compact mass. The α-form is frequently obtained when a solution of europous chloride from a zinc reductor is run into a solution of magnesium sulfate or dilute sulfuric acid. It soon passes into the stable β-form. The latter is but slightly soluble in 3 *N* sulfuric acid, while the former is dissolved by acid of this concentration. The analyses quoted were of the β-form.

The dry β-form keeps surprisingly well. In one case a sample, kept in a corked vial, showed the same permanganate titer after two, sixteen and fifty-five days and but 2.8% less after one hundred and forty-three days. Another sample, known to contain some rare-earth contamination, showed a purity of 94.7% after sixty-four days. The resistance of europous sulfate to oxidation by air is doubtless in large measure due to its marked insolubility.

Europous sulfate can be oxidized by and dissolved in nitric acid.[4,5] It can also be oxidized by chlorine, bromine, bromic acid and other active oxidizing agents. When europous sulfate is boiled for a few minutes with a solution of one equivalent of sodium carbonate and 0.4 equivalent of sodium hydroxide it forms a yellow, compact, easily filtered carbonate (probably $EuCO_3$). The carbonate dissolves readily in most acids.

The Absorption Spectrum of Europous Chloride.—The chloride ($EuCl_2$) solution of 20 to 30% concentration has a greenish yellow color like that of a concentrated solution of chlorine. The absorption spectrum of this solution, in the visible range, differs in a remarkable way from one of the trichloride. It does not show any of the several bands of the latter.[8] Instead, below approximately 4480 Å. all visible light is absorbed. The exact maximum wave length at which complete absorption begins depends upon the concentration of the solution and the thickness of the layer. Characteristic results are obtained when 30 ml. of a 1.2 molar solution of europium trichloride is run through a zinc reductor and viewed in a 20-cm. tube. The spectrometer used was a Bausch and Lomb instrument Cat. no. 2700. The light was that of a 75-watt Mazda bulb. It thus appears that the shift of the valence electron in the change $Eu^{+++} \rightleftharpoons Eu^{++}$ is responsible for a profound change in the absorption spectrum.

Summary

1. New methods permit the electrolytic reduction of trivalent europium to bivalent in simple cells at 6 volts or less.

2. Solutions of bivalent europium do not show any of the bands of the absorption spectrum of the trivalent salts; instead, complete absorption of visible light occurs below 4480 Å.

3. The reduction potential E_0 of Eu^{++}, Eu^{+++} solutions is approximately 0.43 volt.

4. Dilute europous solutions are half oxidized by a rapid stream of air bubbles in about four minutes. Crystalline europous sulfate, $EuSO_4$, is quite stable in air.

5. Iodometric methods for the determination of europium are described.

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[8] If incompletely reduced the two strongest bands of Eu^{+++} may show faintly.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 368, AND THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 141]

The Vibrational Levels of Cyclopropane

BY GILBERT W. KING,[1] ROBERT T. ARMSTRONG AND LOUIS HARRIS

Cyclopropane has considerable interest stereochemically and from the point of view of the mechanics of vibration of polyatomic molecules. A unique assignment of frequencies to its normal vibrations is not possible from its Raman spectrum[2] alone; infra-red data, even of a semi-quantitative nature, would aid in such an assignment. Together, the two spectra permit an analysis of the fundamental modes of vibration of cyclopropane.

Infra-red Absorption.—The preparation and purification of the cyclopropane has been described in a previous paper.[3] The infra-red spectrum has been mapped in the following manner.

Region	Method of measurement	State of cyclopropane
I. 0.8 μ to 2.8 μ	Quartz monochromator. 1000 watt projection lamp. 15 mm. length quartz cell.	Liquid at −78°. Gas at 25° and 1 atm. pressure.
II. 0.8 μ to 1.1 μ	Hilger E1 spectrograph (Glass optics); also 21 ft. grating. 1000 watt projection lamp. 1 meter length cell, quartz windows.	Gas at 25° and 1 atm. pressure.

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[1] Present address, National Research Fellow, California Institute of Technology.

[2] L. Harris, A. A. Ashdown and R. T. Armstrong, THIS JOURNAL, **58**, 852 (1936).

[3] A. A. Ashdown, L. Harris and R. T. Armstrong, *ibid.*, **58**, 850 (1936).

Region	Method of measurement	State of cyclopropane
III. 3.3 μ to 10.0 μ	Low dispersion rock salt spectrometer. Nernst glower. 10 cm. length cell. Rock salt windows.	Gas at 25° and 10 mm. to 1 atm. pressure.

The observed infra-red bands and Raman frequencies (previously reported) are presented in Table I.

TABLE I

THE RAMAN AND INFRA-RED ABSORPTION SPECTRA OF CYCLOPROPANE

Raman (liquid) Cm.$^{-1}$	Intensity	Infra-red (gas) Cm.$^{-1}$	Intensity	Infra-red (liquid) Cm.$^{-1}$	Intensity
382	v. w.				
745	w.				
869	v. s.				
1022	m.	1020 ± 10	s.		
1191[a]	v. s.				
1437	m.	1425 ± 20	m.		
1454	m.				
1505	w.				
1873	v. w.	1800 ± 40	m.		
		2020 ± 40	m.		
2856	w.				
2953	w.	2950 ± 100	m.		
3013	m.				
3030	m.				
3079	m.				
		3580 ± 1%	m.		
		4200	m.		
		4450	s.		
				4760 ± 1%	m.
				4980	s.
		5160	w.	5130	s.
		5260	w.		
				5620	w.
		5950	s.	5930	s.
				6730	m.
		7040	m.	7090	m.
				7350	m.
				8060	w.
		9070 ± 0.2%	m.	9070	s.
				11,100	m.
		11,490 ± 0.2%	m.	11,800	w.

[a] 1191 cm.$^{-1}$ was the only Raman line observed from gas.

Selection Rules.—The symmetry of the molecule may be decided definitely from qualitative considerations. The manner of distribution of the twenty-one ($3N - 6$) fundamental frequencies of cyclopropane among the representations of the most likely symmetry groups is given in the following table, together with their infra-red (IR) or Raman (R) activity.

C_{3v}	C_{2v}	D_{3h}
R, IR, A_1 5	R, IR, A_1 7	R, A_1' 3
A_2 2	R, A_2 4	A_2' 1
R, IR, E 7	R, IR, B_1 5	A_1'' 1
	R, IR, B_2 5	IR, A_2'' 2
		R, IR, E' 4
		R, E'' 3

C_{3v}.—This symmetry group requires twelve frequencies (seven of the twelve being doubly degenerate) active in both the Raman and infra-red spectra, which is not in agreement with our data.

C_{2v}.—This requires seventeen frequencies active in the infra-red, all of them also active in the Raman spectrum, totaling twenty-one different active fundamentals in the latter spectrum, again not in agreement with observation.

Furthermore, of the three groups given, C_{3v} and C_{2v} require strong Raman frequencies (the totally symmetrical A_1) to be active also in the infra-red. No absorption was detected in the region corresponding to the strongest Raman frequency, 1191 cm.$^{-1}$ (absorption was less than 5% with cyclopropane at one atmosphere pressure in a cell with an effective length of 10 cm.), so that these two symmetry groups are not further considered.

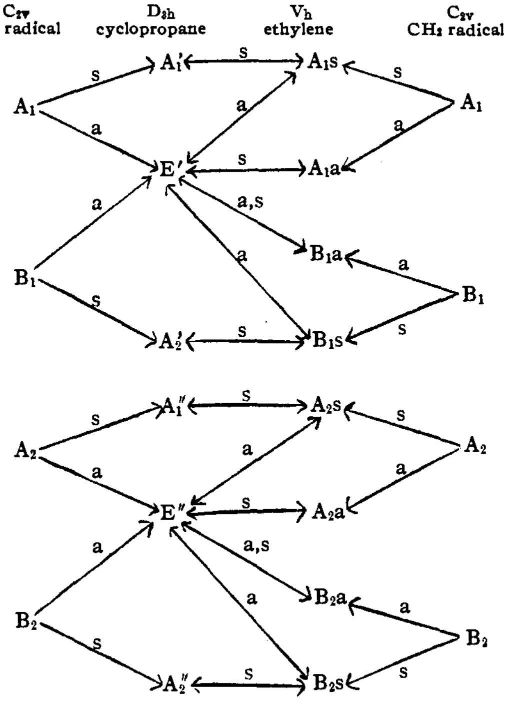
D_{3h}.—This requires six (four doubly degenerate) infra-red active fundamentals, and ten (seven doubly degenerate) Raman active frequencies, which is more compatible with the data. These frequencies may be identified by the following semi-quantitative considerations, pending exact perturbation calculations.

Symmetry Coördinates.—In general there is a correspondence of the representations of a symmetry group of a system and the representations of the symmetry groups of parts of the system, or system under perturbation. If all equivalent bonding energies are permitted to decrease simultaneously (*e. g.*, allow the three CH_2 groups to recede to a large distance yet preserve their geometrical relations) the symmetry of the (enlarged) molecule is unchanged. In the enlarged molecule the normal vibrations are such combinations of the nine orthogonal motions of the isolated radical CH_2 (3 vibrations, 3 rotations, 3 translations) as conform to the symmetry of the group D_{3h}. The fact that the symmetry operators of the combined system (C_3H_6), for example rotation through 120°, must carry any vibration of the enlarged molecule into a linear combination of the vibrations of the same level, indicates that the three isolated CH_2

groups must be vibrating in the same mode, all either in phase (s) or one of the three groups out of phase (a). A more accurate statement concerning the composition of systems from radicals is provided by the resolution of representations into those of component radicals. Table II correlates the representations of CH_2, ethylene and cyclopropane.

TABLE II

CORRELATION OF THE REPRESENTATIONS OF THE SYMMETRY GROUPS OF CYCLOPROPANE, ETHYLENE AND THE CH_2 RADICAL WITH CORRESPONDING RELATIONS FOR THE NORMAL VIBRATIONS



The corresponding relations hold for the actual vibrational states belonging to the various representations. These are described by vector models for CH_2 and $(CH_2)_3$ in Fig. 1.

Figure 1 illustrates the use of the above principles in determining the normal vibrations of cyclopropane from those of its component radicals, 3CH_2's. The nine (3 N) normal vibrations of a non-linear tri-atomic molecule (translations, T_z, T_h and $T_\perp$, and rotations, R_z, R_h and $R_\perp$, may be regarded as vibrations of zero frequency) are described by vector models in the center column of Fig. 1. These vibrations are perturbed by the coupling action of the other two CH_2 groups and each frequency (including the translations and rotations) combines anti-symmetrically (doubly degenerate, a-levels) or symmetrically (s-levels) to give the vibrations of cyclopropane as shown on the left and right of the figure, respectively. Similarly the vibrational levels of the symmetrical triangular C_3 molecule (Group D_{3h}), or of a constrained cyclopropane molecule, where the CH_2 groups are rigid, may be resolved into the levels of the actual cyclopropane molecule.

Assignment of Observed Frequencies to Normal Modes of Vibration

a. Carbon Interaction: (T_{zs} and $T_{\perp a}$).—Calculations based on central forces[4,5] of the frequencies of the constrained cyclopropane molecule identify the intense symmetrical vibration (labeled T_{zs} in Fig. 1) at 1191 cm.$^{-1}$ (properly inactive in the infra-red) and a doubly degenerate deformation frequency at 869 cm.$^{-1}$ (labeled $T_{\perp a}$ from its construction from CH_2 levels). The latter was beyond the spectral region (infra-red) investigated (see note 10 at end of paper).

b. CH_2 (Vibration) Interaction: $\sigma_{s,\,a}$; $\pi_{s,\,a}$; $\delta_{s,\,a}$).—The principles used in deriving the normal modes of vibration lead to further definite assignments. Each of the three normal vibrations of CH_2, σ, π, δ, should split slightly to form a- and s-levels of ethylene, and to almost the same degree to form the corresponding a- and s-levels of cyclopropane, in the same region of the energy scale. These frequencies can be identified more precisely by means of Mecke's Rule II.[6] The infra-red spectrum was not resolved enough to decide, by means of selection rules, which of the Raman frequencies (1505, 1437, 1454 and 2953, 3013, 3030 cm.$^{-1}$) are the a- and s-combinations of the δ_a and π_a levels. The doublets (1437–1454 and 3013–3030) may be the doubly degenerate levels δ_a and π_a whose degeneracy has been removed either by interaction of the angular momentum of the doubly-degenerate motions with that of pure rotation[6] (p. 125), or by resonance due to a slight difference in the C–C bonds requiring both components to be active in the Raman and infra-red spectra.

Dr. E. Bright Wilson, Jr., has kindly suggested that these doublets are more likely to be ascribed to accidental degeneracy of δ_s and 2 × 745 (leading to 1437 and 1454) and of π_s with 2 × 1505 (leading to 3013 and 3030). The frequency 745 cm.$^{-1}$ is probably to be assigned to $R_{\perp a}$ of repre-

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(4) S. Bhagavantam, *Indian J. Phys.*, **5**, 73 (1930).

(5) R. Lespieau, M. Bourguel and R. Wakeman, *Bull. soc. chim.*, [4] **51**, 400 (1932).

(6) Eucken-Wolf, "Hand- und Jahrbuch der chemischen Physik," [9] 11, 1934, p. 338.

TABLE III

Type	$(CH_2)_2O$ ν cm.$^{-1}$	$(CH_2)_2O$ $\nu_a^2 - \nu_s^2$	$(CH_2)_2$ ν cm.$^{-1}$	$(CH_2)_2$ $\nu_a^2 - \nu_s^2$	$(CH_2)_2$ Calcd.	$(CH_2)_3$ ν cm.$^{-1}$	$(CH_2)_3$ $\nu_a^2 - \nu_s^2$	$(CH_2)_3$ Calcd.
σ_a			3107			3079		
				+0.234	+0.2			
σ_s	3047		3069					
π_a	2970		2988			2957		
		−0.227		−0.186	−0.1		−0.461 to −0.368	−0.4
π_s	3008		3019			3013–30		
δ_a			1444			1505		
				+0.283	+0.3		+0.200 to +0.151	+0.2
δ_s			1342			1437–54		

sentation E″, as indicated below. Thus its overtone belongs to E′ and A′, and so may couple with δ_s of A′, both frequencies being active in the Raman, and the component with symmetry *E′* of the overtone being active in the infra-red. An analogous situation obtains for the π_s level. Much greater resolution than was used here will be required to decide whether one or both components of the doublets appear in the infra-red. The relative positions of the a- and s-levels of cyclopropane and ethylene oxide[7] are the same according to this assignment, as shown in Table III. The separations of the a- and s-levels are computed assuming that the coupling of the CH_2 radicals is due predominantly to central forces between the atoms of one radical and those in the other, whose magnitudes are estimated from the types T_{zs}, R_{ha} and $R_{\perp a}$. (No assumptions are necessary regarding the potential function within the CH_2 radicals, other than a rough estimate of the amplitudes of motion in each vibration.) Since the results for ethylene agree in order of magnitude and sign with observation (Table III) some weight may be given to the values obtained for cyclopropane.

c. Hydrogen (CH_2 Rotation) Interaction: ($R_{ha,s}$; $R_{za,s}$; $R_{\perp a,s}$).—All the frequencies of cyclopropane except those that are a and s combinations of the *rotational* modes of the CH_2 radical, have now been assigned and correlated. Of these R_{ha} (of C_3H_6) is to be ascribed to 1022 cm.$^{-1}$, for this is the only vibration of this group that is active in both the infra-red and Raman spectra. Another frequency of this group, $R_{\perp s}$, is also unique since it is the only one predicted to occur in the infra-red alone. The band at 1800 cm.$^{-1}$ was observed only in absorption; but since this is a high frequency for such a (fundamental) mode, it is probably a combination frequency and $R_{\perp s}$ probably lies in the unexplored region < 1000 cm.$^{-1}$. The only permitted combinations and harmonics of appreciable intensity active only in

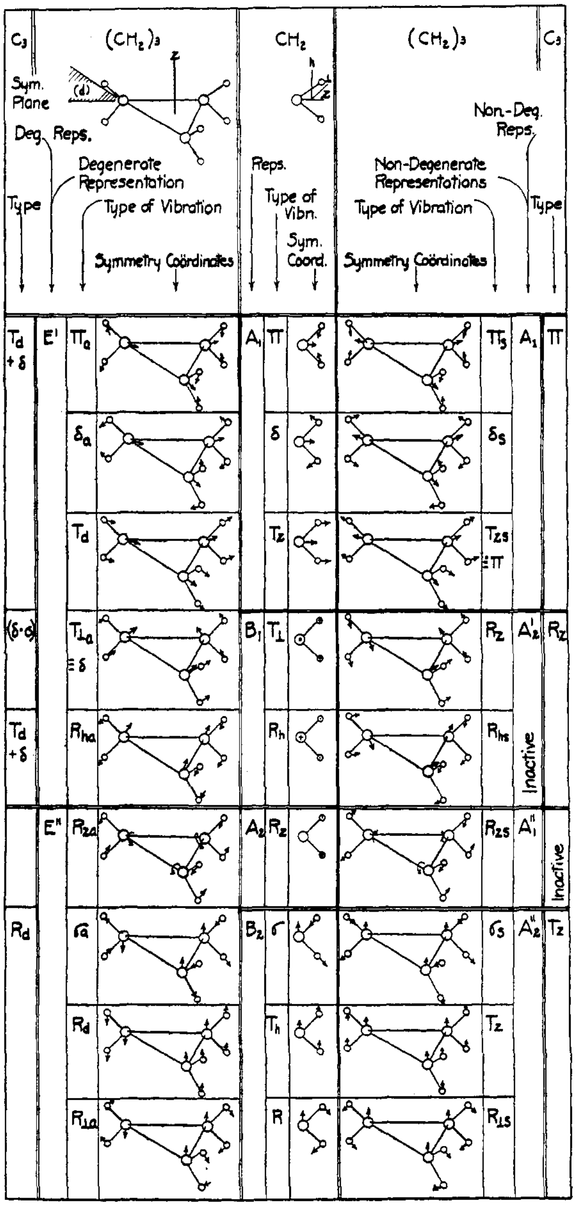

Fig. 1.—Symmetry coördinates and derivation of the fundamental vibrational modes of cyclopropane.

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[7] B. Timm and R. Mecke, *Z. Physik*, **97**, 221 (1935).

absorption are $T_{zs} + R_{\perp s}$ (giving $R_{\perp s} = 1800 - 1191 = 609$ cm.$^{-1}$ + anharmonicity) and the combination $R_{zs} + R_{hs}$. The latter modes should be inactive in both spectra as fundamentals.

The unassigned lines in the Raman spectrum (382, 745 and 1873 cm.$^{-1}$, all of low intensity) are attributed to the two remaining fundamentals, $R_{\perp a}$ and R_{za}. The following tentative assignment is made $R_{\perp a} = 745$ cm.$^{-1}$, $R_{za} = 382$ cm.$^{-1}$, and $R_{ha} + T_{\perp a} = 1873$ cm.$^{-1}$.

Further Confirmation of Assignments.—As indicated in Table II, the anti-symmetrical levels of cyclopropane are composed from the anti- *and* symmetrical levels of ethylene. The anti-symmetrical levels of cyclopropane are, to a first approximation, the mean of the corresponding (squared) frequencies of ethylene

$$\nu_s^2 + \nu_a^2 = 2\nu_s^2$$

Ethylene Cyclopropane

This formula holds quite well for all the levels except R_{za} (giving 500 cm.$^{-1}$ instead of 382 cm.$^{-1}$) and $R_{\perp a}$ (950 cm.$^{-1}$ instead of 745 cm.$^{-1}$).

Similarly the vibrational modes of cyclopropane can also be constructed from the motions of the "radicals," C_3 and H_3. Due to much larger perturbation here the levels more closely related to CH_2 levels are split to such an extent that this composition is purely formal. However, the π and δ (doubly degenerate) levels of C_3 (whose frequency ratio based on central forces[4,5] would be $\sqrt{2}$) are only slightly perturbed to form T_{zs} and and $T_{\perp a}$ (ratio 1.372) and δ_s and R_{ha} (ratio 1.476). The motions of the hydrogen planes (π and δ) are similar in each pair, but are in opposite phase relative to the carbon motions, accounting for the four per cent. perturbation in each direction from $\sqrt{2}$. These ratios confirm the previous method of assignment and may be extended to modes involving only π and δ vibrations of the hydrogen rings. It is interesting to note that the ratio of 1022 to 745 is also 1.372, but it is difficult to attach significance to this.

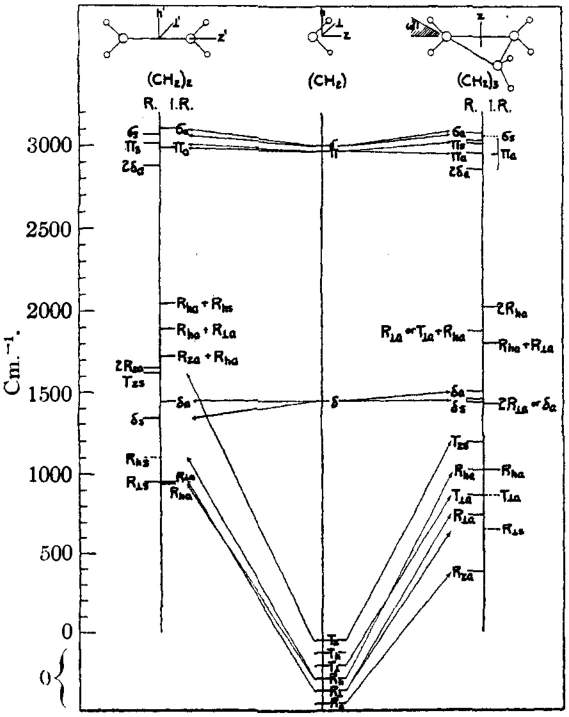

Fig. 2.—Relation of the frequencies of the CH_2 radical, ethylene and cyclopropane.

Acknowledgment

We wish to thank Professor Hoyt C. Hottel for the use of the rock-salt spectrometer.

Summary

The fundamentals of cyclopropane have been identified by group theoretical correlation with the frequencies of ethylene[8] and of the CH_2 radical.[9] The results are summarized in Figure 2. The frequencies predicted but not observed here ($T_{\perp a}$, $R_{\perp s}$) are indicated by dotted lines.[10] Such semi-quantitative analysis should act as a guide in the deduction of a suitable type of potential function for these hydrocarbons.

The measurements reported for the infra-red absorption bands in the 0.8 μ to 3.6 μ region (listed in Table I) are inadequate to justify an assignment of the combination frequencies.

CAMBRIDGE, MASS. RECEIVED MARCH 20, 1936

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[8] L. C. Bonner, THIS JOURNAL, **58**, 34 (1936).

[9] C. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.*, **148**, 258 (1935).

(10) Since this paper was submitted we have learned through the kindness of Professor E. F. Barker, of the University of Michigan, of some measurements of the infra-red absorption of cyclopropane made there by Doctor W. W. Sleator. He observed the following: a strong unresolved triplet at about 675 cm.$^{-1}$, another similar one at 870 cm.$^{-1}$, a strong narrow peak at approximately 1400 cm.$^{-1}$ and several weaker ones at higher frequencies, one near 1437 cm.$^{-1}$. Absorption in the 3 μ region was strong, but was not completely resolved.

Infra-red absorption at 870 cm.$^{-1}$ confirms the assignment of T_{zs} and $T_{\perp a}$ given above. Absorption at 675 cm.$^{-1}$ is probably due to $R_{\perp s}$ (predicted at 609 + cm.$^{-1}$).