi_b \) to be orthogonal to each other, even though \( \phi_a \) and \( \phi_b \) are not. The expression for the cross term, \( H_{12} \), is
considerably more complicated. The derivation is tedious and not particularly enlightening, so the final expression will be presented without any intermediate steps:

\[ <\psi | H | \psi> = 2(1+S^2) \sum_{i} h_{ii} + h_{aa} + h_{bb} + 2S h_{ab} + J_{ab} + K_{ab} \]

\[ + 2(1+S^2) \sum_{i>j} (2J_{ij} - K_{ij}) + \sum_{i} (2J_{ia} - K_{ia} + 2J_{ib} - K_{ib}) \]

\[ + 2S \sum_{i} <a | 2J_i + K_i | b> . \]  

(18)

(Note that the shorthand notation \(|a>\) has been used in place of \(\phi_a\). This convention will be employed hereafter.) The norm of the wavefunction (14) is simply \(<\psi | \psi> = 1 + S^2\), so the energy will be given by

\[ E = <\psi | H | \psi> \]

\[ 1 + S^2 \]  

(19)

Note that if \(S=0\), then expression (18) is indeed identical to the energy expression for an open-shell singlet wavefunction constructed from orthogonal orbitals.\(^{81}\)

Following the method of Roothan\(^{63,70}\) the energy expression (19) must be minimized with respect to any changes in the orbitals \(|i>\), while maintaining the orthonormality conditions (16). Using Lagrange's method of undetermined multipliers, one then minimizes the function

\[ E' = E - \sum_{i,j} \lambda_{ij} <i|j> - \sum_{i} \sum_{j=a} ^{b} [ \lambda_{ij} <i|j> + \lambda_{ji} <j|i> ] \]

\[ - \lambda_{aa} <a|a> - \lambda_{bb} <b|b> \]  

(20)
where the $\lambda_{ij}$ are the undetermined multipliers. Note that this differs from Roothan's expressions in that the term $\lambda_{ab}$ is missing, as there are no restrictions between these orbitals.

The energy is invariant with respect to unitary transformations of the closed-shell orbitals among themselves but not with respect to rotations of the closed and the two open shells among one another. Consequently, three conditions for a minimum energy are required, one for orbitals of each shell. These conditions are:

\begin{align*}
2\mathcal{F}^\alpha |i\rangle &= \sum_j^M \lambda_{ij} |j\rangle + \lambda_{ia} |a\rangle + \lambda_{ib} |b\rangle \quad 1 < i < M \quad (21) \\
\alpha \mathcal{F}^\alpha |a\rangle &= \sum_j^M \lambda_{ja} |j\rangle + \lambda_{aa} |a\rangle \quad (22) \\
\alpha \mathcal{F}^\beta |b\rangle &= \sum_j^M \lambda_{jb} |j\rangle + \lambda_{bb} |b\rangle \quad (23)
\end{align*}

with the following definitions:

\begin{align*}
\alpha &= (1 + S^2)^{-1} \quad (24) \\
\mathcal{F}^0 &= h + \sum_j^M (2J_j - K_j) \quad (25) \\
E^0 &= 2 \sum_i^M h_{ii} + 2 \sum_{i>j}^M (2J_{ij} - K_{ij}) \quad (26) \\
\mathcal{F}^\alpha |i\rangle &= (1 + S^2) \mathcal{F}^0 |i\rangle + (2J_a - K_a) |i\rangle + (2J_b - K_b) |i\rangle
\end{align*}
The various $F^i$ are referred to as the Fock operators for the $i^{th}$ shells.\textsuperscript{63,70}

Now it is necessary to eliminate the off diagonal multipliers, $\lambda_{ij}$. Generally, this is accomplished by concatenating the various Fock operators for each shell into a single operator by one of a number of formalisms,\textsuperscript{70,72,74} and then diagonalizing it. In this case, such a procedure is inapplicable, since these schemes all assume the orbitals to be orthogonal. Instead the 'sequential orthogonalization' method of Davidson\textsuperscript{83} may be employed.

In this technique, the contribution to the various Fock operators of each shell arising from the other two shells is removed by the use of projection operators. These 'projected' Fock matrices may then be solved to give the eigenvalues and the new orbitals for each shell. These operators are given by:\textsuperscript{74,83}

$$G^c = F^c - \frac{1}{2} \left\{ |b><b|F^b + F^b|b><b| + |a><a|F^a + F^a|a><a| \right\}$$  \hspace{1cm} (30)

$$G^a = P F^a P$$  \hspace{1cm} (31)

$$G^b = P F^b P$$  \hspace{1cm} (32)
The new conditions for a stationary energy are given by:

\[ P = 1 - \sum_{I}^{M} |i><i| \] \hspace{1cm} (33)

where the orbitals \( b+1 \) through \( V \) are the virtual (unoccupied) orbitals.

Although \( G^c \) is needed to solve for only the new doubly occupied orbitals, \( |i>^c \), \( G^c \) is in fact solved throughout the entire space, \( 1 < i < V \). Those resulting orbitals lying in the doubly occupied space are stored as the \( |i>^c \), and the remaining orbitals \( a < j < V \) are used in (35). This yields the new orbital for the first open shell, \( |a>^a \). This is stored, and the orbitals are then used in (36) to obtain the \( |j>^b \), \( a < j < V \). Note that this gives two orbitals corresponding to the first open shell, namely \( |a>^a \) and \( |a>^b \). The orbital \( |a>^b \) is discarded; \( |a>^a \) is used to describe the first open shell, and \( |b>^b \) is used to describe the other. The orbitals from \( G^a \) and \( G^b \) are not orthogonal to each other, but the virtual orbital space \( |j>^b \), \( b+1 < j < V \), may be subsequently orthogonalized to \( |a>^a \) without changing the energy. The orbitals \( |a>^a \) and \( |b>^b \) are never orthogonalized, leaving one with the condition \( <a^a|b^b>=S\neq0 \).

This method has been shown to converge variationally to excited states by Davidson and Stenkamp. The excited state singlet
wavefunction may be expressed as:

\[
\psi = \frac{1}{\sqrt{2}} A \left\{ \phi_1^c \phi_1^c \cdots \phi_M^c \phi_M^c \phi_a^b \phi_b^b \right\}
\]

If one considers the CI matrix elements between this configuration and single excitations into the virtual orbitals, \(|j^b\rangle\), then the resulting matrix is diagonal (to zeroth order in \(S\)), with one element corresponding to the SCF energy as given in (18) and (19). The resulting SCF energy is therefore stable, since it can not interact with the ground state.

The non-orthogonal-orbital wavefunction (37) may be shown to be equivalent to a TC SCF wavefunction by the following orbital rotation. One can define two orthogonal orbitals:

\[
|u\rangle = \frac{|a\rangle + |b\rangle}{\sqrt{2(1+S)}}
\]

\[
|v\rangle = \frac{|a\rangle - |b\rangle}{\sqrt{2(1-S)}}
\]

After some algebraic manipulation one can cast the wavefunction in the form:

\[
\psi = C_1 A \left\{ 1 \overline{1} 2 \overline{2} \cdots M \overline{M} u \overline{u} \right\}
\]

\[
- C_2 A \left\{ 1 \overline{1} 2 \overline{2} \cdots M \overline{M} v \overline{v} \right\}
\]
where the coefficients $C_1$ and $C_2$ are given by

$$C_1 = \frac{1 + S}{\sqrt{2(1 + S^2)}}$$  \hspace{1cm} (41)$$

$$C_2 = \frac{1 - S}{\sqrt{2(1 + S^2)}}$$  \hspace{1cm} (42)$$

This transformation is extremely useful. Since all the orbitals are now orthogonal, and since the CI coefficients $C_1$ and $C_2$ may be obtained from the value of $S$, no further modifications are necessary to employ existing TC SCF gradient\textsuperscript{20} and analytic second derivative\textsuperscript{22} techniques.

Further insight into the nature of wavefunction (37) may be gained by a second orbital rotation. By defining the orbitals

$$|x\rangle = \frac{1}{\sqrt{2}} (|u\rangle + |v\rangle)$$  \hspace{1cm} (43)$$

$$|y\rangle = \frac{1}{\sqrt{2}} (|u\rangle - |v\rangle)$$  \hspace{1cm} (44)$$

the wavefunction becomes:

$$\psi = \lambda_1 \ A \{ 1 \bar{1} 2 \bar{2} \cdots x \bar{x} \} + \lambda_2 \ A \{ 1 \bar{1} 2 \bar{2} \cdots y \bar{y} \}$$

$$+ \lambda_3 \ A \{ 1 \bar{1} 2 \bar{2} \cdots (xy - \bar{xy})/\sqrt{2} \}$$  \hspace{1cm} (45)$$

with the CI coefficients given by

$$\lambda_3 = (1 + S^2)^{-\frac{1}{2}}$$  \hspace{1cm} (46)$$
\[
\begin{align*}
\lambda_1 &= \lambda_2 = \frac{s}{\sqrt{2}} \\
\lambda_3 &= \frac{s}{\sqrt{2}}
\end{align*}
\]  
(47)

Since both $S$ (and hence the $\lambda_i$) and the SCF orbitals are fully optimized, the method is seen to be equivalent to an MCSCF in the space of orbitals $|x\rangle$ and $|y\rangle$. Furthermore, since $S$ is generally small, the coefficient $\lambda_3$ is the largest. Hence, (45) is dominated by the open-shell singlet configuration; the method converges to the second root of the MCSCF.

If one chooses the orbital $|a\rangle^b$ instead of $|b\rangle^b$ to represent the second open shell, then $S$ is very large ($S=1$). In such a case, $\lambda_1 = \lambda_2 = \frac{1}{\sqrt{2}}$ and $\lambda_3 = \frac{1}{\sqrt{2}}$, which is not particularly enlightening. However, in wavefunction (40), one can see that $C_1 = 1$ while $C_2$ is very small. Hence if $|a\rangle^b$ is retained in place of $|b\rangle^b$ one obtains a TCSCF description of the closed-shell ground state. This method may be used to converge to either the ground or first excited singlet state of a closed-shell system.

III.3 APPLICATIONS

The method described in the previous section was tested on an excited singlet state of formaldehyde. This molecule has been studied quite extensively in the last several years by both experimentalists and theoreticians. Buenker and Peyerimhoff\textsuperscript{85} demonstrated that excitation into the $\pi^*$ ($2b_1$) orbital caused the molecule to pyramidalize, going from $C_{2v}$ symmetry in the ground state to $C_s$ in the excited states. Although these workers showed that the energies of these excited states were lower in $C_s$ symmetry, they were unable to perform complete geometry optimizations. In particular, they noted that their predictions for the
\( \pi + \pi^* \) \(^1\!\!A_1\) state were probably inaccurate, since they were unable to perform a variational SCF calculation on this state.

Since then there have been a number of increasingly accurate studies of many of the excited states of formaldehyde.\(^{86-89}\) The \( \pi + \pi^* \) state (hereafter designated \(2^1A_1\)) was originally a somewhat controversial state. It was initially assigned to the observed spectral band at about 8 eV\(^{76}\). Since then this band has been assigned to the \( \pi(n + 3p) \) transition, while the \(2^1A_1\) state remains unobserved. More recently, it has been established that this state probably lies energetically above the dissociation threshold,\(^{90,91}\) within a continuum of states.

This last remark notwithstanding, the \(2^1A_1\) state remains of interest. The vertical excitation energy is difficult to predict accurately, because it is of the same symmetry as the ground state. Additionally, the reduction in energy resulting from a geometry optimization is totally unknown. It is possible that this would be sufficient to bring the total energy below the continuum, making this an observable state.

With this end in mind, a full geometry optimization was performed on the \(^1\!\!A_1\) state of formaldehyde arising from the configuration

\[
1a_1^22a_1^23a_1^24a_1^21b_2^25a_2^22b_2^21b_1^2b_1^2
\] (2)

along with a determination of its harmonic vibrational frequencies. For comparison, the \(^3\!\!A_1\) state arising from configuration (2) (which is accessible to ordinary SCF) was also studied. Both of these states were investigated using the DZ basis sets of Huzinaga\(^ {16}\) and Dunning\(^ {17}\),
designated C(9s5p/4s2p), O(9s5p/4s2p), H(4s/2s); hydrogen s functions were scaled by a factor of 1.2. A DZ+P basis was also used; it was formed by augmenting the DZ basis set with the polarization functions $\alpha_d(C)=0.75$, $\alpha_d(O)=0.80$, $\alpha_p(H)=0.75$. Stationary points were initially determined in $C_{2v}$ symmetry, and harmonic vibrational frequencies were obtained at each one by analytic SCF$^{21}$ and TCSCF$^{22}$ second derivative methods. Where necessary, further geometry optimizations were performed in $C_s$ symmetry to determine the absolute energy minimum.

SCF calculations using these basis sets are not expected to give particularly accurate results for the excitation energies. As mentioned earlier, SCF methods are frequently inadequate for open-shell singlet states.$^{76,77}$ Furthermore, the importance of including additional diffuse p functions (Rydberg functions) in the carbon and oxygen atom basis sets has been noted by earlier studies.$^{89}$ The purpose of this study, however, is to establish the effects of a complete geometry optimization on the excitation energy. The basis sets employed should be of sufficient quality to allow a reasonable estimate of this effect.

Vertical excitation energies were calculated at the equilibrium geometry of ground state formaldehyde with each basis set. The results of this study appear in Table III.I with the results of some earlier workers.$^{86-89}$ The vertical excitation energy of the $2^1A_1$ state is predicted to be 10.87 eV with the DZ basis and 10.95 eV with the larger DZ+P basis. These are in remarkably good agreement with the other results, which range from an early SCF result of 10.1 eV$^{87}$ to a fairly recent GVB-CI prediction of 11.31 eV.$^{86}$ The $3A_1$ state is not in quite so good agreement, with SCF predictions of 4.11 eV (DZ) and 4.87 eV (DZ+P). The earlier predictions for this state range between 5.29 eV$^{87}$ and 6.16
The optimized $C_{2v}$ geometries of these two states are given in Table III.II. As expected, the geometry is significantly different from that of the ground state; the C-O bond length has been especially affected by the excitation. A lengthening of this bond is to be expected, since the $\pi$ bond is essentially nullified by exciting an electron into the antibonding orbital. The DZ+P results predict a C-O bond length of 1.189Å in the ground state, only 0.21Å shorter than the experimental value. The excited triplet and singlet states have predicted C-O bond lengths of 1.432Å and 1.537Å, respectively. The latter is a very long bond, even longer than the C-O single bond found in formic acid (1.343Å) or in ethylene oxide (1.436Å).

The harmonic vibrational frequencies of these stationary points (Table III.III) indicate that the $2^1A_1$ state is a local minimum on the potential energy hypersurface, while the $3A_1$ is a transition state. This result is surprising in light of the fact that so many of the excited states of formaldehyde are pyramidal. Comparison of the predicted DZ+P frequencies of the $2^1A_1$, the $3A_1$, and the $3A'$ (the $3A_1$ in $Cs$ symmetry) states shows that all the frequencies are quite similar with the single exception of the C-O stretching fundamental. The $C_{2v}$ $3A_1$ state has a C-O stretch of 1191 cm$^{-1}$ which reduces by a small amount to 1176 cm$^{-1}$ in the optimized $Cs$ structure. The $2^1A_1$ state, on the other hand, has a C-O stretch of only 848 cm$^{-1}$, an extremely low result.

The low value of the C-O stretch in the singlet may be interpreted in terms of the characteristics of the $\pi^*$ orbital. Harding and Goddard observed in their study of vertical excitation energies that this orbital of the $2^1A_1$ state was fairly diffuse. Allowing the bond to relax
from 1.189Å to 1.537Å will make the orbital even more diffuse, decreasing the electron density between the two atoms and weakening the bond.

The observation that the $2^1A_1$ state is a minimum in $C_{2v}$ while the $3^1A_1$ is a transition state can be explained in terms of another feature of the $\pi^*$ orbital. The SCF vector for the triplet indicates that this orbital is more localized on the carbon atom, while in the singlet state, the orbital is spread roughly evenly between the carbon and oxygen atoms. (A Mulliken population analysis could verify this quantitatively but is not available at this time.) It is possible that in the triplet state, the molecule puckers from planarity in order for the C-H $\sigma$ orbitals to interact with the extra electron density on the carbon atom from the $\pi^*$ orbital. In the singlet, however, this orbital provides the carbon atom with substantially less density, hence there is less 'motivation' for the molecule to pucker. In this light, it is not unreasonable that the singlet should be a minimum on the potential energy surface in $C_{2v}$ symmetry.

The energetics of the optimized structures are shown in Table III.IV. As seen there, there is a substantial reduction in the $2^1A_1$ excitation energy when the geometry is optimized. The minimum energy geometry is predicted to lie only 7.97 eV (DZ) or 8.68 eV (DZ+P) above the ground state. These values represent energy lowerings of 2.90 and 2.27 eV for the DZ and DZ+P calculations, respectively. This excitation energy is now comparable to the predicted vertical excitation energies for some of the other observable states of formaldehyde.\textsuperscript{86-89} It is now entirely possible that the $2^1A_1$ state at its equilibrium geometry lies below the continuum.
III.4 CONCLUSIONS

The method for excited singlet states presented here is a useful and convenient technique for studying states previously inaccessible to study by SCF calculations. For the case presented in the previous section, the $^1(\pi + \pi^*)$ state of formaldehyde, the vertical excitation energy predicted with this method gave a result comparable to that obtained by more accurate calculations.\textsuperscript{86-89} The time required for the evaluation of the excited state SCF energy was about 25% to 40% longer than for a normal SCF calculation on, say, the $^3\text{A}_1$ state. Evaluation of the analytic first and second derivatives of the energy (which is by far the most time consuming step) required no more time than in a conventional calculation. This technique is substantially faster than a CI or MCSCF calculation, and is viable first step, even if the accuracy afforded by these latter techniques is required for a particular case.

Even the application of this to such a simple test case as formaldehyde has produced some extremely interesting results. The $^2\text{A}_1$ state of formaldehyde is predicted to be a minimum in $C_{2\nu}$ symmetry, in contrast to the triplet state which has its energy minimum in $C_5$ symmetry. At its equilibrium geometry, this state has an excitation energy of only 8.68 eV (DZ+P), which is 2.27 eV lower than the predicted vertical excitation energy. This state might lie below the continuum\textsuperscript{90,91} at its equilibrium geometry, but it is unlikely that a direct transition could occur from the ground state; the excited state geometry is so different that the overlap with the ground state is probably small, making the transition improbable.


31. J. S. Binkley, M. J. Frisch, Fifth Annual West Coast Theoretical Conference Los Alamos, N.M., 4-6 April, 1984.


60. E. K. C. Lee, private communication, to be published.
66. J. A. Pople, Fifth Triennial Conference on Theoretical Chemistry, Jackson Lake, Wyoming, 15-20 June, 1984. Heats of formation were predicted to < 2 kcal/mole using large basis sets and MP-4 theory.


84. E. R. Davidson, private communication.


Table I. I Total Energies (hartree) and Relative Energies (kcal/mole) for the Lowest Singlet and Triplet Electronic States of Cyclopropyne

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>Number of Configurations</th>
<th>( E ) (hartree)</th>
<th>Relative energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ TCSCF ( ^1A_1 )</td>
<td>2</td>
<td>-114.46490</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ SCF ( ^3B_2 )</td>
<td>1</td>
<td>-114.45179</td>
<td>8.2</td>
</tr>
<tr>
<td>DZ CI ( ^1A_1 )</td>
<td>5724</td>
<td>-114.70296</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ CI ( ^3B_2 )</td>
<td>3816</td>
<td>-114.69290</td>
<td>6.3</td>
</tr>
<tr>
<td>DZ+d TCSCF ( ^1A_1 )</td>
<td>2</td>
<td>-114.53855</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ+d SCF ( ^3B_2 )</td>
<td>1</td>
<td>-114.51936</td>
<td>12.0</td>
</tr>
<tr>
<td>DZ+d CI ( ^1A_1 )</td>
<td>19331</td>
<td>-114.86497</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ+d CI ( ^3B_2 )</td>
<td>12582</td>
<td>-114.84805</td>
<td>10.6</td>
</tr>
</tbody>
</table>
Table I.II Predicted Harmonic Vibrational Frequencies (cm\(^{-1}\)) for the Lowest Singlet and Triplet States of Cyclopropyne

<table>
<thead>
<tr>
<th>Description</th>
<th>(^1\text{A}_1)</th>
<th>(^3\text{B}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asymmetric H str.</td>
<td>(B_1)</td>
<td>3366</td>
</tr>
<tr>
<td>symmetric H str.</td>
<td>(A_1)</td>
<td>3287</td>
</tr>
<tr>
<td>C=C (or C≡C) str.</td>
<td>(A_1)</td>
<td>2049</td>
</tr>
<tr>
<td>CH(_2) scissor</td>
<td>(A_1)</td>
<td>1689</td>
</tr>
<tr>
<td>CH(_2) wag</td>
<td>(B_2)</td>
<td>1246</td>
</tr>
<tr>
<td>ring expansion (^a)</td>
<td>(A_1)</td>
<td>1182</td>
</tr>
<tr>
<td>CH(_2) rock</td>
<td>(B_1)</td>
<td>1167</td>
</tr>
<tr>
<td>ring torsion</td>
<td>(A_2)</td>
<td>435</td>
</tr>
<tr>
<td>ring opening (^b)</td>
<td>(B_2)</td>
<td>6021</td>
</tr>
</tbody>
</table>

\(^a\) May also be called symmetric C-C stretch

\(^b\) May also be called asymmetric C-C stretch
<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>Number of Configurations</th>
<th>E (hartree)</th>
<th>Relative energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ TCSCF (^1A_1)</td>
<td>2</td>
<td>-153.54798</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ SCF (^3B_2)</td>
<td>1</td>
<td>-153.53363</td>
<td>9.0</td>
</tr>
<tr>
<td>DZ CI (^1A_1)</td>
<td>23249</td>
<td>-153.85531</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ CI (^3B_2)</td>
<td>14503</td>
<td>-153.83741</td>
<td>11.2</td>
</tr>
<tr>
<td>DZ+d TCSCF (^1A_1)</td>
<td>2</td>
<td>-153.62504</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ+d SCF (^3B_2)</td>
<td>1</td>
<td>-153.60824</td>
<td>10.5</td>
</tr>
<tr>
<td>DZ+d CI (^1A_1)</td>
<td>74625</td>
<td>-153.05772</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ+d CI (^3B_2)</td>
<td>45623</td>
<td>-153.03731</td>
<td>12.8</td>
</tr>
<tr>
<td>DZ+P SCF (^3B_2)</td>
<td>1</td>
<td>-153.61596</td>
<td></td>
</tr>
</tbody>
</table>
Table I.IV Predicted Harmonic Vibrational Frequencies (cm$^{-1}$) for the Lowest Singlet and Triplet States of Cyclobutyne

<table>
<thead>
<tr>
<th>Description</th>
<th>$^1A_1$ DZ+d</th>
<th>$^1A_1$ DZ</th>
<th>$^3B_2$ DZ+d</th>
<th>$^3B_2$ DZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>in-phase CH$_2$ sym str</td>
<td>B$_1$ 3370</td>
<td>B$_1$ 3378</td>
<td>B$_1$ 3329</td>
<td>B$_1$ 3342</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ sym str</td>
<td>A$_2$ 3355</td>
<td>A$_2$ 3362</td>
<td>A$_2$ 3314</td>
<td>A$_2$ 3326</td>
</tr>
<tr>
<td>in-phase CH$_2$ asym str</td>
<td>A$_1$ 3294</td>
<td>A$_1$ 3295</td>
<td>A$_1$ 3262</td>
<td>A$_1$ 3267</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ asym str</td>
<td>B$_2$ 3285</td>
<td>B$_2$ 3286</td>
<td>B$_2$ 3253</td>
<td>B$_2$ 3256</td>
</tr>
<tr>
<td>C=C (or C=C) str</td>
<td>A$_1$ 1911</td>
<td>A$_1$ 1847</td>
<td>A$_1$ 1779</td>
<td>A$_1$ 1731</td>
</tr>
<tr>
<td>in-phase CH$_2$ scissor</td>
<td>A$_1$ 1640</td>
<td>A$_1$ 1635</td>
<td>A$_1$ 1637</td>
<td>A$_1$ 1636</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ scissor</td>
<td>B$_2$ 1612</td>
<td>B$_2$ 1621</td>
<td>B$_2$ 1614</td>
<td>B$_2$ 1622</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ wag</td>
<td>B$_2$ 1320</td>
<td>B$_2$ 1346</td>
<td>B$_2$ 1375</td>
<td>B$_2$ 1384</td>
</tr>
<tr>
<td>in-phase CH$_2$ wag</td>
<td>A$_1$ 1311</td>
<td>A$_1$ 1314</td>
<td>A$_1$ 1298</td>
<td>A$_1$ 1307</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ twist</td>
<td>A$_2$ 1301</td>
<td>A$_2$ 1299</td>
<td>A$_2$ 1257</td>
<td>A$_2$ 1261</td>
</tr>
<tr>
<td>in-phase CH$_2$ twist</td>
<td>B$_1$ 1163</td>
<td>B$_1$ 1165</td>
<td>B$_1$ 1155</td>
<td>B$_1$ 1162</td>
</tr>
<tr>
<td>out-of-phase CH$_2$ rock</td>
<td>A$_2$ 1053</td>
<td>A$_2$ 1079</td>
<td>A$_2$ 1102</td>
<td>A$_2$ 1119</td>
</tr>
<tr>
<td>in phase C-C str</td>
<td>A$_1$ 1100</td>
<td>A$_1$ 1076</td>
<td>A$_1$ 1127</td>
<td>A$_1$ 1102</td>
</tr>
<tr>
<td>out-of-phase C-C str</td>
<td>B$_2$ 963</td>
<td>B$_2$ 936</td>
<td>B$_2$ 1065</td>
<td>B$_2$ 1025</td>
</tr>
<tr>
<td>unique C-C str</td>
<td>A$_1$ 916</td>
<td>A$_1$ 885</td>
<td>A$_1$ 922</td>
<td>A$_1$ 897</td>
</tr>
<tr>
<td>in-phase CH$_2$ rock</td>
<td>B$_1$ 855</td>
<td>B$_1$ 871</td>
<td>B$_1$ 854</td>
<td>B$_1$ 884</td>
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<tr>
<td>ring deformation</td>
<td>B$_2$ 618</td>
<td>B$_2$ 716</td>
<td>B$_2$ 878</td>
<td>B$_2$ 910</td>
</tr>
<tr>
<td>ring puckering</td>
<td>A$_2$ 276</td>
<td>A$_2$ 320</td>
<td>A$_2$ 371</td>
<td>A$_2$ 381</td>
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Table I.V Total Energies (hartree) and Relative Energies (kcal/mole) for the Lowest One- and Two-Configuration Singlet States and Lowest Triplet State of Cyclopentyne

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>Number of Configurations</th>
<th>E (hartree)</th>
<th>Relative energy (kcal/mole)</th>
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</thead>
<tbody>
<tr>
<td>DZ TCSCF (1A₁)</td>
<td>2</td>
<td>-192.63422</td>
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<tr>
<td>DZ SCF (3B₂)</td>
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<td>-192.57373</td>
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<tr>
<td>DZ CIₐ (1A₁)</td>
<td>65994</td>
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</tr>
<tr>
<td>DZ CI (3B₂)</td>
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<td>-192.97798</td>
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<tr>
<td>DZ CI (1A₁)</td>
<td>33266</td>
<td>-192.98524</td>
<td>17.5</td>
</tr>
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</table>

a. all single and double 1A₁ configurations relative to references (9) and (10)

b. All single and double 1A₁ configurations relative to reference (9)
Table I.VI Predicted Harmonic Vibrational Frequencies for the Lowest One- and Two-Configuration Singlet States and Lowest Triplet State of Cyclopentyne

<table>
<thead>
<tr>
<th>Description</th>
<th>TC $^1A_1$</th>
<th>$^3B_2$</th>
<th>$^1A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α asym str</td>
<td>$B_1$</td>
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<tr>
<td>β out-of-phase asym str</td>
<td>$A_2$</td>
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<td>3280</td>
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<tr>
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<td>$B_1$</td>
<td>3275</td>
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<tr>
<td>α sym str</td>
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<tr>
<td>β out-of-phase sym str</td>
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</tr>
<tr>
<td>β in-phase sym str</td>
<td>$A_1$</td>
<td>3229</td>
<td>3229</td>
</tr>
<tr>
<td>C=C (or C=C) str</td>
<td>$A_1$</td>
<td>1990</td>
<td>1819</td>
</tr>
<tr>
<td>β in-phase scissor</td>
<td>$B_1$</td>
<td>1663</td>
<td>1663</td>
</tr>
<tr>
<td>β out-of-phase scissor</td>
<td>$B_2$</td>
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<td>1651</td>
</tr>
<tr>
<td>α scissor</td>
<td>$A_1$</td>
<td>1636</td>
<td>1637</td>
</tr>
<tr>
<td>α wag</td>
<td>$B_2$</td>
<td>1468</td>
<td>1476</td>
</tr>
<tr>
<td>β in-phase wag</td>
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<tr>
<td>α twist</td>
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<td>1385</td>
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<tr>
<td>β in-phase twist</td>
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</tr>
<tr>
<td>β out-of-phase twist</td>
<td>$A_2$</td>
<td>1247</td>
<td>1253</td>
</tr>
<tr>
<td>β in-phase rock</td>
<td>$B_1$</td>
<td>1154</td>
<td>1129</td>
</tr>
<tr>
<td>ring mode</td>
<td>$B_2$</td>
<td>1115</td>
<td>1112</td>
</tr>
<tr>
<td>ring mode</td>
<td>$A_1$</td>
<td>1047</td>
<td>1041</td>
</tr>
<tr>
<td>ring mode</td>
<td>$B_2$</td>
<td>1023</td>
<td>1042</td>
</tr>
<tr>
<td>β out-of-phase rock</td>
<td>$A_2$</td>
<td>981</td>
<td>1008</td>
</tr>
<tr>
<td>ring mode</td>
<td>$A_1$</td>
<td>911</td>
<td>933</td>
</tr>
<tr>
<td>α rock</td>
<td>$B_1$</td>
<td>801</td>
<td>827</td>
</tr>
<tr>
<td>ring mode</td>
<td>$A_1$</td>
<td>732</td>
<td>722</td>
</tr>
<tr>
<td>ring mode</td>
<td>$B_2$</td>
<td>724</td>
<td>818</td>
</tr>
<tr>
<td>ring torsion</td>
<td>$A_2$</td>
<td>367</td>
<td>416</td>
</tr>
<tr>
<td>ring folding</td>
<td>$B_1$</td>
<td>641</td>
<td>511</td>
</tr>
</tbody>
</table>

α refers to the single CH$_2$ group opposite the multiple bond

β refers to the two equivalent CH$_2$ groups adjacent to the triple bond
Table II.I Absolute Energies (hartree) and Dimerization Energies (kcal/mole) for several Isomers of the Hydroperoxyl Dimer.

<table>
<thead>
<tr>
<th>species</th>
<th>DZ results</th>
<th>DZ+P results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy</td>
<td>ΔE&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2A'' HO&lt;sub&gt;2&lt;/sub&gt; monomer</td>
<td>-150.15752</td>
<td>0.0</td>
</tr>
<tr>
<td>3B&lt;sub&gt;u&lt;/sub&gt; C&lt;sub&gt;2h&lt;/sub&gt; ring</td>
<td>-300.32225</td>
<td>-4.52</td>
</tr>
<tr>
<td>1A&lt;sub&gt;g&lt;/sub&gt; C&lt;sub&gt;2h&lt;/sub&gt; ring</td>
<td>-300.32224</td>
<td>-4.52</td>
</tr>
<tr>
<td>1A&lt;sub&gt;g&lt;/sub&gt; C&lt;sub&gt;2h&lt;/sub&gt; chain</td>
<td>-300.24471</td>
<td>44.13</td>
</tr>
<tr>
<td>1A&lt;sub&gt;g&lt;/sub&gt; C&lt;sub&gt;1&lt;/sub&gt; chain</td>
<td>-300.26073</td>
<td>34.08</td>
</tr>
</tbody>
</table>

<sup>a</sup> ΔE is defined here as E(dimer) - 2xE(monomer), and is reported in kcal/mole
Table II.2: Comparison of Theoretical and Experimental Vibrational Frequencies for the $\text{H}_2\text{O}_2$ Monomer

<table>
<thead>
<tr>
<th>Normal Mode</th>
<th>DZ SCF harmonic</th>
<th>DZ+P SCF harmonic</th>
<th>Experimental anharmonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-H stretch</td>
<td>3991</td>
<td>4105</td>
<td>3436 \textsuperscript{a}</td>
</tr>
<tr>
<td>0-0-H bend</td>
<td>1526</td>
<td>1592</td>
<td>1392 \textsuperscript{b}</td>
</tr>
<tr>
<td>0-0 stretch</td>
<td>1100</td>
<td>1270</td>
<td>1098 \textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yamanda, Endo, and Hirota, reference 59.

\textsuperscript{b} Nagai, Endo, and Hirota, reference 58.

\textsuperscript{c} McKellar, reference 57.
Table II-III Predicted Harmonic Vibrational Frequencies (cm\(^{-1}\)) for the Cyclic Two-Hydrogen-Bonded Form of the Hydroperoxyl Dimer.

<table>
<thead>
<tr>
<th>normal mode</th>
<th>symmetry</th>
<th>DZ SCF</th>
<th>DZ+P SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>out-of-phase O-H str</td>
<td>Bu</td>
<td>3966</td>
<td>4073</td>
</tr>
<tr>
<td>in-phase O-H str</td>
<td>Ag</td>
<td>3953</td>
<td>4061</td>
</tr>
<tr>
<td>in-phase O-O-H bend</td>
<td>Ag</td>
<td>1577</td>
<td>1653</td>
</tr>
<tr>
<td>out-of-phase O-O-H bend</td>
<td>Bu</td>
<td>1555</td>
<td>1626</td>
</tr>
<tr>
<td>in-phase O-O str</td>
<td>Ag</td>
<td>1101</td>
<td>1279</td>
</tr>
<tr>
<td>out-of-phase O-O str</td>
<td>Bu</td>
<td>1099</td>
<td>1278</td>
</tr>
<tr>
<td>out-of-phase H wag</td>
<td>Bg</td>
<td>456</td>
<td>527</td>
</tr>
<tr>
<td>in-phase H wag</td>
<td>Bu</td>
<td>358</td>
<td>439</td>
</tr>
<tr>
<td>in-plane deformation</td>
<td>Ag</td>
<td>182</td>
<td>189</td>
</tr>
<tr>
<td>out-of-phase O•••H str</td>
<td>Bu</td>
<td>157</td>
<td>173</td>
</tr>
<tr>
<td>in-phase O•••H str</td>
<td>Ag</td>
<td>136</td>
<td>135</td>
</tr>
<tr>
<td>ring torsion</td>
<td>Au</td>
<td>92</td>
<td>98</td>
</tr>
</tbody>
</table>
### Table II.IV Predicted Harmonic Vibrational Frequencies (cm⁻¹) for the Open Chain Structure of the Hydroperoxyl Dimer

<table>
<thead>
<tr>
<th>Normal Mode</th>
<th>C₂h</th>
<th>C₁</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DZ</td>
<td>DZ+P</td>
</tr>
<tr>
<td><strong>in-phase 0-H str</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>3988</td>
<td>4157</td>
</tr>
<tr>
<td>Bu</td>
<td>3984</td>
<td>4154</td>
</tr>
<tr>
<td><strong>out-of-phase 0-H str</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1553</td>
<td>1631</td>
</tr>
<tr>
<td>Bu</td>
<td>1469</td>
<td>1541</td>
</tr>
<tr>
<td><strong>in-phase 0-0-H bend</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1144</td>
<td>1253</td>
</tr>
<tr>
<td>Bu</td>
<td>1087</td>
<td>1198</td>
</tr>
<tr>
<td><strong>out-of-phase 0-0-H str</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bu</td>
<td>1027</td>
<td>1147</td>
</tr>
<tr>
<td><strong>unique 0-0 str</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>522</td>
<td>579</td>
</tr>
<tr>
<td>Bu</td>
<td>342</td>
<td>386</td>
</tr>
<tr>
<td><strong>in-phase 0-0-0 bend</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>3121</td>
<td>3621</td>
</tr>
<tr>
<td>Bu</td>
<td>3531</td>
<td>3901</td>
</tr>
<tr>
<td><strong>out-of-phase H wag</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1041</td>
<td>1101</td>
</tr>
<tr>
<td>Bu</td>
<td>342</td>
<td>386</td>
</tr>
</tbody>
</table>

**a.** Symmetry of the normal mode refers to C₂h symmetry. Ag and Bg of C₂h become Ag in C₁; Au and Bu of C₂h become Au in C₁.
Table II.V Experimentally Observed Vibrational Frequencies (cm\(^{-1}\)) for the Hydroperoxyl Monomer and Dimer (from reference 60)

<table>
<thead>
<tr>
<th>mode</th>
<th>HO(_2) (^a)</th>
<th>(HO(_2))(_2) (^a)</th>
<th>(HO(_2))(_2) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch</td>
<td>3400</td>
<td>3329</td>
<td>3322</td>
</tr>
<tr>
<td></td>
<td>3320</td>
<td></td>
<td>3320</td>
</tr>
<tr>
<td>O-O-H bend</td>
<td>1391</td>
<td>1417</td>
<td>1417 (^c)</td>
</tr>
<tr>
<td></td>
<td>1413</td>
<td></td>
<td>1415 (^c)</td>
</tr>
<tr>
<td>O-O stretch</td>
<td>1101</td>
<td>1110</td>
<td>1109 (^c)</td>
</tr>
<tr>
<td></td>
<td>1108</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) from experiment A, photolysis of CH\(_2\)O in O\(_2\)

\(^b\) from experiment B, photolysis of C\(_2\)H\(_2\)O\(_2\) in O\(_2\)

\(^c\) actually a fundamental of (HO\(_2\))•CO
<table>
<thead>
<tr>
<th>source</th>
<th>O-H stretch</th>
<th>O-O-H bend</th>
<th>O-H stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment a</td>
<td>-71 +26</td>
<td>+9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-80 +22</td>
<td>+7</td>
<td></td>
</tr>
<tr>
<td>experiment b</td>
<td>-77 +25</td>
<td>+7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-80 +24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DZ ring II.4</td>
<td>-25 +51</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-37 +28</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>DZ+P ring II.4</td>
<td>-32 +61</td>
<td>+9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-44 +34</td>
<td>+8</td>
<td></td>
</tr>
<tr>
<td>DZ C₁ chain II.1</td>
<td>-7 +12</td>
<td>+16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-10 +6</td>
<td>-3</td>
<td></td>
</tr>
</tbody>
</table>

a. expt. A, photolysis of CH₂O in O₂ (ref 60).
b. expt. B, photolysis of C₂H₂O₂ in O₂ (ref 60).
Table III. Vertical Excitation Energies (eV) of the $^1(\pi^+\pi^*)$ and $^3(\pi^+\pi^*)$ States of Formaldehyde

<table>
<thead>
<tr>
<th>reference</th>
<th>$^1A_1$ energy (eV)</th>
<th>$^3A_1$ energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work DZ basis</td>
<td>10.87</td>
<td>4.11</td>
</tr>
<tr>
<td>this work DZ+P basis</td>
<td>10.95</td>
<td>4.87</td>
</tr>
<tr>
<td>Whitten and Hackmeyer$^{86}$</td>
<td>11.31</td>
<td>5.66</td>
</tr>
<tr>
<td>Yeager and McKoy$^{87}$</td>
<td>10.10</td>
<td>5.29</td>
</tr>
<tr>
<td>Gouyet and Prat$^{88}$</td>
<td>10.43</td>
<td>6.16</td>
</tr>
<tr>
<td>Harding and Goddard$^{89}$</td>
<td>10.77</td>
<td>5.95</td>
</tr>
</tbody>
</table>
Table III.II Predicted Stationary Point Geometries for the Ground State and Several Excited States of Formaldehyde. Bond lengths are given in angstroms.

<table>
<thead>
<tr>
<th>state</th>
<th>$r_e$ (CO)</th>
<th>$r_e$(CH)</th>
<th>$\theta$(HCH)</th>
<th>torsional angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ $^1A_1$ ground</td>
<td>1.217</td>
<td>1.084</td>
<td>116.9°</td>
<td>0.0°</td>
</tr>
<tr>
<td>DZ+P $^1A_1$ ground</td>
<td>1.189</td>
<td>1.096</td>
<td>116.2°</td>
<td>0.0°</td>
</tr>
<tr>
<td>DZ $^1A_1$ ($\pi+\pi^*$)</td>
<td>1.647</td>
<td>1.076</td>
<td>121.5°</td>
<td>0.0°</td>
</tr>
<tr>
<td>DZ+P $^1A_1$ ($\pi+\pi^*$)</td>
<td>1.537</td>
<td>1.078</td>
<td>120.3°</td>
<td>0.0°</td>
</tr>
<tr>
<td>DZ $^3A_1$ ($\pi+\pi^*$)</td>
<td>1.474</td>
<td>1.069</td>
<td>125.9°</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ+P $^3A_1$ ($\pi+\pi^*$)</td>
<td>1.432</td>
<td>1.073</td>
<td>124.9°</td>
<td>0.0</td>
</tr>
<tr>
<td>DZ $^3A'$ ($\pi+\pi^*$)</td>
<td>1.477</td>
<td>1.074</td>
<td>121.0°</td>
<td>32.0°</td>
</tr>
<tr>
<td>DZ+P$^a$ $^1A'$ ($\pi+\pi^*$)</td>
<td>1.434</td>
<td>1.077</td>
<td>119.1°</td>
<td>34.8°</td>
</tr>
</tbody>
</table>

a. from reference 92.
Table III.III Predicted Harmonic Vibrational Frequencies (cm$^{-1}$) for the Ground and Several Excited States of Formaldehyde.

<table>
<thead>
<tr>
<th>normal mode</th>
<th>$DZ^1A_1$, ground</th>
<th>$DZ^1A_1$, $(\pi+\pi^*)$</th>
<th>$DZ^3A_1$, $(\pi+\pi^*)$</th>
<th>$DZ^3A'$, $(\pi+\pi^*)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_2$ asym str</td>
<td>3315</td>
<td>3492</td>
<td>3537</td>
<td>3471</td>
</tr>
<tr>
<td>$CH_2$ sym str</td>
<td>3224</td>
<td>3332</td>
<td>3360</td>
<td>3320</td>
</tr>
<tr>
<td>C=O str</td>
<td>1878</td>
<td>760</td>
<td>1102</td>
<td>1086</td>
</tr>
<tr>
<td>$CH_2$ scissor</td>
<td>1651</td>
<td>1512</td>
<td>1553</td>
<td>1567</td>
</tr>
<tr>
<td>$CH_2$ rock</td>
<td>1350</td>
<td>902</td>
<td>1145</td>
<td>1184</td>
</tr>
<tr>
<td>$CH_2$ wag</td>
<td>1325</td>
<td>769</td>
<td>6261</td>
<td>774</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>normal mode</th>
<th>$DZ+P^1A_1$, ground</th>
<th>$DZ+P^1A_1$, $(\pi+\pi^*)$</th>
<th>$DZ+P^3A_1$, $(\pi+\pi^*)$</th>
<th>$DZ+P^3A'$, $(\pi+\pi^*)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_2$ asym str</td>
<td>3215</td>
<td>3464</td>
<td>3492</td>
<td>3420</td>
</tr>
<tr>
<td>$CH_2$ sym str</td>
<td>3137</td>
<td>3323</td>
<td>3337</td>
<td>3288</td>
</tr>
<tr>
<td>C=O str</td>
<td>2005</td>
<td>848</td>
<td>1191</td>
<td>1176</td>
</tr>
<tr>
<td>$CH_2$ scissor</td>
<td>1651</td>
<td>1567</td>
<td>1578</td>
<td>1590</td>
</tr>
<tr>
<td>$CH_2$ rock</td>
<td>1363</td>
<td>1024</td>
<td>1180</td>
<td>1232</td>
</tr>
<tr>
<td>$CH_2$ wag</td>
<td>1331</td>
<td>721</td>
<td>7341</td>
<td>873</td>
</tr>
</tbody>
</table>

* from reference 92.
Table III.IV Relative Energies (eV) for Several States and Geometries of Formaldehyde

<table>
<thead>
<tr>
<th>state</th>
<th>geometry</th>
<th>relative energy (eV)</th>
<th>DZ</th>
<th>DZ+P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$ ground state</td>
<td>ground state</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$^1(\pi+\pi^*)$</td>
<td>ground state</td>
<td>10.87</td>
<td>10.95</td>
<td></td>
</tr>
<tr>
<td>$^1(\pi+\pi^*)$</td>
<td>$C_2v$ optimized</td>
<td>7.97</td>
<td>8.68</td>
<td></td>
</tr>
<tr>
<td>$^3(\pi+\pi^*)$</td>
<td>ground state</td>
<td>4.11</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>$^3(\pi+\pi^*)$</td>
<td>$C_2v$ optimized</td>
<td>2.36</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>$^3(\pi+\pi^*)$</td>
<td>$C_8$ optimized</td>
<td>2.32</td>
<td>2.99</td>
<td></td>
</tr>
</tbody>
</table>

a. from reference 92.
Figure Captions.

Figure I.1 Predicted equilibrium structures of the lowest singlet and triplet states of cyclopropyne. Bond lengths are in angstroms.

Figure I.2 Predicted equilibrium structures of the lowest singlet and triplet states of cyclobutane. Bond lengths are in angstroms.

Figure I.3 Predicted C2v equilibrium structures of the lowest one- and two-configuration singlet states and the lowest triplet state of cyclopentane. Bond lengths are in angstroms.

Figure II.1 Predicted equilibrium structures of the 2A" ground state of HO2. Bond lengths are in angstroms. Experimental results (ref 51) appear in parentheses.

Figure II.2 Predicted equilibrium structures of the 3Bu state of the cyclic, two-hydrogen-bond form of the hydroperoxyl dimer, (HO2)2. Bond lengths are in angstroms.

Figure II.3 Predicted equilibrium structure of the two-configuration 1Ag state of the cyclic, two-hydrogen-bond form of the hydroperoxyl dimer, (HO2)2. Bond lengths are in angstroms.

Figure II.4 Predicted equilibrium structures of the 1Ag state of the C2h and C1 open chain forms of the hydroperoxyl dimer, (HO2)2. Bond lengths are in angstroms.
Figure I.1

\[ \text{DZ} \]

\[ \text{DZ + d} \]

\[ \text{\( ^3B_2 \) State} \]

\[ \text{\( ^1A_1 \) State} \]

\[ C \]

\[ \begin{align*}
\text{H} & \quad 114.9^\circ & \quad \text{H} \\
\text{C} & \quad 1.075 \\
\text{C} & \quad 1.567 \\
\end{align*} \]

\[ C \]

\[ \begin{align*}
\text{H} & \quad 114.0^\circ & \quad \text{H} \\
\text{C} & \quad 1.077 \\
\text{C} & \quad 1.556 \\
\end{align*} \]

\[ \begin{align*}
\text{C} & \quad 1.298 \\
\text{C} & \quad 1.262 \\
\end{align*} \]

\[ \begin{align*}
\text{C} & \quad 1.276 \\
\text{C} & \quad 1.241 \\
\end{align*} \]

\[ \text{XBL8211-4244} \]
Figure I.2

$^{3}B_2$ State

DZ

$^{1}A_1$ State

DZ + d

DZ + P
Figure II.2

Triplet
DZ+P

H

1.309

0.954

143.0°

2.192

105.6°

111.5°

Triplet
DZ

0.961

107.3°

115.6°

XBL641-7550
Figure II.3

Singlet DZ

H

0.961

1.367

2.243

137.1°

107.3°

115.6°

0.961

XBL641-7548
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