# Lawrence Berkeley National Laboratory 

## Title

ELECTRONIC SYMMETRY BREAKING IN POLYATOMIC MOLECULES. MULTICONFIGURATION SELF-CONSISTENT-FIELD STUDY OF THE CYCLOPROPENYL RADICAL, C3H3

## Permalink

https://escholarship.org/uc/item/0g61j91t

## Author

Schaefer, H.F.
Publication Date
1982-03-01

# L3 Lawrence Berkeley Laboratory UNIVERSITY OF CALIFORNIA 

# Materials \＆Molecular Research Division 

RECEIVED BERKFLEYMENCE

LU 71032 DOClIMENTY AIVD DOCUMENTS SECTION
Submitted to the Journal of Chemical Physics

ELECTRONIC SYMMETRY BREAKING IN POLYATOMIC MOLECULES． MULTICONFIGURATION SELF－CONSISTENT－FIELD STUDY OF THE CYCLOPROPENYL RADICAL， $\mathrm{C}_{3} \mathrm{H}_{3}$ ．

William D．Laidig and Henry F．Schaefer III

March 1982

## TWO－WEEK LOAN COPY

．This is a Library Circulating Copy which may be borrowed for two weeks． For a personal retention copy，call Tech．Info．Division，Ext． 6782.

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefuiness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Electronic Symmetry Breaking in Polyatomic Molecules.<br>Multiconfiguration Self-Consistent-Field Study of the Cyclopropenyl Radical, $\mathrm{C}_{3} \mathrm{H}_{3}$.<br>William D, Laidig* and Henry F, Schaefer III<br>Department of Chemistry and Lawrence Berkeley Laboratory University of California Berkeley, California 94720

## Abstract

For equilateral triangle geometries (point group $D_{3 h}$ ), the $\mathrm{C}_{3} \mathrm{H}_{3}$ radical has a degenerate ${ }^{2} \mathrm{E}$ " electronic ground state. Although the ${ }^{2} A_{2}$ and ${ }^{2} B_{1}$ components separate in energy for $C_{2 v}$ geometries, these two components should have identical energies for equilateral trtangle structures. In fact, when approximate wave functions are used and the orbitals not required to transform according to the $D_{3 h}$ irreducible representations, an energy separation between the ${ }^{2} A_{2}$ and: ${ }^{2} B_{1}$ components is observed. At the single configuration selfeconsistent-field (SCF) level of theory this separation is $2,8 \mathrm{kcal}$ with a double zeta basis set and 2.4 kcal with double zeta plus polarization,

It has been demonstrated that this spurious separation may be greatly reduced using multiconfiguration self-consistent-field (up to 7474 variationally optimum configurations) and configuration
interaction (up to 60,685 space and spin adapted configurations)
techniques. Configurations differing by three and four electrons
from the Hartree-Fock reference function are found necessary toreduce the ${ }^{2} A_{2}-{ }^{2} B_{1}$ separation to below 0.5 kcal .*Present address: Quantum Theory Project, University of Florida,Williamson Hall, Gainesville, Florida 32607

The cyclopropenyl radical $\mathrm{C}_{3} \mathrm{H}_{3}$ has received much attention because it is a simple example of a molecule that is expected to undergo a Jahn-Teller distortion. ${ }^{1-8}$ If an electron is added to the lowest unoccupied molecular orbital (LUMO) of the $D_{3 h}$ ground state of the cyclopropenyl cation it will enter a degenerate $e^{\prime \prime}$ orbital to form the lowest ${ }^{2} E$ " state of the radical. According to the Jahn-Teller Theorem ${ }^{10}$ a non-linear molecule of E symmetry will spontaneously distort in such a way as to lift the degeneracy. In the case of the $\mathrm{C}_{3} \mathrm{H}_{3}$ radical this distortion will lower the symmetry to $C_{2 v}$ or possibly $C_{s}$ or $C_{2}$. If the true wavefunction within the Born-Oppenheimer approximation were known at the $D_{3 h}$ and surrounding geometries it would be easy to find out what the "real" equilibrium structure looks like, However, when this exact wavefunction is not known, certain complications arise. If a full configuration interaction (CI) within a given basis set could be computed at any $D_{3 h}$ geometry it would lead to a wavefunction having $D_{3 h}$ symnetry whether $\Psi$ was forced to be of this symmetry or not. However, for theoretical treatments carried out below the full CI level, the wavefunction symmetry may break (i.e., belong to a point group of lower symmetry) unless the correct symuetry is forced by the method. Just such a situation arises for the $\mathrm{C}_{3} \mathrm{H}_{3}$ radical, ${ }^{1-8}$

In the case of the cyclopropenyl radical, if self-consistentfield (SCF) or truncated CI or multiconfiguration (MC) SCF theory is applied at a $D_{3 h}$ geometry, the resulting wavefunctions will be
at best of $C_{2 v}$ symmetry unless otherwise constrained. ${ }^{11}$ The ${ }^{2} E$ " state corresponds to a pair of states in the lower $C_{2 v}$ point group: ${ }^{2} \mathrm{~A}_{2}$ and ${ }^{2} \mathrm{~B}_{1}$, which should physically be degenerate in energy at the $D_{3 h}$ geometry. However, if the calculations are carried out in $C_{2 v}$ symmetry (i.e., the wavefunctions not constrained to transform according to the irreducible representation $\left.E^{\prime \prime}\right)$, the energies of the two states will be different. The purpose of this research is to study the effects of using different CI expansions and orbital basis sets on the ${ }^{2} B_{1}-{ }^{2} A_{2}$ energy splitting. Since Nature requires this splitting to be identically zero, the values obtained at various levels of theory provide a practical lower limit to the sort of errors one should expect in energy differences (i.e., electronic excitation energies) for moderate-sized organic systems such as $\mathrm{C}_{3} \mathrm{H}_{3}$.

## Theoretical Approach

In the present study of the cyclopropenyl radical we employed the standard HuzinagarDunning ${ }^{12,13}$ contracted Gaussian double-zeta (DZ) basis set, the precise designation of which is $C(9 s 5 p / 4 s 2 p)$ and $H(4 s / 2 s)$, All calculations were performed at a single $D_{3 h}$ geometry with the three $C-C$ bond distances fixed at $1.40 \AA$ and the $C-H$ bond lengths set at $1.08 \AA$, as seen in the Figure. The exact cartesian geometry used was ( $0.0,0.0,0.0$ ), $(0,0, \pm 1,322826,-2,291202)$ for the three carbion atoms and ( 0,0 , $0.0,2.040932),(0.0, \pm 3,090325,-3.311668)$ for the three hydrogen atoms. Since the geometry was not optimized in this
study and our primary purpose was to determine the ${ }^{2} B_{1}{ }^{-}{ }^{2} A_{2}$ energy splitting at a representative $D_{3 h}$ geometry, we deemed a DZ basis set to be adequate. Subsequent studies (see below) with a larger basis set confirmed our intuition that the double zeta basis set is indeed large enough to avoid misleading results with respect to the $\mathrm{C}_{3} \mathrm{H}_{3}$ symmetry breaking problem. Note in this vein that the geometry selected does not correspond to the minimum on the $D_{3 h}$ surface for this basis set, but was picked because it is in the range of previous theoretical work. ${ }^{1-8}$

To determine how the spurious electronic splitting (at the chosen $D_{3 h}$ geometry) varies as the level of theory is changed, a series of variational wavefunctions were determined for the lowest ${ }^{2} \mathrm{~B}_{1}$ and ${ }^{2} A_{2}$ states of $\mathrm{C}_{3} \mathrm{H}_{3}$. All of these calculations were done in $\mathrm{C}_{2}$ v symmetry (i,e., the molecular orbitals were constrained to transform according to the $C_{2 v}$ irreducible representations, and the total wavefunctions constrained to transform according to $B_{1}$ or $A_{2}$ symmetry species) at the $D_{3 \hbar}$ geometry, Initially single configuration self-consistent-field (SCF) calculations were performed on these two states with the ${ }^{2} B_{1}$ and ${ }^{2} A_{2}$ reference configurations being

$$
\begin{align*}
& \Phi_{1}\left({ }^{2} \mathrm{~B}_{1}\right)=\ldots 5 \mathrm{a}_{1}^{2} 3 \mathrm{~b}_{2}^{2} 1 \mathrm{~b}_{1}^{2} 6 \mathrm{a}_{1}^{2} 2 \mathrm{~b}_{1}  \tag{1}\\
& \Phi_{1}\left({ }^{2} \mathrm{~A}_{2}\right)=\ldots 5 \mathrm{a}_{1}^{2} 3 \mathrm{~b}_{2}^{2} 1 \mathrm{~b}_{1}^{2} 6 \mathrm{a}_{1}^{2} \mathrm{la}_{2} \tag{2}
\end{align*}
$$

Beyond the SCF level a number of CI and MCSCF treatments were
pursued. First a set of three single and double excitation CI wavefunctions were computed for each state. In the largest, involving 11,829 and 11,800 configurations for the ${ }^{2} B_{1}$ and ${ }^{2} \mathrm{~A}_{2}$ states respectively, all orbitals were included in the CI. In the second the 18 orbitals with the highest orbital energies were forced to have zero occupancy in the CI (in other words, one half of the orbitals of each symmetry type were.frozen) reducing the number of configurations to 1069 for either state. In the third CI the three lowest occupied SCF orbitals (in an energetic sense) were frozen in addition, resulting in 549 configurations in both the ${ }^{2} \mathrm{~B}_{1}$ and ${ }^{2} \mathrm{~A}_{2}$ cases. These three calculations will be abbreviated as CIALL, CIMIN and CI549. In this last CI the orbitals are partitioned such that there are 18 of the virtual, 3 of the core and 15 of the active varieties. Such a small CI limits excitations to within the valence space. The concept of the valence space is easy to visualize if one envisions the $C-C$ and C-H bond lengths being stretched to infinity. When this happens the set of 15 active orbitals reduces to the 2 s and 2 p shells on the carbon atoms and the ls orbitals on the hydrogens.

In addition to these three types of configuration interaction, a number of further calculations were performed within the valence space on both the ${ }^{2} A_{2}$ and ${ }^{2} B_{1}$ states. The first of these involves an MCSCF optimization within the same 549 configuration space defined above and is called MC549. To investigate the effect of higher than double excitations in this subspace on the ${ }^{2} B_{1} \Gamma^{2} A_{2}$ splitting, four further sets of calculations were carried out.

Initially standard CIs (using the canonical SCF orbitals) with configuration set composed of the reference plus all single, double and triple excitations within the valence space were performed. This increased the number of configurations to 7470 or 7474 for the ${ }^{2} A_{2}$ or ${ }^{2} \mathrm{~B}_{1}$ states, respectively. These were followed by MCSCF calculations employing the same configuration list to ascertain the effect of optimizing the orbitals. These two theoretical procedures will be labeled CISDT and MCSDT. Single, double, triple and quadruple excitation (SDTQ) CI using the SCF orbitals were next performed and will be identified as CISDTQ, To estimate the energetic effect of optimizing the orbitals for the SDTQ configuration set, CIs employing the MC549 (instead of single configuration SCF) orbitals were carried out. Henceforth the latter level of theory will be designated MCSD+TQ. The SDTQ CIs were relatively large, containing 60645 and 60685 configurations for the ${ }^{2} A_{2}$ and ${ }^{2} \mathrm{~B}_{1}$ states, respectively.

Thus far this investigation has concerned itself only with changes in the ${ }^{2} B_{1}-{ }^{2} A_{2}$ splitting as a function of the orbital type or the configuration set employed in CI calculations. Another important factor to consider is the effect of basis set size on the energy difference. To investigate this aspect of the problem, polarization functions were added to both the carbon and hydrogen basis sets, For carbon a set of gaussian $d$ functions was added with exponents $\alpha=0.75$. For hydrogen a set of gaussian $p$ functions was added with exponents $\alpha=1.0$. This more complete basis set will be designated $D Z+P$ and was employed only at the SCF level of theory.

All the research described above was carried out using the system of unitary group CI and MCSCF programs described in references 14-19 and was performed on a Harris Series 800 minicomputer.

## Results and Discussion

In Table I the total energies for the levels of theory specified in the preceeding section are presented. First, the $D Z$ SCF results are examined. For the ${ }^{2} A_{2}$ state a total energy of -115.104667 hartrees was obtained and for the corresponding ${ }^{2} B_{1}$ state a lower energy of -115.109144 hartrees was found. This leads to a splitting of 0.004477 hartrees or $2.81 \mathrm{kcal} / \mathrm{mole}$. This difference is of the same order as the minimum basis SCF results of Davidson and Borden ${ }^{7}$ in which a value of around 5 kcal/mole was reported. Poppinger, Radom and Vincent ${ }^{8}$ (PRV) also published SCF ${ }^{2} \mathrm{~B}_{1}-{ }^{2} \mathrm{~A}_{2}$ splittings for both the minimum and the split valence $4-31 \mathrm{G}$ basis sets, for which they obtained 4.79 and $3.23 \mathrm{kcal} / \mathrm{mole}$ respectively.

The spurious separation between ${ }^{2} \mathrm{~A}_{2}$ and ${ }^{2} \mathrm{~B}_{1}$ electronic states was next considered with the larger DZ + P basis set, For the ${ }^{2} A_{2}$ and ${ }^{2} B_{1}$ states DZ + PSCF energies of -115.174127 and -115.178000 hartrees were obtained respectively. The ${ }^{2} B_{1} V^{2} A_{2}$ splitting is thus 0.003873 hartrees or $2.43 \mathrm{kcal} / \mathrm{mole}$, or approximately 0.4 kcal below the corresponding $D Z$ value. This leads to the following basis set trend, $\Delta E_{M B}>\Delta E_{4-31 G}>\Delta E_{D Z}$ $>E_{D Z+P}$ where $\Delta E$ is the ${ }^{2} B_{1}-{ }^{2} A_{2}$ energy splitting and $M B$ stands for minimum basis set. Since the $M B$ results of Davidson and Borden ${ }^{7}$
and the $M B$ and 4-31G results of Poppinger, Radom and Vincent were carried out at geometries different from ours, their values for $\Delta E$ will be slightly different from values calculated at our geometry. However, the geometry differences are very small and it seems likely that qualitative trend will remain the same. Thus, while improvement of the basis set does reduce the artificial energy difference between the two degenerage components of the 2E" state of $\mathrm{C}_{3} \mathrm{H}_{3}$, the effect nevertheless persists.

Moving on to the straight CI results, the energies of the ${ }^{2} B_{1}$ and ${ }^{2} A_{2}$ states are found to be -115.389963 and -115.387954 hartrees, respectively, in the all orbital single and double excitation $C I$ treatment. These calculations which involve nearly 12,000 configurations reduce the splitting to 0.002009 hartrees or $1.26 \mathrm{kcal} / \mathrm{mole}$. This energy difference is less than half the comparable SCF value. If the 18 highest reference unoccupied orbitals are now frozen in the single and doubles $C I$ the corresponding ${ }^{2}{ }_{B}{ }_{1}$ and ${ }^{2} \mathrm{~A}_{2}$ energies are -115.165587 and -115.167098 hartrees. This leads to a splitting of -0.001512 hartrees or $-0.95 \mathrm{kcal} / \mathrm{mole}$, where the minus sign indicates that the ordering of the two states has changed. This state reversal is most likely due to the choice of the frozen orbitals in the CI, If all the molecular orbitals unoccupied in the reference configuration (1) or (2) are kept in the CI, the energy is invariant to unitary transformations within this orbital subset. However, if any of these orbitals are frozen, the energy is no longer invariant in this respect. From the SCF point of view, however, the unoccupied orbitals are only required to be orthogonal to the occupied space
and amongst themselves and are thus rather arbitrary, particularly so when compared to MCSCF or natural orbitals. ${ }^{20}$ A likely explanation of this sign reversal is that by chance the set of ${ }^{2} A_{2}$ unoccupied orbitals retained in the $C I$ were energetically more favorable (with respect to the correlation energy) than the corresponding ${ }^{2} B_{2}$ orbitals. If, in addition to the 18 virtual orbitals, 3 core orbitals are frozen the single and doubles CI energies are found to be -115.165484 and -115.166984 hartrees for the ${ }^{2} B_{1}$ and ${ }^{2} A_{1}$ states, Here one notices that the ordering of the states is again reversed, with the splitting being -0.001510 hartrees or $-0.94 \mathrm{kcal} / \mathrm{mole}$. This result confirms the view that core electron correlation effects are of little importance in the theoretical prediction of valence properties, such as the energy difference between a pair of lowlying electronic states.

Continuing to the first of the MCSCF results the ${ }^{2} B_{1}-{ }^{2} A_{2}$ energy gap is found to be +0.001336 hartrees for the valence space singles and doubles MCSCF (MC549), This $0.84 \mathrm{kcal} / \mathrm{mole}$ difference is roughly $2 / 3$ of the analogous CIALL splitting ( $1.26 \mathrm{kcal} / \mathrm{mole}$ ), but the CI contains only about $1 / 20$ of the number of configurations. This result is encouraging since MCSCF calculations of this variety can be performed on nearly all systems that can be handled using SCF theory alone, ${ }^{17}$ In terms of absolute energies, -115.290106 and -115.288770 hartrees were obtained for the ${ }^{2} B_{1}$ and ${ }^{2} A_{2}$ states respectively. These results are perhaps surprising in that the small 549 configuration MCSCF calculations recovered around $65 \%$ of the full CI singles
plus doubles correlation energy while the CIs using SCF orbitals in the same formal valence space recovered about $20 \%$. Optimizing the orbitals then leads to roughly 3 times as much correlation energy and the "correct" (by comparison with more complete levels of theory) prediction of the state ordering. Four additional sets of calculations were carried out within the valence space to test the effect of inclusion of higher than double excitations. The first two of these employed a configuration set consisting of all valence single, double and triple excitations. The total energies for the straight CISDT computations are -115.166563 and -115. 168311 hartrees for the ${ }^{2} B_{1}$ and ${ }^{2} A_{1}$ states, respectively, which leads to a splitting of -0.001748 hartrees or $-1.10 \mathrm{kcal} / \mathrm{mole}$. The ordering of the two states is again inverted as in the CIMIN and CI549 cases with the gap now larger by roughly 0.15 kcal . This result is at first glance surprising since the CISDT calculation is much more extensive than either of the CIMIN or CI549 calculations, On closer examination, however, since the ${ }^{2} A_{2}$ state is above the ${ }^{2} B_{1}$ state in the SCF approximation, one would expect that as the size of the CI increases so will the ratio of the ${ }^{2} A_{2}$ and ${ }^{2} B_{1}$ correlation energies,

The second level of theory attained using the all valence single, double and triple configuration set was MCSDT. Since the orbitals used in these MCSCF wavefunctions are optimal and the configuration lists increased ${ }_{\mathrm{r}}$ it is not surprising that the results represent an improvement with respect to the earlier
discussed MCSD (or MC549) treatment, As with the CIALL and MCSD levels of theory, MCSDT predicts the ${ }^{2} B_{1}$ electronic state to lie slightly below the ${ }^{2} A_{2}$. This separation is reduced from 0.84 kcal in MCSD to 0.70 kcal in MCSDT. An error of this magnitude is now compatible with the elusive goal of "chemical. accuracy", typically designated as one kcal/mole.

Straight configuration interaction employing all valence single, double, triple and quadruple excitations for both the two states of cyclopropenyl radical were next carried out: As in the other three CIs with 18 frozen SCF virtual orbitals, CISDTO predicts the ${ }^{2} A_{2}$ state to lie below the ${ }^{2} B_{1}$ state. This time an energy splitting of -0.002207 hartrees or $-1.38 \mathrm{kca} / \mathrm{mole}$ is found. What these four theoretical treatments (CIMIN, CI549, CISDT and CISDTQ) demonstrate is that when the CI expansion is restricted to the minimum basis or valence space, it is necessary to optimize the orbitals if properties such as the ${ }^{2} A_{2}{ }^{2}{ }^{2} B_{1}$ energy ordering are to be correctly predicted. Inclusion of a very large number of configurations does not in such cases compensate for the poor choice of a small virtual orbital space.

Lastly the MCSD+TQ calculations were carried out. For the ${ }^{2} A_{1}$ and ${ }^{2} B_{2}$ states energies of -115.309306 and -115.309002 hartrees were computed, respectively. This leads to a ${ }^{2} \mathrm{~B}_{1}{ }^{-}{ }^{2} \mathrm{~A}_{2}$ energy splitting of just 0,000304 hartrees or $-0.19 \mathrm{kcal} / \mathrm{mole}$. This difference is by far the smallest obtained, being less than one-third of the MCSDT result of $0.70 \mathrm{kcal} / \mathrm{mole}$. The magnitude of the splitting suggests (but by no means proves) that the MC.549
orbitals employed in this calculation-were-nearly optimal. Comparing the ${ }^{2} \mathrm{~A}_{2}$ and ${ }^{2} \mathrm{~B}_{1}$ MCSD+TQ and MC549 energies energy lowerings of 0.0205 and 0.0189 hartrees are found respectively. The same differences between the MCSDT and MC549 calculations are 0.0026 and 0.0024 hartrees for the ${ }^{2} \mathrm{~A}_{2}$ and $2_{1}{ }_{1}$ states respectively, or almost an order of magnitude less. This suggests that triple excitations are considerably less important than quadruple excitations in valence subspace CIs employing optimized or nearly optimized orbitals. This finding tends to differ from previous results on the importance of triple and quadruple excitations in MCSCF calculations in the water molecule, ${ }^{19}$ In that study triple excitations could be made more important (via the MCSCF procedure) than quadruple excitations, Such a contrast may be due to the restriction of the CI to only the valence orbital space in this investigation or it may be related to the fact that the SCF reference is a poorer zeroth order wavefunction for cyclopropenyl radical than for water, (This can be seen by comparing the first few CI coefficients in a CI singles and doubles calculation).

In addition to the variational results, if CIALL is corrected for the effects of unlinked clusters using the Davidson"s correction ${ }^{21}$ a splitting of $0.55 \mathrm{kcal} / \mathrm{mole}$ is obtained. This result is less than one-half of the straight CIALL difference and maintains the "correct" ordering of the two states. This seems to suggest the validity of employing this correction to all singles and doubles CI energies.

Before closing this section certain features of the CI and MCSCF wave functions should be discussed. In the course of this study it was discovered that even though cyclopropenyl radical is adequately described by one reference, two additional configurations for each of the ${ }^{2} A_{2}$ and ${ }^{2} \mathrm{~B}_{1}$ states are moderately important also. For the ${ }^{2} \mathrm{~A}_{2}$ state these configurations are

$$
\begin{align*}
& \Phi_{2}\left({ }^{2} A_{2}\right)=\ldots 5 a_{1}^{2} 3 b_{2}^{2} 1 b_{1} 6 a_{1}^{2} 2 b_{1} 1 a_{2} \quad\left(1 b_{1}-2 b_{1}\right)  \tag{3}\\
& \Phi_{3}\left({ }^{2} A_{2}\right)=\ldots 5 a_{1}^{2} 3 b_{2}^{2} 1 b_{1}^{0} 6 a_{1}^{2} 2 b_{1}^{2} l a_{2} \quad\left(1 b_{1}^{2} \rightarrow 2 b_{1}^{2}\right) \tag{4}
\end{align*}
$$

while for the ${ }^{2} B_{1}$ state the other two important configurations are

$$
\begin{align*}
& \Phi_{2}\left({ }^{2} \mathrm{~B}_{1}\right)=\ldots 5 a_{1}^{2} 3 \mathrm{~b}_{2}^{2} 1 \mathrm{~b}_{1}^{0} 6 \mathrm{a}_{1}^{2} 2 \mathrm{~b}_{1} 1 \mathrm{a}_{2}^{2} \quad\left(1 \mathrm{~b}_{1}^{2}+1 \mathrm{a}_{2}^{2}\right)  \tag{5}\\
& \Phi_{3}\left({ }^{2} \mathrm{~B}_{1}\right)=\ldots 5 a_{1}^{2} 3 \mathrm{~b}_{2}^{2} 1 \mathrm{~b}_{1} 6 a_{1}^{2} 1 \mathrm{a}_{2}^{2} \cdot\left(1 \mathrm{~b}_{1} 2 \mathrm{~b}_{1}-1 \mathrm{a}_{2}^{2}\right) \tag{6}
\end{align*}
$$

The values of the coefficients of these configurations plus those of the SCF references are compiled in Table II.

In all the CI and MCSCF wavefunctions except MCSD+TQ the principal coefficients were roughly 0,95 , while the absolute values of the other two coefficients are between 0.06 and 0.17 in every case. In the four calculations involving frozen SCF virtual orbitals and in MCSD+TQ, the values of $C_{2}$ are somewhat higher ( $\sim 0.15$ for ${ }^{2} A_{2}$ and $\sim 0.12$ for ${ }^{2} B_{1}$ )
than in the remaining wave functions. Also $C_{3}$ for the $2_{B_{1}}$ state is larger (roughly 0.10 ) compared to the MCSCF values of around 0.08. The two MCSCFs (MC549 and MCSDT) are quite similar in this regard, though the importance of single excitations in the former is far greater. The MCSCF results differ somewhat, however, from MCSD+TQ, which is very similar to the CIs involving the SCF virtual orbitals except that $C_{1}$ for MCSD+TQ is much smaller, being 0.932 and 0.939 in the ${ }^{2} A_{2}$ and $2_{B_{1}}$ cases. The magnitude of $C_{1}$ for MCSD+TQ implies that the MC549 orbitals are a reasonable choice for use in the SDTQ CI expansion and also that the quadruple excitations are relatively important. This can be seen by comparing $C_{1}$ for the MC549, MCSDT and MCSD + TQ theoretical treatments.

Concluding Remarks

For the cyclopropenyl radical it was found at at a representative $D_{3 h}$ geometry an artifical energy splitting of nearly 3 kcal/mole exists for the truly degenerate ${ }^{2} \mathrm{~A}_{2}$ and ${ }^{2} B_{1}$ states at the SCF level of theory. This energy gap can be substantially lessened if subsequent CI calculations are performed. In the case of all single and double excitation CIs the splitting is reduced by over $50 \%$. If these two energies are corrected for unlinked cluster effects ${ }^{21}$ the ${ }^{2} A_{2}-{ }^{2}{ }^{B}{ }_{1}$ difference is only $0.55 \mathrm{kcal} / \mathrm{mole}$.

Significantly improved results are also obtained for valence space MCSCF calculations, In the MCSCF employing all valence single and double excitations, the spurious splitting is roughly
two thirds of the CISD result and only about $1 / 20$ of the number of configurations are needed. If triple excitations are added the gap is reduced still more to around 0.70 kcal/mole. The best results were obtained if the MCSCF orbitals obtained in the valence space singles and doubles procedure
are used in a valence space singles, doubles, triples, and quadruples CI. In this case the ${ }^{2} \mathrm{~A}_{2}-{ }^{2} \mathrm{~B}_{1}$ splitting is found to be only $0.19 \mathrm{kcal} / \mathrm{mole}$ which is nearly 4 times smaller than the MCSDT value.

The value of this research lies in the provision of guidelines for the prediction of electronic energy differences. The errors found here at various levels of theory refer to, in essence, a model problem for which the exact answer is known. Of course one should not take these results too literally, assuming for example that all Davidson corrected CISD excitation energies will lie within 0.55 kcal of the full CI result for the chosen basis set. But it probably is fair to conclude that when relative energy predictions to within less than 0.5 kcal are required, an explicit treatment of triple and quadruple excitations will be necessary.

The present study may be considered preliminary to a definitive theoretical examination of the equilibrium geometries (not $D_{3 h}$, of course) and actual energy separation between the ${ }^{2} A_{2}$ and ${ }^{2} B_{1}$ electronic states of $\mathrm{C}_{3} \mathrm{H}_{3}$. As long as an inherent error of 2-5 kcal in the $D_{3 h}$ energy difference persists (as is found at the SCF level of theory), then one is deprived of real
confidence in the predicted adiabatic separation: the energy difference between the ${ }^{2} A_{2}$ state at its $C_{2 v}$ equilibrium geometry and the ${ }^{2} B_{1}$ state at its equilibrium geometry. The same uncertainty clouds the prediction of the barrier in the three-fold degenerate $\mathrm{C}_{3} \mathrm{H}_{3}$ potential surface, an important question recently explored experimentally by Closs and co-workers. 9 However, the MCSCF and CI techniques explored here for the model $\mathrm{C}_{3} \mathrm{H}_{3}$ problem should provide quite reasonable predictions for both of these important problems.

Acknowledgments

This research was supported by the U.S. National Science Foundation under grant CHE-8009320, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-ACO3-76SF00098.

## References

1. L. C. Snyder, J. Phys. Chem. 66, 2299 (1962).
2. M. Shansal, Z. Naturforsch. 26A, 1336 (1971).
3. T. K. Ha, F. Graf and H. S. Gưnthard, J. Mol. Struct. 15, 335 (1973).
4. G. Cirelli, F. Graf and H. S. Günthard, Chem. Phys. Lett. 28, 494 (1974).
5. N. C. Baird, J. Org. Chem: 40, 624 (1975).
6. J. Pancir and R. Zahradnik, Tetrahedron 32, 2257 (1976).
7. E. R. Davidson and W. T. Borden, J. Chem. Phys. 67, 2191 (1977).
8. D. Poppinger, L. Radom and M. A. Vincent, Cher. Phys. 23, 437 (1977).
9. The unsubstituted cyclopropenyl radical $\mathrm{C}_{3} \mathrm{H}_{3}$ has apparently not been identified in the laboratory to date. However, the C-13 ESR spectrum of the tri-tert-butylcyclopropenyl radical has been observed by K, Schreimer and A. Berndt, Angew. Chem. Int. Ed. Engl. 15, 698 (1976). Very recently the structure and dynamics of the simpler trimethylcyclopropenyl radical have been studied using magnetic resonance techniques by G. L. Closs, W. T. Evanochko, and J. R. Norris, J. Amer. Chem. Soc. 104, 350 (1982).
10. H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A 161 , 220 (1937).
11. R. Manne, Mol. Phys. 24, 935 (1972).
12. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
13. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
14. B. R. Brooks and H. F. Schaefer, J. Chem. Phys. 70, 5092 (1979).
15. B. R. Brooks, W. D. Laidig, P. Saxe, N. C. Handy are H. F. Schaefer, Phys. Scripta 21, 312 (1980).
16. B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard and H. F. Schaefer, in Proceedings of the Conference on the Unitary Group for the Evaluation of Electronic Energy Matrix Flements, edited by Jürgen Hinze (Springer, Berlin, 1980).
17. B. R. Brooks, W. D. Laidig, P. Saxe and H. F. Schaefer, J. Chem. Phys. 72, 3837 (1980).
18. W. D. Laidig and H. F. Schaefer, in Recent Developments and Applications of Multi-Configuration Hartree-Fock Methods, NRCC Proceedings No. 10, edited by M. Dupuis (1981).
19. W. D. Laidig, P. Saxe and H, F. Schaefer, J. Chem.Phys. 73, 1765 (1980).
20. H. F. Schaefer, The Electronic Structure of Atoms and Molecules:

A Survey of Rigorous Quantum Mechanical Results (AddisonWesley, Reading, Mass., 1972).
21. E. R. Davidson, in The World of Quantum Chemistry, editors R. Daudel and B. Pullman, (Reidel, Dordrecht, Holland,1974), p. 17; S. R. Langhoff and E. R. Davidson, Int. J. Quant. Chem. 8, 61 (1974).

## Figure Caption

Assumed geometrical structure of the cyclopropenyl radical, $\left(\therefore H_{3}\right.$. Bond distances are in A .

Table I. Summary of energetic results for the cyclopenyl radical, $\mathrm{C}_{3} \mathrm{H}_{3}$

| Theoretical Method | $\mathrm{A}_{2}$ Symmetry |  | ${ }^{8} 1$ Symmetry |  | Energy Difference$E\left(A_{2}\right)-E\left(B_{1}\right)$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | No. of Configurations | Total Energy (hartrees) | No. of Configurations | Total Energy (hartrees) | hartrees | kcal/mole |
| SCF-DZ | 1 | -115.104667 | 1 | -115.109144 | +0.004477 | 2.81 |
| ST:F-DZ + P | 1 | -115.174127 | 1 | -115.178000 | +0.003873 | 2.43 |
| CI-all orbitals-SD ${ }^{\text {a }}$ | 11800 | -115.387954 | 11829 | -115.389963 | +0.002009 | 1.26 |
| ```CI-all orbitals-SD plus Davidson's Correction``` | 11800 | -115.417994 | 11829 | -115.418878 | +0.000884 | 0.55 |
| CI-18 virtual-SD | 1069 | -115.167098 | 1069 | -115.165587 | -0.001512 | -0.95 |
| ```CI-18 virtual-SD 3 core frozen``` | 549 | -115.166984 | 549 | -115.165484 | -0.001510 | -0.94 |
| MCSCF-18 virtual-SD <br> 3 core frozen | 549 | -115.288770 | 549 | -115.290106 | +0.001336 | 0.84 |
| CI-18 virtual-SDT | 7470 | -115.168311 | 7474 | -115.166563 | -0.001748 | -1.10 |
| MCSCF-18 virtual-SDT | 7470 | -115.2914 | 7474 | -115.29252 | +0.0011 | $\sim 0.70$ |
| $\begin{aligned} & \text { CI-18 virtual-SDTQ } \\ & \text { SCF orbitals } \end{aligned}$ | 60645 | -115.170483 | 60685 | -115.168276 | -0.002207 | -1.38 |
| CI-18 $\quad$ irtual-SDTO MC549 orbitals | 60645 | -115.309306 | 60685 | -115.309002 | -0.000304 | -0.19 |

${ }^{\text {a }}$ Symbols $S, D, T$, and $Q$ represent all single, double, triple and quadruple configurations, respectively.

Table II. Tabulated coefficients for the three most important ${ }^{2} B_{1}$ and ${ }^{2} A_{2}$ configurations appearing in the 549 configuration MCSCF wave functions.

|  |  | SCF | CIALL | CIMIN | CI549 | MC549 | CISDT | MCSDT | CISDTQ | $\underline{M C S D+T O}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{C}_{1}$ | 1.0000 | 0.945 | 0.967 | 0.967 | 0.950 | 0.965 | 0.947 | 0.962 | 0.932 |
| ${ }^{2} \mathrm{~A}_{2}$ | $\mathrm{C}_{2}$ |  | 0.087 | -0.152 | -0.152 | -0.124 | -0.156 | -0.128 | -0.164 | -0.158 |
|  | $\mathrm{C}_{3}$ |  | -0.070 | -0.105 | -0.105 | -0.099 | -0.106 | -0.100 | -0.109 | -0.115 |
| ${ }^{2} \mathrm{~B}_{1}$ | $\mathrm{C}_{1}$ | 1.0000 | 0.947 | 0.973 | 0.973 | 0.953 | 0.972 | 0.951 | 0.969 | 0.939 |
|  | $\mathrm{C}_{2}$ |  | 0.080 | -0.120 | -0.120 | -0.111 | -0.121 | -0.112 | -0.125 | -0.129 |
|  | $\mathrm{C}_{3}$ |  | 0.058 | -0.101 | -0.101 | 0.078 | 0.104 | 0.083 | 0.110 | 0.099 |



Figure 1
XBL823-3664

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720

