The chemical inertness of the polyether Pluracol toward the solution was checked by measuring its effect on the temporal frequencies in stirred solutions. Concentrations of the oscillatory solution differed from the excitable solutions; however, the content and the mechanisms are similar. The oscillatory composition followed the suggestion of Field and Noyes.[10] The addition of the polyether Pluracol did not affect significantly the period of the oscillation, 70 ± 5 s. Although this is not a proof that the polyether is inert in the Belousov–Zhabotinskii reaction, it nevertheless indicates that the interactions are small and the main effect is the change in the viscosity of the solution. It is possible that the change in viscosity affects the rate of diffusion of oxygen from the atmosphere. However, the experiments were performed in a thin layer between two glass plates; hence oxygen diffusion is minimal during the trigger wave experiments.

Quantative comparison of the experimental data and theoretical models of Field and Noyes,[10] Reusser and Field,[11] and Murray[12] indicates large numerical discrepancies. The rate constants are $k_5 = 1 \times 10^{-4}\ \mathrm{M^{-2}\ s^{-1}}$, $k_4 = 4 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$, and $k_2 = 2 \times 10^{9}\ \mathrm{M^{-2}\ s^{-1}}$.[8] The diffusivity can be estimated for the nonviscous solution as $1.8 \times 10^{-5}\ \mathrm{cm^2/s}$.[8] Hence the velocity of propagation is given by Field and Noyes[10] and Murray.[13]

$$v\ (\mathrm{mm/min}) = 509(\mathrm{H^+})^{1/2}(\mathrm{BrO_3^-})^{1/2}$$

In the present investigation $(\mathrm{H^+}) \sim 0.02$ M and $(\mathrm{BrO_3^-}) = 0.05$ M; therefore, the propagation velocity is on the order of $v = 16$ mm/min, an order of magnitude larger than the experimental data. The numerical discrepancy is probably due to uncertainties in the rate constants and the effects of various physical parameters such as the depth of the layer and exposure to oxygen.

The mechanism of Field and Noyes[7-10] essentially consists of three intermediate species, $\mathrm{Br^-}$, $\mathrm{HBrO_2}$, and $\mathrm{Fe^{3+}}$. The orange region in front of the propagating front contains a modest amount of bromide ion which reacts according to

$$\mathrm{BrO_3 + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr} \qquad \text{(R3)}$$

$$\mathrm{HBrO_2 + Br^- + H^+ \rightarrow 2HOBr} \qquad \text{(R2)}$$

The product HOBr is destroyed by the brominating malonic acid, and the bromous acid is maintained at very low steady-state concentration. When the bromide concentration becomes low so reaction R2 is slow, then bromous acid can react with bromate ion to initiate a second sequence of reactions:

$$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O} \qquad \text{(R5)}$$

$$\mathrm{BrO_2\cdot + Fe^{2+} + H^+ \rightarrow HBrO_2 + Fe^{3+}} \qquad \text{(R6)}$$

$$\mathrm{BrO_2\cdot \rightarrow BrO_3^- + HOBr + H^+} \qquad \text{(R4)}$$

Step R5 is the rate-determining step and $\mathrm{HBrO_2}$ is autocatalytically generated as ferroin (red) is rapidly oxidized to ferriin (blue). The bromide ion is consumed therefore triggering the autocatalytic formation of bromous acid. The color change is due to the oxidation of ferroin Fe(II) to ferriin Fe(III) by the radical $\mathrm{BrO_2\cdot}$. In the oxidation band (blue) the ferriin reacts with the bromomalonic acid to form bromide again which in turn inhibits the autocatalytic formation of the bromous acid.

From the present work and previous theoretical and experimental studies it appears that trigger wave propagation is caused by the coupling between the autocatalytic mechanism and diffusion. Field and Noyes[10] verified experimentally that the propagation is proportional to

$$v = k[\mathrm{H^+}]^{1/2}[\mathrm{BrO_3^-}]^{1/2}$$

The present study shows that for given composition and temperature

$$v \propto D^{1/2}$$

Therefore there is good reason to believe that the velocity is given by

$$v = K\{D[\mathrm{H^+}][\mathrm{BrO_3^-}]\}^{1/2}$$

in a qualitative agreement with the theoretical prediction[10-12] based on kinetics–diffusion coupling.

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Theoretical Study of the Optical Absorption and Magnetic Circular Dichroism Spectra of Cyclopropane

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Abstract: Ab initio configuration interaction calculations have been carried out for the absorption and magnetic circular dichroism (MCD) spectra of cyclopropane. Since the MCD was computed to result from the interference of several states, the calculated results were fitted to Gaussian line-shape functions with experimental widths. The resultant calculated spectrum is in good agreement with the observed, although the interpretation afforded by these calculations differs in many respects from that obtained through a moment analysis of the experimental spectrum. The advantages and dangers of the moment analysis approach to the interpretation of MCD spectra are epitomized and discussed.

A. Introduction

Although cyclopropane is the smallest of the cyclic hydrocarbons, it is atypical of the series in that it often behaves more like a conjugated than a saturated molecule. It has long been noted, for instance, that it resembles ethylene in many of its chemical reactions and that its first major ultraviolet absorption band displays a maximum at 7.8 eV, far to the red of most saturated absorbers and in the region of the $\pi \rightarrow \pi^*$ transitions of unsaturated molecules.

This behavior can be rationalized[1] from the observation that its HCH angles are not far from 120°, a fact which implies something approaching $\mathrm{sp^2}$ hybridization at the carbons. Two of these hybrids are directed toward the hydrogens, while the third points into the center of the equilateral triangle forming the so-called "internal" system of in-plane valence orbitals. The remaining p orbital lies perpendicular to both the C_3 axis and the

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[1] C. A. Coulson and W. E. Moffitt, *Phil. Mag.* (*Ser. 7*), **40**, 1 (1949).

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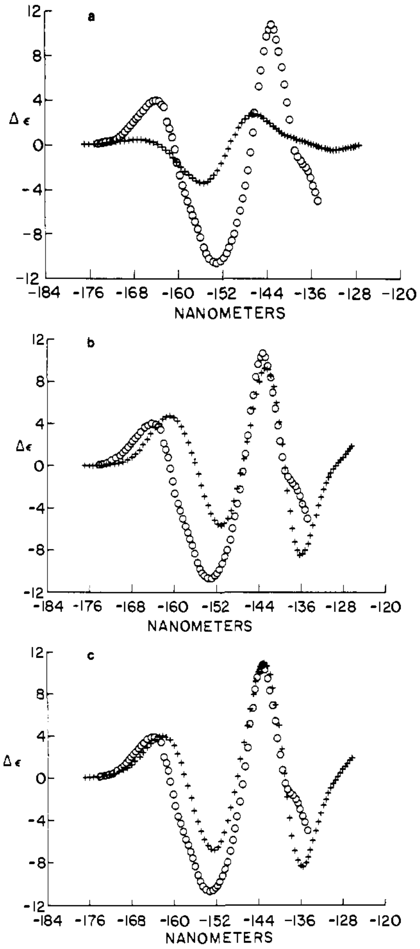

Figure 1. (a) Calculated *A* term contribution to the MCD spectrum of cyclopropane: O, experimental spectrum; +, calculated *A* term contribution. (b) Calculated *B* term contribution to the MCD spectrum of cyclopropane: O, experimental spectrum; +, calculated *B* term contribution. (c) Calculated MCD spectrum of cyclopropane: O, experimental spectrum; +, calculated spectrum.

bisector of the CCC angle, forming an "external" system comprised of orbitals belonging to irreducible representations e′ and a_2' within the D_{3h} point group of the molecule. In this simple valence model, the external e′ orbitals form the HOMO set while the e′ combinations of the internal orbitals are antibonding and form the LUMO set.

As a result of this basic orbital structure, early attempts at the theoretical calculation of the spectrum encountered an extraordinarily dense manifold of electronic states, rendering definite assignment of the absorption spectrum problematical. Thus Basch et al.,[2] using virtual orbitals from SCF calculations, found no less than nine singlet excited states within the lowest computed 3-V absorption region, 11.5–14.8 eV. Early ab initio SCF plus limited CI calculations by Buenker and Peyerimhoff[3] were unable to satisfactorily assign the observed spectrum. Similar difficulties were encountered by Meyer,[4,5] Clark,[6] and Brown and Krishna,[7] using semiempirical methods.

The observed[8,9] absorption spectrum of cyclopropane consists of three broad bands. The first band extends from 60 000 to 66 000 cm^{-1} (7.44–8.18 eV) with a maximum at 63 000 cm^{-1} (7.8 eV) and an observed oscillator strength of 0.12, while the second, extending from 67 000 to 72 000 cm^{-1} (8.3–8.9 eV), displays an oscillator strength of 0.04 and a maximum at 70 000 cm^{-1} (8.68 eV). Finally the third and most intense band ($f = 0.7$) has a maximum at 83 000 cm^{-1} (10.3 eV) and extends over the energy region from 9.2 to 10.5 eV. The first and third of these bands have a discrete structure superimposed on a broad continuous background. The lowest band disappears entirely in the solid-phase spectrum as does the sharp structure on the low-energy side of the third band, confirming the Rydberg character of both the first band and the sharp structure superimposed on the third.[2] A weak band is reported to have been observed at 80 000 cm^{-1} by Sandorfy and seems to correspond to another Rydberg transition.[9]

The bands at 70 000 cm^{-1} (8.7 eV) and 83 000 cm^{-1} (10.3 eV) have been identified by Basch et al. as valence transitions on the basis of the comparison of gas- and condensed-phase spectra;[2] however, the lower energy transition (8.7 eV) may be of either Rydberg or valence character, since the condensed-phase studies on this band are by no means conclusive. Finally, a very weak system composed of 12 sharp bands is observed between 6.56 and 7.1 eV.[8,10] The integrated intensity of this system is about 10^{-4} of the intensity of the strongest other electronic transition, so it is clearly either spin or symmetry forbidden.

A considerable amount of additional information about the excited states of this molecule can be obtained from the magnetic circular dichroism (MCD) spectrum since the ubiquity of degenerate excited states renders cyclopropane a particularly favorable subject for study by this technique. This spectrum has been recorded by Gedanken and Schnepp.[11]

To a reasonable approximation, the dichroism $\Delta\epsilon$ exhibited by a molecule under the influence of a magnetic field for excitation from a nondegenerate ground state A, as in cyclopropane, to an excited state J, is given by[12,13]

$$\frac{\Delta\epsilon}{\nu} = -1.02 \times 10^{-2}(-\mathrm{A}f' + \mathrm{B}f^0)H \tag{1}$$

where

$$A(\mathrm{A} \rightarrow \mathrm{J}) = \tfrac{1}{2}\sum_{\lambda,\lambda'} Im(\langle \mathrm{A}|\bar{m}|\mathrm{J}_\lambda\rangle x \langle \mathrm{J}_{\lambda'}|\bar{m}|\mathrm{A}\rangle \cdot \langle \mathrm{J}_\lambda|\bar{\mu}|\mathrm{J}_{\lambda'}\rangle) \tag{2}$$

$$B(\mathrm{A} \rightarrow \mathrm{J}) = \sum_{\lambda} Im(\sum_{\mathrm{K}_\kappa \neq \mathrm{A}} \langle \mathrm{A}|\bar{m}|\mathrm{J}_\lambda\rangle x \langle \mathrm{J}_\lambda|\bar{m}|\mathrm{K}_\kappa\rangle \cdot \langle \mathrm{K}_\kappa|\bar{\mu}|\mathrm{A}\rangle / \bar{h}\omega_{\mathrm{KA}} + \sum_{\mathrm{K}_\kappa \neq \mathrm{J}} \langle \mathrm{A}|\bar{m}|\mathrm{J}_\lambda\rangle x \langle \mathrm{K}_\kappa|\bar{m}|\mathrm{A}\rangle \cdot \langle \mathrm{J}_\lambda|\bar{\mu}|\mathrm{K}_\kappa\rangle / \bar{h}\omega_{\mathrm{KJ}}) \tag{3}$$

The subscripts λ and κ denote the individual members of the possibly degenerate excited states, $\bar{m}$ is the electric dipole moment, μ the magnetic dipole moment, H the magnetic field, and f^0 is a line-shape function, while f' is its derivative with respect to frequency ν. The coefficient in eq 1 is consistent with units of debyes, Bohr magnetons, gauss, and reciprocal centimeters for these quantities.

The $A(\mathrm{A} \rightarrow \mathrm{J})$ term arises from the first-order Zeeman splitting of the members of a degenerate excited state and vanishes if the excited state possesses no magnetic moment. An important feature of this term is that it appears multiplied by the first derivative of the line-shape function with respect to frequency. The appearance of dispersive line shapes in MCD spectra is therefore diagnostic for a degenerate excited state.

Whereas the *A* term exists only for degenerate states, the *B* term is generally present for all transitions and is due to a second-order Zeeman effect. The *B* term arises from the mixing of excited states with each other through the perturbation of the magnetic field. In eq 3, the infinite sum K_κ runs over all electronic states. As a result of this, unless very few states dominate the

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(13) There is a misprint in ref 12 in that the coefficient 1.02 is given as 1.002. P. J. Stephens, private communication.

mixing process, usually for the reason that they lie very close to each other in energy, theoretical analysis through standard perturbation theory will not be possible.

Fortunately, the first sum in the B term will generally be small relative to A terms due to the denominators ω_{KA}. If, however, other excited states lie close to the state of interest J and are magnetically coupled to it as well as electrically coupled to the ground state, the second term in eq 3 can lead to sizable B terms. This, as we shall see, is certainly the case in cyclopropane.

The observed MCD spectrum in the 175–135-nm region is shown in Figure 1. It exhibits two broad bands, the first of which appears to represent a strong A term centered about 7.87 eV and the second a B term with maximum dichroism at 8.63 eV. A higher resolution study of the first band reveals that troughs in the MCD correspond to peaks in the absorption. There is therefore strong evidence for the existence of two transitions with MCD of opposite sign. Gedanken and Schnepp have fit this entire spectrum by using moment analysis and Gaussian line shapes as the sum of two A and two B terms and attempted assignments on the basis of this two-state analysis.

Moment analysis has been applied to many simple spectra and seems to yield valuable information. When, however, the bands are broad and overlapping as in cyclopropane, problems may arise due to the model dependence of the method. In particular, if all the contributing transitions are not included in the analysis, the method of moments may yield erroneous results,[12] as will be further discussed below.

In this paper we report extensive ab initio configuration interaction calculations directed toward the elucidation of both the absorption and MCD spectra of cyclopropane. In particular, since our results turn out to be somewhat at variance with the simple analysis of the MCD to which Gedanken and Schnepp were necessarily limited, we have attempted the direct reproduction of the experimental MCD spectrum by appending suitable line-shape functions to our calculated results.

B. Computational Details

The geometry of cyclopropane[14] was assumed to be of D_{3h} symmetry with $r_{CC} = 1.5138$ Å, $r_{CH} = 1.0820$ Å, $\angle CCC = 60°$, and $\angle HCH = 116.2°$. In the coordinate system chosen, the origin is at the center of the equilateral triangle and z coincides with the C_3 figure axis.

The AO basis chosen was a (9s,5p) carbon basis contracted to [4s,2p] as defined by Dunning.[15] Dunning's (5s) hydrogen basis contracted to a single function was used with a scale factor of 1.414. A set of s, p, and d single Gaussian functions of exponent 0.02 was placed at the origin of the coordinate system at the center of the molecule, the d set being comprised of six functions. It is therefore to be expected that these calculations should be accurate through $n = 3$ Rydberg states. The SCF orbital energies are given in Table I.

This basis set generates 46 molecular orbitals. Of these, 40 were considered in the configuration interaction calculation. The three carbon 1s molecular orbitals were held as a frozen core and the three highest energy virtual orbitals, their antibonding complement, were ignored.

The configuration interaction calculations, which range up to a CI basis of 32 542 spin eigenfunctions, were carried out by using the perturbational configuration interaction techniques which we have described elsewhere.[16-18] The configuration interaction calculations which we report here were carried out by generating all single- and double-hole-particle excitations of the proper symmetry from up to 10 base configurations belonging to the same irreducible representation.

In these calculations, the 50 dimensional zero-order function comprised about 95% of the modulus squared weight of the wave function. The perturbational correction was therefore about 5% of the total eigenfunction for each state. Since this was so, all requisite matrix elements over the electric and magnetic moment operators were computed by using only the 50-dimensional portion of the wave function, omitting the perturbational tail. It is estimated that this procedure, while obviously cost efficient, will entail no more than a 10% error in our computed values, a level of accuracy fully consistent with the accuracy of the experimental data and other errors in the calculation.

Table I. SCF Results for Cyclopropane[a]

symmetry	eigenvalue, au	$\langle r^2 \rangle$[b]	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
1. $1a_1'$	−11.2247				
2. $1e'$	−11.2237				
3. $1e'$	−11.2237				
4. $2a_1'$	−1.1348				
5. $2e'$	−0.8153				
6. $2e'$	−0.8153				
7. $1a_2''$	−0.6748				
8. $3a_1'$	−0.6192				
9. $1e''$	−0.5122				
10. $1e''$	−0.5122				
11. $3e'$	−0.4135				
12. $3e'$	−0.4135				
13. $4a_1'$	0.02670	94.4	28.8	28.8	36.7
14. $2a_2''$	0.0512	68.9	13.7	13.7	41.6
15. $4e'$	0.0541	72.6	43.3	14.5	14.8
16. $4e'$	0.0541	72.6	14.5	43.3	14.8
17. $5a_1'$	0.0655	87.5	24.6	24.6	38.4
18. $2e''$	0.0702	90.8	38.9	12.9	38.9
19. $2e''$	0.0702	90.8	12.9	38.9	38.9
20. $5e'$	0.0723	91.4	39.1	39.1	13.1
21. $5e'$	0.0723	91.4	39.1	39.1	13.1
22. $6a_1'$	0.1403	59.2	16.4	16.4	26.5
23. $1a_2'$	0.2818	14.7	6.6	6.6	1.5
24. $6e'$	0.2991				
25. $6e'$	0.2991				
26. $7a_1'$	0.4395				
27. $3a_2''$	0.5071				
28. $7e'$	0.5157				
29. $7e'$	0.5157				
30. $3e''$	0.5258				
31. $3e''$	0.5258				
32. $2a_2'$	0.7040				
33. $4a_2''$	0.7397				
34. $8e'$	0.7752				
35. $8e'$	0.7752				
36. $8a_1'$	0.8398				
37. $9e'$	0.8677				
38. $9e'$	0.8677				
39. $9a_1'$	0.9742				
40. $4e''$	1.1643				
41. $4e''$	1.1643				
42. $10e'$	1.3750				
43. $10e'$	1.3750				
44. $10a_1'$	23.7693				
45. $11e'$	24.0074				
46. $11e'$	24.0074				

[a] Total SCF energy: −117.00998 au. [b] In units of au.^{2}

The calculated vertical transition energies and oscillator strengths for the electric-dipole-allowed states of cyclopropane are given in Table II and the detailed nature of all computed states is reported in Table III.

As will be discussed in the next section, these results are at variance with the assignments of the MCD in ref 11, differing principally in that more states are found to be of importance to the MCD than was assumed to be the case by Gedanken and Schnepp. Because more states are found to be of importance and because it is not obvious, on inspection, that the states in Table II will interfere to yield the observed MCD, we have chosen to reconstruct the actual spectrum.

The method of moments was used in the experimental analysis, and a brief discussion of this approach is necessary to an understanding of our results, where the discussion we present is limited to the case of allowed transitions A → J under the as-

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Table II. Comparison of Calculated Results and Experimental Absorption

state	primary excitatn	calcd excitatn energy, eV	f^r	f^∇	$f^{r\cdot\nabla}$	expt
1E′	3e′ → 4a$_1$′	7.61	0.009	0.013	0.011	7.4–8.2, $f = 0.12$
2E′	3e′ → 4e′	8.11	0.127	0.101	0.113	
1A$_2$″	3e′ → 2e″	8.72	0.007	0.001	0.005	8.3–8.9, $f = 0.04$
3E′	3e′ → 5a$_1$′	8.85	0.002	0.001	0.002	
4E′	3e′ → 5e′	9.08	0.002	0.001	0.001	
5E′	3e′ → 6a$_1$′	9.92	0.001	0.004	0.002	weak Rydberg at 9.9 eV, 9.2–10.5, maximum 10.3 valence with Rydberg superimposed, $f = 0.7$
6E′	1e″ → 2a$_2$″	10.56	0.135	0.076	0.102	
2A$_2$″	1e″ → 4e′	10.79	0.072	0.053	0.062	
7E′	3e′ → 1A$_2$′	11.94	0.376	0.244	0.303	

sumption of both the Born–Oppenheimer and Franck–Condon approximations. The reader is referred to ref 12 for a fuller discussion of these matters. Following the notation of Stephens, this method involves the integrated properties of absorption and MCD bands. The nth moment of the molar extinction coefficient ϵ, for a transition A → J, is defined by eq 4, where ν_0 is the origin

$$\langle\epsilon\rangle_n = \int \frac{\epsilon}{\nu}(\nu - \nu_0)^n \, d\nu \tag{4}$$

of the moment expansion of the band. From eq 4, the zeroth moment about ν_0 for absorption is

$$\langle\epsilon\rangle_0 = \int \frac{\epsilon}{\nu} \, d\nu \tag{5}$$

where

$$\frac{\epsilon}{\nu} = 1.089 \times 10^2 D_0 f^0 \tag{6}$$

D_0 is the dipole strength in debyes^2 and frequency is in reciprocal centimeters.

$$D_0 = \sum_\lambda \langle A|\vec{m}|J_\lambda\rangle \cdot \langle J_\lambda|\vec{m}|A\rangle \tag{6a}$$

f^0 is a normalized line-shape function, $\int f^0 \, d\nu = 1$. Equation (5) therefore simplifies to

$$\langle\epsilon\rangle_0 = \int 1.089 \times 10^2 D_0 f^0 \, d\nu = 1.089 \times 10^2 D_0 \tag{7}$$

Similarly, for the MCD band, if $\Delta\epsilon$ is defined as the difference

$$\Delta\epsilon = \epsilon_{\text{left}} - \epsilon_{\text{right}}$$

then

$$\langle\Delta\epsilon\rangle_n = \int \frac{\Delta\epsilon}{\nu}(\nu - \nu^0)^n \, d\nu \tag{8}$$

The zeroth moment in MCD is

$$\langle\Delta\epsilon\rangle_0 = \int \frac{\Delta\epsilon}{\nu} \, d\nu \tag{9}$$

and

$$\langle\Delta\epsilon\rangle_0 = -1.02 \times 10^{-2} B_0 \tag{10}$$

where $B_0(A \rightarrow J)$ is given by eq 3, with units of μ_B debye^2/cm^{-1} where μ_B is the Bohr magneton. The first moment is given by eq 11, where $A_1 = -A(A \rightarrow J)$ as defined in eq 2 and has units

$$\langle\Delta\epsilon\rangle_1 = -1.02 \times 10^{-2}[A_1 + (B_1 - \nu_0 B_0)] \tag{11}$$

of μB debye^2, and

$$B_1(A \rightarrow J) = \sum_{\lambda,\lambda'} Im(b_{\lambda\lambda'} x_{\lambda\lambda'}) \tag{12}$$

where $x_{\lambda\lambda'}$ relates to energy differences between the ground- and excited-state potential energy surfaces. Choosing ν_0 to be the average absorption frequency,[12] eq 11 simplifies to

$$\langle\Delta\epsilon\rangle_1 = -1.02 \times 10^{-2} A_1 \tag{13}$$

Table III. Summary of CI Results for All Calculated States

excited states	main contributions[a]	CI coeff	excitatn energy, eV
1^{3}E′	11 → 13	0.85	7.47
	11 → 22	0.39	
	12 → 15	0.14	
1^{1}E′	11 → 13	0.90	7.61
	11 → 15	0.15	
	12 → 16	0.07	
	11 → 17	0.14	
	11 → 22	0.30	
1^{1}A$_2$′	11 → 15	−0.68	8.07
	12 → 16	0.68	
	11 → 24	0.11	
	12 → 25	−0.11	
1^{1}A$_1$′	11 → 16	0.68	
	12 → 15	0.68	8.08
	11 → 25	0.09	
	12 → 24	−0.09	
2E′	12 → 13	−0.19	8.11
	11 → 16	0.66	
	12 → 15	−0.66	
	12 → 17	−0.08	
1A$_2$″	11 → 19	0.68	8.72
	12 → 18	0.68	
1A$_1$″	12 → 19	0.67	8.79
	11 → 18	0.67	
3E′	12 → 13	0.12	8.85
	12 → 17	0.95	
	12 → 22	0.10	
1E″	11 → 19	−0.68	8.96
	12 → 18	0.68	
4E′	11 → 20	−0.69	9.08
	12 → 21	0.69	
2A$_2$′	11 → 21	−0.69	9.09
	12 → 20	0.69	
2A$_1$′	11 → 20	0.69	9.19
	12 → 21	0.69	
5E′	11 → 13	0.34	9.92
	11 → 17	0.18	
	11 → 22	−0.88	
6E′	10 → 14	0.97	10.56
	12 → 23	0.13	
2A$_2$″	9 → 15	−0.63	10.79
	10 → 16	0.63	
	11 → 19	0.30	
	12 → 18	0.30	
2E″	9 → 16	0.70	10.62
	10 → 16	0.70	
7E′	12 → 23	0.64	11.94
	10 → 14	−0.19	
	9 → 19	−0.50	
	10 → 18	0.50	
	11 → 24	0.12	
	12 → 25	0.12	

[a] Only one of two vectors given for degenerate states.

The experimentally determined moments, $\langle\Delta\epsilon\rangle$, were used by Gedanken and Schnepp to find the ratios

$$A_1/D_0 = -1.072 \times 10^4(\langle\Delta\epsilon\rangle_1/\langle\epsilon\rangle_0) \tag{14}$$

$$B_0/D_0 = -1.072 \times 10^4(\langle\Delta\epsilon\rangle_0/\langle\epsilon\rangle_0) \tag{15}$$

Table IV. Calculated MCD

	$-A_1/D_0$[a]	eigenvalue	10^4B_0[b]	D_0[c]	$-A_1$[d]
1E′	0.573	7.61	2.8	0.309	0.177
2E′	−0.172	8.11	−2.4	3.890	−0.670
$1A_2''$		8.72	5.3	0.050	
3E′	0.582	8.85	−3.8	0.067	0.039
4E′	0.100	9.08	−1.1	0.066	0.007
5E′	0.618	9.92	−0.8	0.068	0.042

[a] $-A_1/D_0$ is the calculated value of $-\frac{1}{2}\langle\psi_y|(\bar{r} \times \bar{\nabla})_z|\psi_x\rangle$. [b] μ_B debye^2/cm^{-1}. [c] Debye.^{2} [d] μ_B debye.^{2}

which were then related to theoretically evaluable quantities through eq 2 and 3.

In particular, from eq 2, the magnetic moment of an excited state J is given by eq 16, and these quantities were extracted on the basis of the moment analysis of the experimental spectrum.

$$A_1/D_0 = -\tfrac{1}{2}\sum_{\lambda,\lambda'} Im(\langle J_\lambda|\bar{m}|J_{\lambda'}\rangle) \tag{16}$$

We have computed values for the A_1 and B_0 terms through eq 2 and 3, utilizing calculated wave functions and energies. The results are reported in Table IV, and details of the B_0 calculations are given in Table V. As previously mentioned, we have limited ourselves to the 50-dimensional portion of the wave function, omitting the perturbational tail in evaluating all matrix elements.

The evaluation of the A term is straightforward and requires no further comment. The B term, eq 3, however, involves an infinite sum over states and is made up of two sums, one involving the denominator W_{KA} and the other, W_{KJ}. The first sum in eq 3 will have value for any excited state J to which transition from the ground state is electric dipole allowed, A_2'' or E′ in cyclopropane, interacting with excited states K which are electrically coupled to J and magnetically coupled to the ground state. This summation was found to be small in all cases, principally because the denominator involves energy differences of more than 8 eV as displayed in Table III. For example, the magnetic-dipole-allowed E″(*xz*,*yz*) states must be considered in the first sum. Coupling via the electric dipole field with the E′ state is allowed:

$$\langle A_1'|\bar{m}|E'\rangle x\langle E'|\bar{m}|E''\rangle\cdot\langle E''|\bar{\mu}|A_1'\rangle/h\omega_{E''A_1'}$$

When matrix elements of this type are calculated, they are found to be nearly 2 orders of magnitude smaller than those of the second summation in the B term. They have therefore been treated as negligible and omitted from the calculation.

The second summation in eq 3 links A_2'' excited states with E′ states and E′ states among themselves. Our calculations (Table III) lead to the conclusion that the denominators W_{KJ} are frequently very small in cases where the numerators are of reasonable magnitude. These interactions are given in Table V and, as can be seen from Figure 1, lead to B term contributions to the MCD which dominate the A terms. We have therefore assumed that the extreme density of excited states over a narrow energy range which is found in cyclopropane renders this molecule a particularly favorable case for the truncation of the infinite summations of eq 3 to a finite set of terms. The states included are listed in Table V. Under these circumstances, the computed B terms obey, within this subset of states, the sum rule that B terms sum to zero.

It has been pointed out by Seamans and Moscowitz[19] that if the infinite summation in eq 3 is not fully carried out, the B terms may be origin dependent in molecules belonging to certain point groups. Fortunately, D_{3h} is not one of these, and our results are origin invariant.

The line shapes f' and f^0 were described by Gaussians, equations (17) and (18) with $\int f^0{}_G\, d\nu = 1$ and $\int f'{}_G\nu\, d\nu = -1$.

$$f^0{}_G = \frac{1}{\pi^{1/2}\Delta}\exp[-(\nu-\nu_0)^2/\Delta^2] \tag{17}$$

$$f'{}_G = [2(\nu_0-\nu)/\pi^{1/2}\Delta^3]\exp[-(\nu-\nu_0)^2/\Delta^2] \tag{18}$$

Although each state should have a different width, these are unknown. The band widths, Δ, were therefore taken to be those found by Gedanken and Schnepp for the 157.5- and 144.5-bands, 3270 and 2000 cm^{-1}, respectively, so that the calculated B and A terms were fitted to the line-shape factors given by eq 17 and 18 with 1E′ and 2E′ having a width of 3270 cm^{-1} and all others having a width of 2000 cm^{-1}.

The resultant terms were then summed at each frequency and the spectrum plotted. The computed MCD is given in Figure 1. It must be emphasized, however, that these plots involve interference between terms and are sensitive to the assumptions made as to line widths and transition frequencies. The figures displayed, which use computed frequencies and the probably improper widths just described, are close to an optimal fit to experiment, given our calculated matrix elements. The width of each contributing state should certainly be an independent parameter in computing the MCD, but we have chosen not to attempt to optimize the fit since it is clear that our computations yield the experimental curve for the first two bands.

C. Discussion of Results

The calculations reported here find the first optical absorption band in cyclopropane to be made up of two states, 1E′ and 2E′, excitations to the 3s and $3p_{x,y}$ Rydberg orbitals, respectively. The calculated oscillator strength to the 3s Rydberg (0.009) is 1 order of magnitude smaller than that to the 3p Rydberg (0.127), while the latter is in good agreement with the experimentally observed value. We therefore conclude that the 3s Rydberg state is not resolved in absorption in the vicinity of the calculated vertical excitation energy, 7.61 eV, because it is obscured by the broad and strongly absorbing 2E′ transition. The entire band vanishes in condensed-phase spectra[2] and may therefore be taken to be of Rydberg character. This is in agreement with our assignment as is the observation of Gedanken and Schnepp that the peaks in absorption correspond to minima in the MCD under higher resolution. The computed radial extents of the excited electrons are summarized in Table I.

The first MCD band requires more discussion, for this is fundamentally a case of two B terms, one from each state, masquerading as an A term or, alternatively, two distinct MCD bands which appear to be one. This is a situation mentioned by Stephens[12] as particularly favorable for the detection of a weak transition under a strong band, but it results in the breakdown of the entire moment analysis procedure if the pseudo-A term is not recognized and the MCD is considered to be due to a single excitation to a degenerate state.

From all appearances (Figure 1), this band represents a classic A term, i.e., a dispersive line shape, which is skewed to shorter wavelengths by the perturbation of a B term. Gedanken and Schnepp, reasonably assuming this to represent a single transition, carried out a moment analysis decomposition about a ν_0 of 7.87 eV, close to the absorption maximum, and found $B_0 = -6.1 \times 10^{-4}$ and $A_1 = -2.22$. When fitted to the same Gaussian line shapes used by us, this led to A and B contributions of roughly equal magnitudes and a reasonable fit to the MCD band. The reader is referred to ref 11 for the details of this procedure, but it led to the conclusion that the excited state has a magnetic moment of 0.53 μ_B.

Examination of Figure 1, however, will show that our calculations lead to the conclusion that the lowest frequency positive peak of this apparent A term is due to the B term of the 3e′ → 3s transition (our 1E′) and that the A term from this state is very small. The source of the size of the A term is, of course, the fact that D_0 is small; this is a weak optical transition. These numbers lead to a value of $-A_1/D_0 = 0.573\ \mu_B$ in fortuitous but meaningless agreement with the value of 0.53 obtained by Gedanken and Schnepp for the upper-state magnetic moment. The 1E′ state is calculated to have a relatively large magnetic moment, but its product with a weak electric dipole oscillator strength produces a small A term.

The 2E′ (3e′ → 3p) transition displays a calculated oscillator strength of 0.127, in good agreement with experiment for this band. Although the magnetic moment of the excited state is smaller than

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(19) L. Seamans and A. Moscowitz, *J. Chem. Phys.*, **56**, 1099 (1972).
(20) O. Schnepp, private communication.

Table V. *B*-Term Components (μ_B debyes^2/cm^{-1})

	1E′, 7.61 eV	2E′, 8.11 eV	1A_2″, 8.72 eV	3E′, 8.85 eV	4E′, 9.08 eV	5E′, 9.92 eV
1E′	. . .	2.8×10^{-4}	0.0	0.0	0.0	0.0
2E′	-2.8×10^{-4}	. . .	0.0	0.3×10^{-4}	0.8×10^{-5}	0.0
1A_2″	0.0	0.0	. . .	3.6×10^{-4}	0.9×10^{-4}	0.8×10^{-4}
3E′	0.0	-0.3×10^{-4}	-3.6×10^{-4}	. . .	0.1×10^{-4}	0.0
4E′	0.0	-0.8×10^{-5}	-0.9×10^{-4}	-0.1×10^{-4}	. . .	0.0
5E′	0.0	0.0	-0.8×10^{-4}	0.0	0.0	. . .

that for the 3s Rydberg state, this leads to a more significant *A* term (−A = 0.670) but to one centered at 8.11 eV (153 nm).

Table V shows that the *B* term due to the 1E′ transition is dominated by its interaction with the 2E′ state and that the inverse is true for the 2E′ state. This is reasonable in that these two states lie relatively close in energy (as will be common for 3s and 3p Rydberg states in polyatomic molecules) and the product of the two electric dipole matrix elements (eq 3) results in compensating effects.

In the situation where the *B* terms are effectively due to the interaction of two close lying states, they will be of equal magnitude but opposite in sign (Table IV). The result of the superposition of these two terms, fitted to line shapes and using the same width for each state, can be seen in Figure 1b which displays only the *B* term contribution to the MCD. It is qualitatively indistinguishable from an *A* term. The negative lobe of the *A* term from 2E′ is of the same sign as the *B* term for this transition, a situation which results in the apparent skewed *A* term displayed in Figure 1c.

Proper moment analysis of this MCD band, therefore, would require the decomposition of these two overlapping bands with the use of two different values of ν_0 corresponding to the average absorption frequency of the 1E′ and 2E′ states, respectively. This is not a unique decomposition in absorption, and cannot, in fact, be done, but our argument leads to the conclusion that ν_0 (1E′) should be at about 165.5 nm (7.49 eV), the maximum of the first experimental MCD peak, while that for the 2E′ state would be at about the absorption maximum, the value used by Gedanken and Schnepp.

The optical absorption maximum for the unresolved 3s Rydberg state may therefore be taken to lie at about 7.5 eV. Robin and Kuebler[10] have recently reported a multiphoton ionization study of cyclopropane and conclude that the extremely weak system of 12 sharp bands in the 51 000–56 000-cm^{-1} region (6.32–6.94 eV) is due to the 3e′ → 3s (1E′) Rydberg transition under the influence of a Jahn–Teller distortion in the excited state. Our results support this assignment.

In order to rule out the possibility that these bands are due to the lowest cyclopropane triplet, we have carried out a calculation of the vertical excitation energy to this state, 1^3E′, and find it to be close to the singlet at 7.47 eV. The only experimental evidence on the location of this state is the trapped electron spectrum obtained by Brongersma,[21] who found a shift in the maximum of the first band from 7.8 eV in the optical absorption spectrum to 7.4 eV in electron scattering. If this is taken to be due to a predominance of scattering from the triplet state as suggested by Robin,[9] our computed energy is in good agreement. In any case, it would seem that the singlet–triplet splitting is small and that the long wavelength band system is unlikely to be due to lowest triplet state in cyclopropane.

On the other hand, Buenker and Peyerimhoff[3] have studied the variation of energy of the excited states of cyclopropane with bond angle and find that distortion to C_{2v} symmetry in this way results in a rapid drop in the energy of both members of the 1^1E′ state, a result consistent with a vibronically induced shift of the order of 1 eV in the 3s Rydberg state due to Jahn–Teller splitting. Our present calculations have been limited to the D_{3h} symmetry point on the cyclopropane electronic energy surface, and further calculations on the 1^1E′ and 2^1E′ states at other geometries are clearly indicated both to study the Jahn–Teller distortion which is to be expected and to evaluate the effect of these splittings on the MCD. It would appear, however, that our description of the 7.8-eV absorption and its MCD is consistent with the interpretation of the multiphoton ionization spectrum.

The positive ion in which the *n*s Rydberg series terminates will undergo a Jahn–Teller distortion similar to that experienced by the 3s (1^1E′) state. Robin and Kuebler have argued[10] that the adiabatic ionization potential of cyclopropane is 9.75 eV so that the term value of the 6.32-eV transition is 3.43 eV. This term value is consistent with that for the 3s Rydberg transition in other C_3 hydrocarbons. The vertical ionization potential of cyclopropane is 10.53 eV.[2] If one assumes that the difference between the vertical and adiabatic (Jahn–Teller distorted) energies of the 3s Rydberg state is that of the ion, 0.78 eV, one is led to the conclusion that the vertical energy of the 3s Rydberg state should be approximately 7.1 eV. On the other hand, the first weak band in single photon absorption falls at 6.58 eV. The same argument using this origin would lead to a vertical energy of 7.36 eV. Given the uncertainties in this argument, it can reasonably be concluded that the two-photon absorption spectrum represents transitions to the lower vibrational levels of the Jahn–Teller distorted 3s Rydberg state, especially since this series merges at higher energy with much stronger absorption from the 2^1E′ state which finally obscures it. The maximum in the MCD, which is primarily due to the *B* term, lies at the vertical transition energy, 7.49 eV, *B* terms being due to the mixing of states under the influence of the magnetic field.

The second principal optical absorption band in cyclopropane extends from 8.3 to 8.9 eV (f = 0.04). This oscillator strength is consistent with Rydberg character, but the band seems to persist in the condensed-phase spectrum[2] as would be expected if it had some valence character. The third optical absorption band, however, is significantly broadened and red-shifted in the condensed phase and examination of this spectrum, as noted by Robin,[9] is inconclusive as to the nature of the second band. It is possible that one of the states contributing to the third band is red-shifted into this region in the polycrystalline film.

We calculate three dipole-allowed singlet states in this region, 1A_2″, 3E′, and 4E′, all of which are of approximate 3d Rydberg character (Table I). The principal oscillator strength is carried by the 1A_2″ state (f = 0.007), but the total oscillator strength calculated for the three states taken together is only 0.011. The source of this discrepancy between experiment and calculation is unclear, but this is a reasonably broad, unstructured absorption band and some vibronic borrowing may take place from the much more intensely absorbing transitions of the first and third bands. On the other hand, our Gaussian orbital basis set may be insufficient to properly describe these states although this is less likely in our view. In any case, there is order of magnitude agreement between calculation and experiment as to the overall oscillator strength attributable to this band.

The MCD of this band is well reproduced by our calculation (Figure 1c). The 1A_2″ gives rise to a large positive *B* term, primarily through its interaction with the 3E′ state which is calculated to lie only 0.15 eV away. As Figure 1b shows, this accounts for essentially all the MCD of the second band, in agreement with the moment analysis of Gedanken and Schnepp, who find a B_0 value of 5.3×10^{-4}, a number in exact agreement with the computed B_0. In view of the disparity between the calculated and observed oscillator strength and considerable interference between this state and the 3E′ and 4E′ transitions, this agreement must be viewed as fortuitous. Our computed value of $-A_1$ for the 3E′ and 4E′ states taken together is 0.046 while

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[21] H. H. Brongersma and L. J. Oosterhoff, *Chem. Phys. Lett.*, 3, 437 (1969).

the experimental value is 0.086, a small *A* term. Since the principal optical absorption intensity and hence D_0 for this band seems to be due to a different state ($1A_2''$) than that leading to the value of A_1 ($3E'$), the experimentally determined value of $-A_1/D_0$, 0.05 μ_B, must be viewed with suspicion. The moment analysis procedure is apt to be breaking down here in a manner similar to that found for the first band in this molecule.

The third optical absorption band in cyclopropane is the most intense transition of all, $f = 0.7$. It displays a maximum at 10.3 eV, and some superimposed Rydberg structure to low frequencies. The principal transition usually has been assigned to the transition $3e' \rightarrow 1a_2'$, but all theoretical values for the energy of this state have been 2–3 eV higher than experimental values. No MCD data exist this far into the vacuum ultraviolet.

Our computations find three optically allowed states in this region, $6E'$ ($1e'' \rightarrow 2a_2''$), $2A_2''$ ($1e'' \rightarrow 4e'$), and $7E'$ ($3e' \rightarrow 1a_2'$, $1e'' \rightarrow 2e''$) at 10.56, 10.79, and 11.94 eV, respectively. The first of these is a transition to the $3p_z$ Rydberg state with a large oscillator strength ($f = 0.135$), while the second also has considerable Rydberg character and a computed oscillator strength of 0.072. The principal valence transition, $7E'$, with an oscillator strength of 0.376 is found at 11.94 eV.

Our results are thus somewhat at variance with experiment for this band, since our total computed oscillator strength in this region is 0.2 whereas the experimental value is 0.7. Our calculations lead us to assign the third band as due to transitions to the $6E'$ and $2A_2''$ states with considerable configurational mixing between the $6E'$ (Rydberg) and $7E'$ (valence) elementary configurations.

This absorption band lies at rather high energies, and it is probable that the situation is complicated by the interaction of the states mentioned with Rydberg states of higher principal qunatum number since the first ionization potential lies within the band and near to the absorption maximum. Examination of this question would require a larger Gaussian orbital basis set than that used here. Since no MCD data exist and we are in order of magnitude agreement with the experimental oscillator strength, we have not chosen to pursue the matter further. In view of this limitation, our results on the third band should be viewed as tentative; however, it does seem clear that this band cannot be assigned to the ($3e' \rightarrow 1a_2'$) transition in any simple fashion.

D. Conclusions

As described in the first section of this report, cyclopropane exhibits both a large number of degenerate electronic energy levels and an unusually high density of electronic states in the energy region between the onset of optical absorption and the first ionization potential. The D_{3h} point group of the molecule implies that only transitions from the ground state to the A_2'' and E' members of the excited electronic state manifold will be electric dipole allowed. The extensive configuration interaction calculations which we have carried out lead to the conclusion that eight states, six E' and two A_2'', are involved in the first three absorption bands.

The assignments of the absorption and MCD spectra which these calculations afford seem convincing in view of the extensive agreement with the available experimental data, particularly for the first two bands, and the extent of coincidence between experiment and the ab initio calculation of the MCD spectrum is gratifying.

Since the calculations which we present lead to an interpretation of the MCD which is strongly at variance with that afforded by moment analysis of the experimental spectrum and since cyclopropane, while complex, is not atypical of other polyatomic molecules, one is led to the conclusion that the interpretation of MCD spectra under the assumption that a single electronic state is responsible for each band is fraught with danger. States which are undetectably weak in optical absorption may lead to a strong MCD band, and situations like the interaction between the 3s and $3p_{x,y}$ ($1E'$ and $2E'$) Rydberg states in cyclopropane will often be encountered.

This danger is of course the obverse of the power of MCD spectroscopy to generate new and unique information about molecular excited states. Coupled with calculations of sufficient quality as to provide dependable guidance, MCD spectroscopy is a valuable source of information about the electronic states of polyatomic molecules. In the case of cyclopropane, we have argued that the first MCD band consists of two *B* terms masquerading as an *A* term, an interpretation which leads to the conclusion that the vertical excitation energy of the previously unobserved but much discussed 3s Rydberg state is 7.49 eV.

Finally, the perturbational configuration interaction approach which we have used in these calculations, while quite economical, would appear to be sufficiently accurate as to allow the ab initio calculations of the MCD of a molecule like cyclopropane as well as the assignment of its absorption spectrum.

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Triplet Methylnitrene: An Indefinitely Stable Species in the Absence of Collisions

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Abstract: The isomerizations of triplet and singlet CH_3–N to CH_2–NH have been studied by molecular electronic structure theory. Stationary point geometrical structures have been determined and characterized (by their harmonic vibrational frequencies) at the double ζ basis set self-consistent field level of theory. At these geometries, correlation effects have been explicitly evaluated by using a basis set expanded to include polarization functions. The triplet CH_3N isomerization to methylenimine is predicted to be endothermic by 18 kcal, with an activation energy of 48 kcal. It may be concluded that ground-state methylnitrene is a relatively stable species in the absence of collisions. However, singlet $CH_2{=}NH$ lies 46 kcal below $^3A_2$ CH_3N and might be accessible if the spin–orbit coupling were substantial. There appears to be little or no barrier separating ^1E CH_3N from ground state $CH_2{=}NH$.

In many ways the reactions of nitrenes parallel those of carbenes.[1] However at present nitrenes must be considered a much less completely characterized class of free radicals. In fact, nitrene rearrangements are so rapid that it is often difficult to exclude