

The Microwave Spectrum, Hindered Rotation Potential Function, and Dipole Moment in 1-Methylcyclopropene

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Abstract: The microwave spectrum of 1-methylcyclopropene ($\text{CH}_3\text{-C}_3\text{H}_5$) has been observed in the ground and first excited torsional states. The A-level ground state rotational constants are $A = 20,556.19 \pm 0.09$ MHz, $B = 6356.98 \pm 0.02$ MHz, and $C = 5176.42 \pm 0.02$ MHz. The first excited state A-level rotational constants are $A = 20,322.35 \pm 0.10$ MHz, $B = 6342.62 \pm 0.02$ MHz, and $C = 5172.44 \pm 0.02$ MHz. The value of the first two terms in the hindered rotation potential function, determined from splittings in rotational transitions for the $v = 0$ and $v = 1$ torsional states, are $V_3 = 1381 \pm 2$ cal/mole and $V_6 = 39 \pm 30$ cal/mole. Analysis of the Stark effect yields molecular dipole moment components of $\mu_a = 0.818 \pm 0.008$ D and $\mu_b = 0.19 \pm 0.02$ D with the total moment $\mu = 0.84 \pm 0.01$ D.

In view of the divergent views²⁻⁴ on the origin of the barrier to internal rotation in molecules containing a methyl group, a study of 1-methylcyclopropene was undertaken in order to add new data on the subject. The objective was to obtain both the threefold and sixfold components in the potential function governing the hindered rotation of the methyl group. Comparison of the sixfold component in 1-methylcyclopropene with that found in propylene⁵ should shed some light on the intramolecular forces involved in hindered rotation.

In addition to barrier data, the structure obtained from the rotational constants is useful in discussing the bonding within the ring.⁶ The bonding scheme obtained can then be compared to that in other small-ring compounds in order to obtain a qualitative but useful description of the bonding in these structures.

The molecular dipole moment was also obtained by observing the Stark effect on several rotational transitions.

Experimental Section

The preparation and purification of the 1-methylcyclopropene has been described previously.⁶ Portions of the microwave spectrum were recorded between 4 and 40 GHz. The microwave spectrometer employed in this work is a Stark modulated spectrometer with 12-ft S-, X-, and L-band absorption cells utilizing both 5- and 100-kHz square-wave modulation. The detection system and klystron stabilization system (for X- and Ku-band frequencies) have been described elsewhere.⁷

For frequencies above 18.0 GHz (K and Ka band) Micronow plug-in units containing Varian backward wave oscillators (BWO) are used. To stabilize these oscillators a Polarad KSS power supply with a S-48 plug-in (4-8 GHz) is used as a secondary standard. An external 100-kHz signal is used to control a General Radio Type 1112-A standard frequency multiplier which gives 1-, 10-, and 100-MHz outputs. The Polarad unit is stabilized by mixing its signal with the 100-MHz multiplier output in a Melab M-3 crystal mixer. Difference frequencies between the Polarad signal and harmonics of the 100-MHz signal are then fed into a 30-MHz phase stabilization network which locks the Polarad unit frequency to either +30 or -30 MHz from some harmonic of the 100-MHz

signal. Thus, stabilized signals from the Polarad unit are available in intervals of $[n(100) \pm 30]$ MHz, where n is an integer.

The Polarad unit output and the output from a Hewlett-Packard 608C variable frequency oscillator (VFO: 10-480 MHz) are mixed in a Micronow crystal mixer and harmonic generator (Model 603 for K band and Model 605 for Ka band) to give a signal approximately 58 MHz above the desired BWO output. The 58-MHz IF (intermediate frequency) is fed into a Micronow Model 201C frequency stabilizer, a frequency discriminator device, which controls the BWO frequency. Once the BWO frequency is stabilized by this unit, the microwave frequency can be changed by varying the VFO frequency with a synchronous motor. The output of the VFO is continuously counted using a Northeastern frequency counter. Thus, stabilized frequencies are available at intervals of $[m\{n(100) \pm 30\} \pm \text{VFO} - 58]$ MHz which makes it possible to stabilize any frequency between 18 and 40 GHz.

With this method, it was found that stabilized sweeps of about 100 MHz were possible before readjustment was necessary. The 58-MHz intermediate frequency can be determined to ± 0.05 MHz. Since the external 100-kHz reference is stable to 1 part in 10^8 per day, the IF uncertainty represents the absolute error in the measurement of any frequency by this method. However, difference frequencies can be measured with much higher accuracy.

All frequency measurements were made at Dry Ice temperatures at pressures from 1 to 30 μ . For the highest resolution, measurements were carried out with pressures below 5 μ .

The dipole moment was measured by observing the Stark effect as a function of field in an X-band absorption cell for several transitions. The absorption cell and the 100-kHz square-wave generator were calibrated by observing the Stark effect for the $J = 0 \rightarrow 1$ transition in OCS.

Ground Torsional State Rotational Assignment and Structure

A preliminary report on the assignment of the ground torsional state has been published.⁶ Several additional transitions have been recorded. Table I contains the observed A-level and E-level transitions and calculated A-level transitions for the ground torsional state. Table II and Figure 1 contain the structural data obtained by an adjustment procedure explained in ref 6. The ground torsional state A-level rotational constants are $A = 20,556.19$ MHz, $B = 6356.98$ MHz, and $C = 5176.42$ MHz.

Bonding in small-ring compounds has been summarized and discussed by Bennett⁸ in which he considers the Walsh⁹ (W) and Coulson and Moffitt¹⁰ (CM) bonding schemes. The Walsh bonding scheme for small-ring

(1) Author to whom correspondence should be addressed.

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(7) W. H. Flygare, *J. Chem. Phys.*, **41**, 206 (1964); **42**, 1157 (1965).

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(9) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(10) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

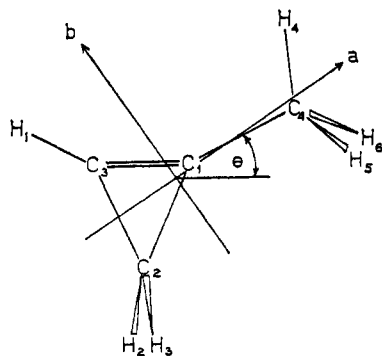


Figure 1. Orientation of the principal inertial axes and atom numbering in 1-methylcyclopropane.

compounds is illustrated in Figure 2 for cyclopropane along with the Coulson and Moffitt bonding scheme. Walsh forms the cyclopropane ring by bringing together three ethylenic ($H_2C=$) links to form the molecule,

Table I. Calculated and Observed A-Level Transitions and Observed E-Level Transitions in 1-Methylcyclopropane in the Ground Torsional State^a

Rotational transition	Obsd frequencies, MHz		Calcd frequencies, MHz
	A	E	
0 ₀₀ → 1 ₀₁	11,533.51	11,533.51	11,533.38
0 ₀₀ → 1 ₁₁	25,732.61	25,721.74	25,732.63
1 ₀₁ → 1 ₁₀	15,379.86	15,371.52	15,379.80
1 ₀₁ → 2 ₀₂	22,996.37	22,996.37	22,996.18
1 ₁₁ → 2 ₁₂	21,886.30	21,887.22	21,886.21
1 ₁₀ → 2 ₁₁	24,247.53	24,246.60	24,247.34
1 ₀₁ → 2 ₁₂	36,085.55	36,075.46	36,085.45
2 ₀₂ → 2 ₁₁	16,630.94	16,621.89	16,630.95
2 ₀₂ → 3 ₀₃	34,319.62	34,319.78	34,319.46
2 ₂₀ → 3 ₂₁	34,880.95	34,847.38	34,880.87
2 ₁₂ → 3 ₁₃	32,786.23	32,786.00	32,796.45
2 ₁₁ → 3 ₁₂	36,325.49	36,325.16	36,325.49
2 ₂₁ → 3 ₂₂	34,599.99	34,633.68	34,600.16
2 ₁₂ → 3 ₀₃	21,230.55	21,240.35	21,230.18
3 ₀₃ → 3 ₁₂	18,636.95	18,627.85	18,636.98
4 ₀₄ → 4 ₁₃	21,539.86	21,531.01	21,539.91
4 ₁₄ → 4 ₁₃	11,787.68	11,787.58	11,787.14
5 ₁₅ → 5 ₁₄	17,635.13	...	17,634.83
5 ₂₃ → 6 ₁₆	9,311.70	...	9,310.59
6 ₀₆ → 6 ₁₅	30,629.55	30,621.58	30,629.80
6 ₁₆ → 6 ₁₆	24,572.15	24,572.59	24,572.49
8 ₂₇ → 8 ₂₆	12,453.93	12,461.36	12,455.68
11 _{2,10} → 11 _{2,9}	33,398.01	33,407.93	33,403.37
12 _{3,10} → 12 _{3,9}	10,715.37	10,727.09	10,718.05
17 _{4,14} → 17 _{4,13}	12,435.58	...	12,444.95

^a Calculated with $A = 20,556.19$ MHz, $B = 6356.98$ MHz, and $C = 5176.42$ MHz.

Table II. Structural Parameters for 1-Methylcyclopropane^a

Bond	Length, Å	Angle	Value
Assumed Structural Parameters			
C ₃ -H ₁	1.070	H ₁ C ₃ C ₁	150°
C ₃ -C ₂	1.515	H ₂ C ₂ H ₃	114° 42'
C ₃ -C ₁	1.300	C ₃ C ₂ C ₁	50° 48'
C ₂ -H _{2,3}	1.087	C ₁ C ₂ H ₄	111°
C ₄ -H ₄	1.085		
C ₄ -H _{5,6}	1.098	H ₄ C ₄ H _{5,6}	109°
Calculated Structural Parameters			
C ₁ -C ₄	1.476	C ₃ C ₁ C ₄	152° 48'
		$\theta = 33° 8'$	

^a See Figure 1 for numbering of atoms.

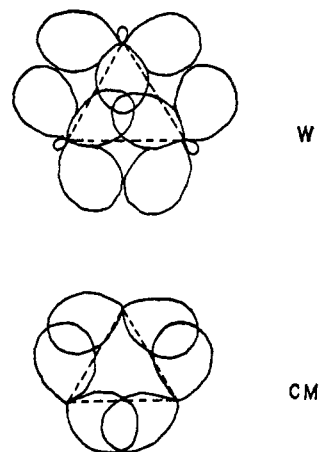


Figure 2. Walsh (W) and Coulson and Moffitt (CM) orbitals for cyclopropane. Orbitals pointing toward hydrogen are not shown.

yielding a completely delocalized system. On the other hand, Coulson and Moffitt allow hybridized C orbitals to overlap outside the ring forming some angle with the internuclear line.

Bennett has pointed out that the two schemes are equivalent under certain circumstances. However, the necessary linear transformation between W and CM orbitals is valid only if atomic orbitals do not overlap with their neighbors and there are an equal number of electrons in each combining hybrid orbital in the W scheme. The W orbital description used here is equivalent to the CM orbital picture only if the two criteria mentioned above are satisfied.

An sp-type hybrid at C₁ (see Figure 1) is indicated by the structural data on 1-methylcyclopropane. The C₁-C₄ bond distance of 1.476 Å is closer to the C-C bond distance of 1.459 Å found in methylacetylene¹¹ than the distance of 1.501 Å found in propylene.¹² This can be explained by allowing more p character in the C₁-C₄ bond with a corresponding lengthening over a pure sp bond. This change leads to more s character in the orbital directed into the ring. The HCH angle at C₂ can also be explained with similar reasoning using sp² orbitals with one lobe directed into the center of the ring.

Nuclear magnetic resonance data on $J_{13C,H}$ spin-spin coupling constants^{13,14} support the above interpretation. Table III lists some relevant $J_{13C,H}$ spin-spin coupling constants. The values of 157 in ethylene and 248 in methylacetylene are typical for sp² and sp hybridization, respectively. Thus, the value of 221 in 2,2-dimethylcyclopropane indicates approximately sp hybridization for the ring carbons involved in the double bond. The fact that the coupling constant is less than for pure sp is consistent with the interpretation given for the C₁-C₄ bond length in 1-methylcyclopropane. That is, slightly more p character is found in the =C-H bond in 2,2-dimethylcyclopropane than in the C₁-C₄ bond of 1-methylcyclopropane.

Thus, it appears that W orbitals are very successful in explaining a considerable body of data for small-ring compounds. A satisfactory bonding scheme in

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Table III. $J^{13}\text{CH}$ Spin-Spin Coupling Constants for Selected Molecules

Molecule	$J^{13}\text{CH}$, cps	Ref
CH_4	125	14
CH_2CH_2	157	14
Benzene	159	14
	221	13
$\text{H}-^{13}\text{C}=\text{C}-\text{CH}_3$	248	14

1-methylcyclopropene would have sp hybrids with one lobe pointed toward the center of the ring at C_3 and C_1 and an sp^2 hybrid at C_2 with one lobe pointed toward the center. We have come to similar conclusions by analyzing the ^{33}S nuclear quadrupole coupling constants in ethylene sulfide¹⁵ and the ^{14}N nuclear quadrupole coupling constants in ethylenimine.¹⁶

First Excited Torsional State Rotational Assignment

Assignment of the rotational spectrum for the first excited torsional state was made on the basis of the Stark effect. The A-level transition Stark effect in the first excited torsional state should be the same as in the ground state. To find each first excited state A-level transition, a frequency sweep about a ground state A-level transition was taken until a weaker absorption having the same Stark effect was observed.

The $0_{00} \rightarrow 1_{01}$ and three $1 \rightarrow 2$ transitions were assigned. Then, with the resulting rotational constants, other transitions were predicted. Measurement of many more transitions served to refine the rotational constants. In most cases the A-E level transition splitting was so large that the E level could be found only after determining V_3 from ground state A-E splittings. The observed A- and E-level transitions and calculated A-level transitions are given in Table IV.

Table IV. Calculated and Observed A-Level Transitions and Observed E-Level Transitions in 1-Methylcyclopropene in the First Excited Torsional State

Rotational transition	Obsd frequencies, MHz		Calcd frequencies, ^a MHz
	A	E	
$0_{00} \rightarrow 1_{01}$	11,515.16	11,515.16	11,515.03
$0_{00} \rightarrow 1_{11}$	25,494.80	24,828.50	25,494.77
$1_{01} \rightarrow 2_{02}$	22,959.79	22,961.32	22,959.64
$1_{11} \rightarrow 2_{12}$	21,859.99	22,322.66	21,859.88
$1_{10} \rightarrow 2_{11}$	24,200.36	23,729.21	24,200.24
$1_{01} \rightarrow 2_{02}$	35,839.23	...	35,839.63
$2_{11} \rightarrow 3_{12}$	36,255.04	36,018.91	36,254.94
$2_{12} \rightarrow 3_{13}$	32,747.21	32,986.28	32,747.06
$2_{20} \rightarrow 3_{21}$	34,824.96	34,680.80	34,825.11
$2_{21} \rightarrow 3_{22}$	34,544.95	34,684.4	34,545.09
$2_{02} \rightarrow 3_{03}$	34,265.23	34,272.90	34,265.07
$2_{12} \rightarrow 3_{03}$	21,384.95	21,577.29	21,385.08
$3_{03} \rightarrow 3_{12}$	18,380.64	19,024.97	18,380.38

^a Calculated with $A = 20,322.25$ MHz, $B = 6342.62$ MHz, and $C = 5172.44$ MHz.

The first excited A-level torsional state rotational constants are $A = 20,322.25$ MHz, $B = 6342.62$ MHz, and $C = 5172.44$ MHz.

(15) R. L. Shoemaker and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 6263 (1968).

(16) M. K. Kemp and W. H. Flygare, *ibid.*, **90**, 6267 (1968).

Hindered Rotation Potential Function

The Hamiltonian which describes the rotational energy levels in the presence of internal rotation may be written as

$$H = H_r + F(p - P)^2 + V(\alpha)$$

where the notation of Table I in Herschbach is appropriate.¹⁷ In addition, the usual rigid-rotor Hamiltonian, H_r , is written as

$$H_r = AP_a^2 + BP_b^2 + CP_c^2$$

where $A = \hbar^2/(2I_a)$, etc., are the rotational constants. The inverse of the reduced moment of inertia is defined as $F = \hbar^2/(2rI_\alpha)$ and $V(\alpha)$ is the potential which is a function of the torsional angle, α .

The rotational energy levels are affected primarily through the coupling of the total angular momentum of the internal top, p , along its symmetry axis, and the angular momentum of the frame, P . That is, the effect on the rotational energy levels is due to the cross term ($-2FPp$) in the $F(p - P)^2$ term in the Hamiltonian. This Hamiltonian gives an energy matrix which is nondiagonal in the torsional quantum number, v ; these nondiagonal elements arise from the ($-2FPp$) cross term. Formally, one can apply successive Van Vleck transformations which will reduce those matrix elements which are nondiagonal in v to a low enough value that they may be neglected. One may then factor the transformed Hamiltonian matrix into smaller rotational matrices, $H_{v\sigma}$, one for each torsional state. These may be written as

$$H_{v\sigma} = H_r + F \sum_n W_{v\sigma}^{(n)} P^n$$

where the $W_{v\sigma}^{(n)}$'s are perturbation coefficients which may be obtained from Herschbach's tabulation of $W_{v\sigma}^{(n)}$ as a function of the reduced barrier parameter, $s = 4.66139(V_3/F)$.¹⁷ V_3 is the barrier height expressed in cal/mole and F is expressed in kHz. The P^n matrix elements up to $n = 4$ are also tabulated in Herschbach's paper.

Therefore, to calculate the effect of internal rotation on the rotational spectrum of a molecule with a high barrier (>500 cal/mole), one must (1) determine F from assumed structural parameters; (2) estimate the barrier height, V_3 , and obtain the necessary $W_{v\sigma}^{(n)}$ coefficients; (3) calculate the P^n matrix for as high as n as necessary; (4) compute the $H_{v\sigma} = H_r + \sum_n W_{v\sigma}^{(n)} P^n$ matrix elements in a symmetric top basis; (5) diagonalize the result; and (6) calculate the spectra using the $J = 0 \pm 1$, $\Delta\sigma = 0$ selection rules. We have used a computer program written by Lett for our calculations.¹⁸ The program makes corrections up to fourth order and includes a denominator correction for an assumption made in the derivation of the $H_{v\sigma}$ formula. To fit the observed splittings, the value of I_α was calculated from the structural data given in Table II, and the appropriate $W_{v\sigma}$ coefficients were interpolated from Herschbach's tables.¹⁷ Values of $\partial(\nu_A - \nu_E)/\partial V_3$ were calculated for each transition which showed a resolvable splitting. Then $(\nu_A - \nu_E)_{\text{calcd}}$ was least-squares fitted to $(\nu_A - \nu_E)_{\text{obsd}}$, yielding the best value for V_3 possible for each torsional state independently.

(17) D. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

(18) R. G. Lett, Ph.D. Thesis, University of Illinois, 1966.

To ensure that round-off errors within the computer were not affecting the calculated splittings, the barrier program written by Lett was converted to double precision. Table V contains $(\nu_A - \nu_E)_{\text{obsd}}$ and $(\nu_A -$

Table V. Observed and Calculated Internal Rotation Splittings for the Ground and First Excited Torsional States in 1-Methylcyclopropene.

Rotational transition	$\nu_A - \nu_E$, MHz		
	Obsd	Calcd ^a	Calcd ^b
Ground Torsional State			
0 ₀₀ → 1 ₁₁	10.87	10.75	9.91
1 ₀₁ → 1 ₁₀	8.34	7.96	7.50
1 ₁₁ → 2 ₁₂	-0.91	-0.89	-0.78
1 ₀₁ → 2 ₁₂	10.35	9.85	9.14
1 ₁₀ → 2 ₁₁	0.93	0.93	0.81
2 ₀₂ → 2 ₁₁	9.05	8.82	8.25
2 ₂₁ → 3 ₂₂	-33.69	-33.89	-31.09
2 ₂₀ → 3 ₂₁	33.57	33.77	31.00
2 ₁₂ → 3 ₀₃	-9.80	-9.57	-8.87
3 ₀₃ → 3 ₁₂	9.10	8.88	8.31
4 ₀₄ → 4 ₁₃	8.85	8.62	8.10
First Excited Torsional State			
0 ₀₀ → 1 ₁₁	666.30	660.52	661.05
1 ₁₀ → 2 ₁₁	461.15	470.62	470.02
1 ₁₁ → 2 ₁₂	-462.67	-472.31	-472.36
2 ₁₁ → 3 ₁₂	236.13	239.82	239.04
2 ₁₂ → 3 ₁₃	-239.07	-244.55	-244.68
2 ₀₂ → 3 ₀₃	-7.67	-7.85	-8.12
2 ₁₂ → 3 ₀₃	-192.34	-198.58	-199.59
2 ₂₀ → 3 ₂₁	144.16	154.88	154.49
2 ₂₁ → 3 ₂₂	-139.45	-150.04	-150.56
3 ₀₃ → 3 ₁₂	-644.33	-628.72	-628.57
4 ₁₄ → 4 ₁₃	-353.88	-351.02	-352.42

^a See Table VI for parameters. ^b See Table VII for parameters.

$\nu_E)_{\text{calcd}}$ for the ground and first excited torsional states using the least-squares values of V_3 . The parameters used for both the ground and first excited torsional state calculations are given in Table VI. In this

Table VI. Internal Rotation Parameters for the Ground and First Excited Torsional States of 1-Methylcyclopropene^a

Parameter	Ground state	First excited state
$\angle C_4-C_1-a$ axis	5° 56'	5° 56'
$\angle C_4-C_1-b$ axis	95° 56'	95° 56'
λ_a^b	0.99423	0.99423
λ_b^b	-0.10722	-0.10722
I_α	3.124	3.124
F , MHz	185,154.9	184,852.5
s	35.07	34.87
V_3 , cal/mole	1393 ± 1	1383 ± 2
Effective A-level rotational constants (MHz)		
A_{eff}	20,556.191	20,322.247
B_{eff}	6356.981	6342.620
C_{eff}	5176.421	5172.440
x	-0.846479	-0.845520

^a The error limits are one standard deviation. ^b λ_a and λ_b are the direction cosines between the top axis and the a and b axes, respectively.

analysis, it was assumed the structural parameters were the same in both the ground and first excited torsional states.

The results in Table VI indicate that the value of the barrier height (V_3) for the ground and first excited torsional state differ by more than the experimental

uncertainty. Of course, the total uncertainty is greater than the experimental deviations because of the uncertainty in the structure and in I_α . As pointed out by Hirota⁵ in his work on propylene, values of V_3 cannot be brought into agreement by changing I_α alone. However, inclusion of a V_6 term was very effective in propylene in bringing the values for V_3 of the various torsional states into coincidence.

Before including a V_6 term in the potential function for the hindered rotation, the direction cosine (λ_a') for the first excited torsional state was used as a parameter. The best least-squares fit for the first excited torsional state was obtained with $V_3 = 1383 \pm 3$ cal/mole and $\lambda_a' = 0.9937 \pm 0.0095$. Thus, it appears that the value of the direction cosine for the ground state is approximately the same as that for the first excited state.

All 22 splittings given in Table V and three parameters (V_3 , V_6 , and λ_a') were used to obtain a final least-squares fit for $(\nu_A - \nu_E)_{\text{obsd}} - (\nu_A - \nu_E)_{\text{calcd}}$. These results are given in Tables VI and VII.

Table VII. Final Parameters for the Internal Rotation Problem in 1-Methylcyclopropene^a

Parameter	Ground state	First excited state
A , MHz	20,556.191	20,322.347
B , MHz	6356.981	6342.620
C , MHz	5176.421	5172.440
I_α , amu Å ² ^b	3.124	3.124
λ_a	0.99423 ^b	0.9922 ± 0.0065
λ_b	-0.10722 ^b	-0.1262 ± 0.0052
V_3 , cal/mole	1381 ± 2	1381 ± 2
V_6 , cal/mole	39 ± 30	39 ± 30
s	34.77	34.84
F , MHz	185,154.9	184,772.3

^a The error limits are one standard deviation. ^b Assumed parameters.

It is interesting to point out that in the first excited state, the value of $\partial(\nu_A - \nu_E)/\partial V_3$ is one to two order of magnitude greater than $\partial(\nu_A - \nu_E)/\partial V_6$, whereas in the ground state the two derivatives are comparable. Thus, the first excited state determines V_3 ; then the ground state serves to fix V_6 with only minor changes in V_3 .

Table VII indicates that the inclusion of a V_6 term does bring the values of V_3 for both the ground and first excited states into coincidence. However, when V_3 is used as the only parameter for all 22 splittings given in Table V, a value of $V_3 = 1383 \pm 2$ cal/mole is obtained.

Using Hirota's data on propylene and the same method of calculation, values of $V_3 = 1987 \pm 2$ cal/mol and $V_6 = -24 \pm 18$ cal/mole were obtained compared to Hirota's values of $V_3 = 1996 \pm 2$ cal/mole and $V_6 = -37 \pm 6$ cal/mole.⁵ Thus, the best that can be said is that V_6 appears to be a small positive number in 1-methylcyclopropene in contrast to a small negative number in propylene. We feel that this statement will remain true in the presence of a more sophisticated treatment of the data. The fit between experiment and theory given in Table V is not very good, and the discrepancies probably arise because of other vibrational-rotational interactions than the torsional mode treated here. In any event, the relative V_3 - V_6 signs in both

propylene and 1-methylcyclopropene are insensitive to structural uncertainties.

Electric Dipole Moment

The dipole moment of 1-methylcyclopropene was measured by observing the frequencies of the Stark components of several transitions as a function of applied electric field. The difference between the unperturbed line and the Stark components as a function of field for the $0_{00} \rightarrow 1_{01}$, $1_{01} \rightarrow 2_{02}$, and $1_{10} \rightarrow 2_{11}$ transitions are given in Figure 3.

In order to accurately determine the electric field, the X-band wave guide used for these measurements was calibrated using OCS as a standard. The Stark component shift for the $J = 0 \rightarrow 1$ transition was observed in the X-band wave guide at various voltage settings on the 100-kHz square-wave generator. The splittings observed along with the accurately known dipole moment in OCS¹⁹ of 0.715 D determine the field at each voltage setting. The electric field strengths determined for the various voltage settings were then used for determining the dipole moment in 1-methylcyclopropene.

From the data shown in Figure 3, values of $\Delta\nu_{J \rightarrow J+1, M}/E^2$ were obtained by a least-squares fit. These slopes are given in Table VIII. Also given are the calculated

Table VIII. Stark Effect and Dipole Moment Data^a

Transition $J \rightarrow J + 1$	Obsd slope ^b	Calcd slope ^b
$0_{00} \rightarrow 1_{01} (M = 0)$	0.798 ± 0.011	0.791
$1_{10} \rightarrow 2_{11} (M = 0)$	0.1744 ± 0.0027	0.1741
$1_{01} \rightarrow 2_{02} (M = 0)$	-0.1985 ± 0.0015	-0.1986
$1_{01} \rightarrow 2_{02} (M = 1)$	0.2100 ± 0.0016	0.2091
	$\mu_a = 0.818 \pm 0.008$ D	
	$\mu_b = 0.19 \pm 0.02$ D	
	$\mu_{\text{total}} = 0.84 \pm 0.01$ D	
	$\theta_{1,a} = 13.5 \pm 2.0^\circ$	

^a The error limits are one standard deviation. ^b $\Delta\nu_{J \rightarrow J+1, M}/E^2 \times 10^6$ with units of MHz/(V cm)².

slopes obtained with $\mu_a^2 = 0.6691$ D² and $\mu_b^2 = 0.0361$ D². The values for μ_a , μ_b , and the total molecular dipole moment along with the angle between the total molecular dipole moment and the a principal inertial axis are also given in Table VIII.

The ratio $\mu_a^2/\mu_b^2 = 18.5$ explains why the b dipole transitions were so weak since the line strength of a g dipole transition is proportional to μ_g^2 . The small angle of 13.5° between μ_{total} and the a axis indicates that the total dipole moment vector is about 19.5° from the C_1-C_4 bond (see Figure 1).

Discussion

The molecular and electronic structures were discussed in the section, Ground Torsional State Rotational Assignment and Structure. We will now discuss the barrier to internal rotation of the methyl group.

(19) J. S. Muentner, *J. Chem. Phys.*, **48**, 4544 (1968).

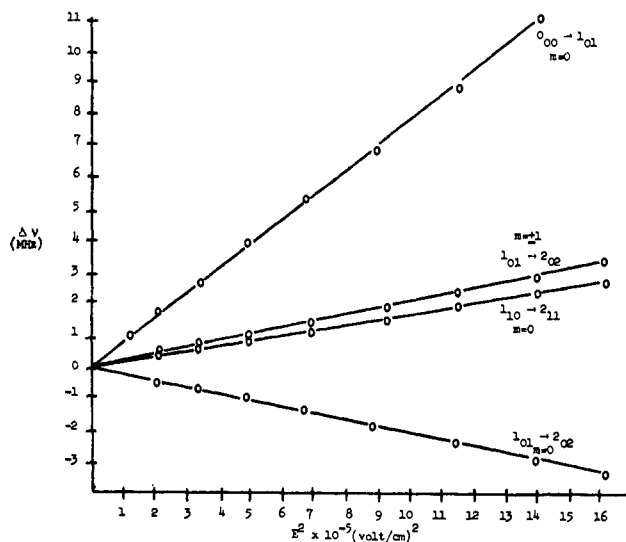


Figure 3. Stark splittings as a function of applied electric field in 1-methylcyclopropene.

In propylene the value of the sixfold term in the hindered rotation potential function is negative ($V_6 = -37$ cal/mole).⁵ A small negative V_6 correction to a positive threefold term yields a potential function which has broader minima and sharper maxima compared to a pure threefold function. For 1-methylcyclopropene V_6 is positive (39 cal/mole), leading to broader maxima and sharper minima compared to pure V_3 . In spite of inadequacies in the theory, we feel that the relative signs of V_3 and V_6 in these two molecules are significant. Assuming that the relative sign information will survive a more sophisticated treatment of internal rotation problem, we offer the following interpretations of this observation.

Since the equilibrium configuration of the methyl group in propylene (a minimum) occurs with a methyl proton eclipsed with the double bond, the sharpened maxima in propylene's hindered rotation potential function indicates a fairly strong repulsion occurs as a methyl group proton eclipses the proton on the adjacent carbon. The distance between the methyl proton and the adjacent carbon proton at a maximum is about 1.5 \AA less than that between the methyl proton and the *cis* proton at a minimum. As repulsion has an e^{-r} or $1/r^{12}$ dependence, the slightly smaller proton-proton distance at a maximum would lead to a sharper interaction than at a minimum resulting in a negative V_6 .

In contrast to the above discussion on propylene, the adjacent carbon atom's proton is not present in 1-methylcyclopropene. Thus, we would now predict that the sharpest part of the potential would be due to repulsion between the methyl protons and the *cis* proton. This expectation coupled with the experimental observation that V_3 and V_6 have the same sign requires that the potential minima occur with the methyl group protons eclipsed with the double bond as in propylene.

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