

InfraRed and Raman Spectra of Polyatomic Molecules IX. Dimethyl Acetylene, C₄H₆

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Infra-Red and Raman Spectra of Polyatomic Molecules

IX. Dimethyl Acetylene, C_4H_6 *

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The infra-red absorption of gaseous C_4H_6 has been measured from 2 to 24μ , and the Raman spectrum of the liquid studied. Analysis of the data permits the determination of all the fundamental frequencies of the molecule. The frequencies are fitted closely with a modified valence-force potential function in which the methyl-group force constants are those previously determined for ethane.

THE dimethyl acetylene molecule, like the ethane molecule, contains one degree of freedom which corresponds to the internal rotation of one methyl group relative to the other. In ethane this rotation is hindered by a barrier of about 2750 cal./mole (assuming the cosine form). It is of interest to determine the magnitude of the barrier in dimethyl acetylene; here the methyl groups are quite far removed, so that we may expect this case to give the smallest restricting potential.

The spectroscopic study which is reported here was undertaken in order to obtain the knowledge of the vibrational frequencies of the molecule which is necessary if the magnitude of the restricting potential is to be accurately determined. The results obtained are also of interest in that the normal coordinate calculations are distinctly encouraging to the hope that certain bond force constants can be transferred from one molecule (ethane) to another of similar structure (dimethyl acetylene).

Studies on the heat capacity of the gas are now in progress, and preliminary results indicate that the restricting potential is less than 500 cal./mole.¹

EXPERIMENTAL

Infra-red absorption

The material used was made available through the generosity of Professor G. B. Kistiakowsky; it was prepared by Dr. J. B. Conn for use in the hydrogenation calorimeter, and its preparation and purity will be described in a future publication of the series on heats of hydrogenation.

The infra-red absorption of the gas was studied from 2 to 24μ ; fluorite, rocksalt, and KBr prisms were used in the appropriate spectral regions. The infra-red spectrometer has been previously described.² The absorption spectrum is shown in Fig. 1; the frequencies of the minima are tabulated in Table I. The extremely weak shoulder at 1664 cm^{-1} is doubtful. The accuracy

* A preliminary report of this study was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Baltimore, April, 1939.

† National Research Fellow in Chemistry.

¹ B. L. Crawford, Jr., and W. W. Rice, *J. Chem. Phys.* **7**, 437 (1939).

² H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 197, 247 (1938).

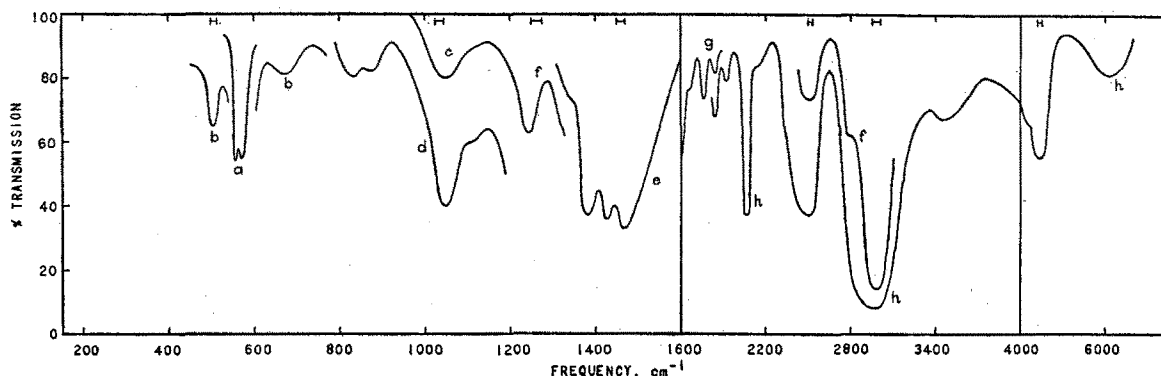
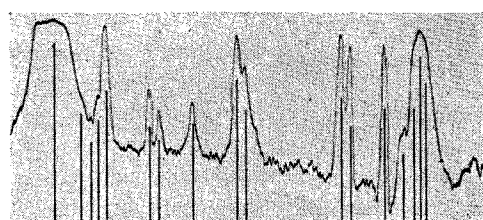


FIG. 1. Infra-red absorption of dimethyl acetylene vapor. Cell length, 30 cm. Pressures : KBr prism: *a*, 100 mm; *b*, 412 mm. NaCl prism: *c*, 103 mm; *d*, 392 mm. CaF₂ prism: *e*, 44 mm; *f*, 98 mm; *g*, 255 mm; *h*, 530 mm. Slit widths are indicated near the top of the plot.



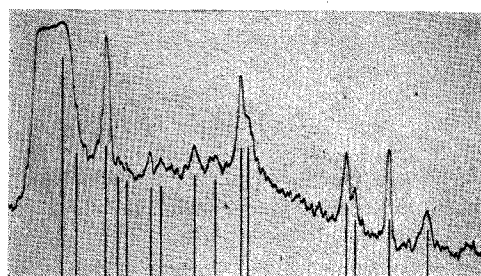
Hg 4358
213 *e*
371 *f, g*
693 *e*
774 *e*
1029 *e*
1380 *e*
1448 *e*
2233 *e*
2310 *e*
Hg 4916
2737 *e*
2857 *e*
2916 *e*
2966 *e*

FIG. 2. Microphotometer tracing of the Raman spectrum of liquid dimethyl acetylene, excited by the Hg 4358 triplet. Notation for the exciting lines: *e*, 22938; *f*, 22995; *g*, 23039; *k*, 24705 cm⁻¹.

of the frequency measurements may be estimated from the slit widths shown in Fig. 1.

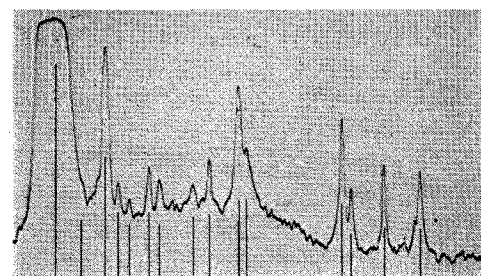
Raman effect

The Raman effect of the liquid was also studied, using the apparatus previously described.² Polarization studies³ were also made. A microphotometer tracing of the Raman spectrum is shown in Fig. 2; tracings of the polarization plates are shown in Fig. 3. The frequency shifts observed, compared with those found by previous investigators,⁴⁻⁷ are tabulated in



Hg 4358
213 *e*
371 *e D*
2233 *k P*
2310 *k P*
693 *e P*
774 *e P*
1029 *e D*
2916 *k P*
1380 *e P*
1448 *e D*
2233 *e P*
2310 *e P*
Hg 4916
2916 *e P*

FIG. 3a. Microphotometer tracing of Raman plate taken with the exciting light plane polarized *parallel* to the axis of the Raman tube. Notation for exciting lines as in FIG. 2. *P*, polarized ($\rho < 6/7$); *D*, depolarized ($\rho = 6/7$).



Hg 4358
213 *e*
371 *e D*
2233 *k P*
2310 *k P*
693 *e P*
774 *e P*
1029 *e D*
2916 *k P*
1380 *e P*
1448 *e D*
2233 *e P*
2310 *e P*
Hg 4916
2916 *e P*

FIG. 3b. Microphotometer tracing of Raman plate taken with the exciting light plane polarized *perpendicular* to the axis of the Raman tube. Notation as in FIG. 3a.

³ J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938).

⁴ G. Glockler and H. M. Davis, J. Chem. Phys. **2**, 881 (1934).

⁵ G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 408 (1938).

⁶ B. Gredy, Comptes rendus **197**, 327 (1933).

⁷ K. W. F. Kohlrausch, A. Pongratz and R. Seka, Monatshefte **70**, 213 (1937).

Table II. The 2114 cm⁻¹ shift found by Kohlrausch, Pongratz, and Seka, and attributed by them to ethyl acetylene, is omitted from Table II. The intensity estimates are those given by the

several authors. The agreement is quite satisfactory with regard to the frequencies of the principal lines; the relative intensity estimates, however, differ markedly in some cases.

THE VIBRATION FREQUENCIES

Symmetry

The dimethyl acetylene molecule has the same symmetry as the ethane molecule, and the treat-

ment given by Howard⁸ is appropriate. Using his notation for the point group D_{3h}' , we have for the structure of the normal coordinate representation

$$\Gamma = 4A_1 + 3\bar{A}_2 + \bar{A}_1 + 4E + 4\bar{E},$$

where the coordinate for the internal rotation

⁸ J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

TABLE I. The infra-red spectrum of dimethyl acetylene, observed and calculated.

OBSERVED FREQUENCY AND INT'Y*	CALC'D FREQ'Y	ASSIGNMENT AND SYMMETRY	OBSERVED FREQUENCY AND INT'Y*	CALC'D FREQ'Y	ASSIGNMENT AND SYMMETRY
	158	371-213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$	1763 W	1775	1050+725, E
	213	Fund., E		1819	1448+371, $\bar{A}_1 + \bar{A}_2 + E$
	426	213 ² , $A_1 + E$		1839	1468+371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
	481	694-213, E§			
507 W	529	371 ² -213, $A_1 + A_2 + 2E$	1842 MW	1851	1126+725, \bar{A}_2
	561	774-213, E§	1920 W	1948	1380+(568), $\bar{A}_1 + \bar{A}_2 + \bar{E}^\dagger$
561 } S†				2058	1029 ² , $A_1 + E$
575 }	584	213+371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$			
			2066 MS	2057	2270-213, E
	658	1029-371, $A_1 + A_2 + E$		2079	1029+1050, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
671 VW	679	1050-371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2100	1050 ² , $A_1 + E$
—	742	371 ² , $A_1 + E$ §			
			2140 W	2105	1380+725, \bar{A}_2
	755	1126-371, E		2155	1029+1126, E
	816	1029-213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2193	1468+725, E
835 W	837	1050-213, $A_1 + A_2 + E$			
				2409	1029+1380, E
877 W	880	1448-(568), $A_1 + A_2 + 3E^\dagger$		2430	1050+1380, E
—	938	725+213, E		2477	1448+1029, $A_1 + A_2 + E$
—	1009	1380-371, E			
				2483	2270+213, E
				2497	1468+1029, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
				2498	1050+1448, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
1050 M	1050	Fund., E			
	1077	1448-371, $A_1 + A_2 + E$	2500 MS	2506	1380+1126, \bar{A}_2
	1097	1468-371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2518	1468+1050, $A_1 + A_2 + E$
				2574	1448+1126, E
1126 W	1126	Fund., \bar{A}_2		2595	2966-371, $A_1 + A_2 + E$
	1167	1380-213, E		2605	2976-371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
	1235	1448-213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2703	2916-213, E
1240 M	1242	1029+213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2753	2966-213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
	1255	1468-213, $A_1 + A_2 + E$		2760	1380+1380, \bar{A}_2
	1263	1050+213, $A_1 + A_2 + E$	2785 W	2763	2976-213, $A_1 + A_2 + E$
1340 W	1337	1029+1050-371 ² , $2\bar{A}_1 + 2\bar{A}_2 + 4\bar{E}$		2828	1448+1380, E
1380 M	1380	Fund., \bar{A}_2		2848	1468+1380, E
	1400	1029+371, $A_1 + A_2 + E$		2896	1448+1448, $A_1 + A_2 + E$
1425 MW	1421	1050+371, $\bar{A}_1 + \bar{A}_2 + \bar{E}$		2916	1448+1468, $\bar{A}_1 + \bar{A}_2 + \bar{E}$
1468 S	1468	Fund., E		2936	1468+1468, $A_1 + A_2 + E$
	1497	1126+371, E	2976 VS	2976	Fund., E, \bar{A}_2
	1593	1380+213, E			
1664 ?	1661	1448+213, $\bar{A}_1 + \bar{A}_2 + \bar{E}$	3450 MW		} various combinations
	1681	1468+213, $A_1 + A_2 + E$	4140 W		
	1751	1380+371, E	4425 MS		
			6100 MW		

* W=weak; VW=very weak; M=medium; S=strong; VS=very strong.

† Resolved doublet; calculated P-R separation, 14.2 cm⁻¹. See text.

‡ 568 is the combination level (213+371), $\bar{A}_1 + \bar{A}_2 + \bar{E}$.

§ The A_1 component of (371²) interacts with the A_1 fundamental at 725 to give two levels, both A_1 , at 694 and 774.

TABLE II. The Raman spectrum of dimethyl acetylene. Frequencies in cm^{-1} .§

GLOCKLER*	GREDY ⁶	KOHLRAUSCH†	PRESENT WORK	ASSIGNMENT AND SYMMETRY
213 (1, b)	212 (W, b) 351 (W)	144 (2, ?) 209 (2, b)	213 (VW)	371-213=158, $\bar{A}_1 + \bar{A}_2 + \bar{E}$ Fund., \bar{E}
374 (5, b) 400 (00)	375 (S)	371 (10) 508 (0)	371 (VVS, D)	Fund., \bar{E} (213 ² =426, $A_1 + E$) 371 ² -213=529, $A_1 + A_2 + 2E$
{ 687 (3, b) 697.4 (4) 773.5 (4) 788.5 (3) }	695 (W) 773 (VW)	692 (3) 767 ($\frac{1}{2}$)	693 (M, P) 774 (M, P)	{ Fund., 725, A_1 371 ² =742, $A_1 + E$
1029 (3)	971 (W)	834 ($\frac{1}{2}$) 1025 (0)	1029 (M, D)	1050-213=837, $A_1 + A_2 + E$ Fund., \bar{E}
1243 (0) 1379 (5, b) 1447 (4, b)	1383 (S) { 1441 (W) 1455 (W) }	1380 (7) 1466 (2, b)	1380 (S, P) 1448 (MS, D)	1468-213=1255, $A_1 + A_2 + E$ † Fund., A_1 Fund., \bar{E}
2201.40 (1) 2280.2 (1) 2234.60 (6) 2312.65 (6)	2238 (S) 2316 (M)	2233 (8) 2311 (5)	2233 (VS, P) 2310 (VS, P)	{ C^{13} isotope effect, shifted from the 2270 doublet. Fund., 2270, A_1 1126 ² =2252, A_1
2736.8 (3) 2861.8 (4) 2920 (7)	2862 (M) 2923 (VS)	2737 (2) 2860 (4, b) 2918 (12, b)	2737 (MW) 2857 (M) 2916 (VS, P)	1380 ² =2760, A_1 ‡ 1448 ² =2896, $A_1 + E$ ‡ Fund., A_1
2961 (4, b)	2961 (VW) 2996	2958 (5, b)	2966 (MW)	Fund., \bar{E}

* Glockler and Davis (reference 4) as corrected by Glockler and Renfrew (reference 5).

† Kohlrausch, Pongratz, and Seka, reference 7.

‡ For other possible assignments, see Table I in the appropriate frequency range.

§ Intensities are given in parentheses: b=broad, S=strong, M=medium, W=weak, VW=very weak, P=polarized ($\rho \leq 6/7$), D=depolarized ($\rho = 6/7$).

(symmetry \bar{A}_1) is included, but those for the over-all translations and rotations are omitted. The A vibrations are nondegenerate, the E vibrations doubly degenerate; the unbarred vibrations are symmetrical, the barred vibrations antisymmetrical, to reflection in a plane perpendicular to the figure axis and bisecting the C—C triple bond. (For a rigorous discussion of this symmetry operation, see Howard's paper.⁸)

The selection rules are also the same (see Table III). The ambiguity with respect to the Raman activity of the E vibrations arises from the same source as in the ethane case. If the internal rotation is free, the E vibrations will be Raman-active; if the rotation is restricted, they will be active or inactive in the Raman effect according as the equilibrium position corresponds to the D_{3h} (eclipsed) or the D_{3d} (staggered) configuration.

Frequency types

If we consider the various types of "bond frequencies" to be expected in dimethyl acetylene, we may apportion them among the symmetry classes as shown in Table III. (The internal rotation is omitted.) The frequencies to be expected for the several vibrations may be estimated by analogy with other molecules, in particular the methyl halides and ethane for the methyl group frequencies, and acetylene for the triple bond stretching frequency. The C—H and C≡C stretching frequencies need no comment. The ethane assignment recently proposed by Barker⁹ would require changes in the expected frequencies for C—H bending; it will appear, however, that the polarization data for dimethyl acetylene leave no doubt as to the correctness

⁹ E. F. Barker, J. Chem. Phys. 7, 277 (1939).

of these values in Table III. The CH_3 rocking frequencies should lie near 1000 cm^{-1} . In ethane, these two frequencies are split apart (827 and 1170 cm^{-1})¹⁰ by the strong interaction between methyl groups; in dimethyl acetylene, the methyl groups being far apart, we should expect these frequencies to lie quite close together.

The C—C stretching frequencies are more uncertain. Despite the shorter C—C bond length in dimethyl acetylene, we may expect these frequencies to lie near 1000 cm^{-1} . The effect of the different masses involved in the two vibrations will split them, however, so that we may expect the symmetrical one (A_1) to lie somewhat below 1000 cm^{-1} , and the unsymmetrical one (\bar{A}_2) somewhat above.

The carbon chain bending frequencies may be estimated from the case of methyl acetylene.¹¹ This molecule has two bending frequencies at 333 and 642 cm^{-1} . The latter may be identified with the bending of the $\text{C}\equiv\text{C}-\text{H}$ angle, since it lies near the bending frequencies of C_2H_2 (605 and 730 cm^{-1}); the 333 cm^{-1} frequency is then associated with the $\text{C}\equiv\text{C}-\text{CH}_3$ angle, and the bending frequencies in dimethyl acetylene should lie near this value.

Assignment

The selection rules (Table III) allow but four polarized Raman lines arising from fundamentals; actually six such lines are found at 693 , 774 , 1380 , 2233 , 2310 , and 2916 cm^{-1} (Table II). Two cases of accidental degeneracy are indicated: one arising from interaction between a fundamental at about 725 cm^{-1} and the first overtone of the 371 Raman line ($371^2=742$); the other from a fundamental at about 2270 cm^{-1} and the first overtone of a frequency near 1135 cm^{-1} . We thus have determined the A_1 frequencies to be 725 , 1380 , 2270 , and 2916 cm^{-1} , as given in Table IV. It is to be noted that in this case, unlike that of ethane, the 1380 cm^{-1} fundamental appears in the Raman effect.

Comparison of the observed frequencies with the estimates and selection rules of Table III allows us immediately to assign the fundamentals above 1300 cm^{-1} as shown in Table IV. (The

2976 cm^{-1} infra-red band is undoubtedly an unresolved complex containing both the \bar{A}_2 and E fundamentals; our resolution in this region is quite low.)

The two carbon-chain bending frequencies may be assigned to the Raman lines at 213 and 371 cm^{-1} ; since we should expect the E vibration to be the more weakly Raman-active, we assign this fundamental to the 213 cm^{-1} line. The depolarized Raman line at 1029 cm^{-1} , obviously a fundamental, may be assigned to the \bar{E} CH_3 rocking frequency; thus the assignment of the \bar{E} fundamentals is completed.

The two remaining unassigned fundamentals are the E CH_3 rocking vibration and the \bar{A}_2 C—C stretching. One of these must lie near 1135 cm^{-1} , as is shown by the resonance splitting of the 2270 cm^{-1} A_1 Raman line, discussed above. The only observed frequency near this value is the 1126 cm^{-1} infra-red band.¹² For the other un-

TABLE III. Types of vibrations in dimethyl acetylene and their distribution among the symmetry classes.

TYPE OF VIBRATION	A_1	\bar{A}_2	E	\bar{E}	EXPECTED FREQUENCY
C—H stretching	1	1	1	1	2900–3000
$\text{C}\equiv\text{C}$ stretching	1	0	0	0	2100–2200
C—H bending, \perp^*	0	0	1	1	1440–1480
C—H bending, \parallel^*	1	1	0	0	1380
CH_3 rocking	0	0	1	1	ca. 1000
C—C stretching	1	1	0	0	ca. 1000
C—C \equiv C—C bending	0	0	1	1	ca. 300
Totals	4	3	4	4	
Activity†	R, P	I, \parallel	I, \perp $R, D?$	R, D	

* \parallel or \perp to the axis of the CH_3 group.
† R, P = Raman active, polarized ($\rho \ll 6/7$); R, D = Raman active, depolarized ($\rho = 6/7$); I, \parallel = infra-red-active, parallel bands; I, \perp = infra-red-active, perpendicular bands.

¹² It would seem more natural to assign 1126 to the overtone of the 568 cm^{-1} band ($568^2=1136$). However, the 568 cm^{-1} band cannot be a fundamental; it is a parallel-type band and would therefore have to be assigned to the A_2 C—C stretching frequency, which surely lies much higher. If 568 cm^{-1} is a combination tone, 1126 cm^{-1} would have to be a quaternary combination if it were not a fundamental, and since the resonance splitting mentioned above demands a fundamental near 1135 cm^{-1} , the assignment given seems the most satisfactory. The possibility of the resonance splitting arising from a binary combination near 2270 cm^{-1} , instead of an overtone, has not been overlooked. Such a combination, however, would have to be of type ($A_2 \times \bar{A}_2$), ($E \times E$), or ($\bar{E} \times \bar{E}$), in order to have a component of symmetry A_1 . A study of the frequencies will show the impossibility of finding a reasonable assignment which satisfies this condition; we have accordingly assumed an overtone to be responsible for the resonance splitting.

¹⁰ B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, J. Chem. Phys. **6**, 682 (1938); and reference 17.

¹¹ B. L. Crawford, Jr., J. Chem. Phys. **7**, 140 (1939).

assigned fundamental, we choose the 1050 cm^{-1} infra-red band, partly because of its fairly strong intensity, and partly because combination assignments indicate this frequency (e.g., the 671 and 835 cm^{-1} bands). We assign 1050 to the E , and 1126 to the \bar{A}_2 class, thus completing the assignments of fundamentals as given in Table IV.

Using the fundamentals thus assigned, the frequencies of all infra-red-active binary combinations and overtones below 3000 cm^{-1} were calculated; difference tones involving the 213 and 371 cm^{-1} fundamentals were included (the Boltzmann factors at 298°K being 0.35 and 0.17 , respectively). These calculated frequencies are compared with the observed spectrum in Table I. Certain ternary and quaternary combinations have been added, to account for all the observed bands.

The doublet structure observed in the 568 cm^{-1} band indicates that this is of the parallel type, in agreement with the selection rules. The observed $P-R$ branch separation of 14 cm^{-1} agrees quantitatively with the value of 14.2 cm^{-1} calculated from Gerhard and Dennison's formula¹³ (interatomic distances used in finding the moments of inertia were those given below); the nonappearance of the Q branch also agrees with their treatment.

Since combination tones appear more weakly in the Raman effect than in infra-red absorption, the complete table of calculated Raman-active combination frequencies was not drawn up; Table II gives the assignments for the observed Raman lines. The assignment of the 2201.40 and 2280.2 cm^{-1} lines, found by Glockler and Davis,⁴ to the C^{13} isotope effect was suggested by Glockler and Renfrew.⁵ This assignment agrees with calculated isotope shifts, as will be discussed below.

The doublet structures found by Glockler and Davis⁴ in the 694 and 774 cm^{-1} lines are not inconsistent with the curves given by Placzek and Teller¹⁴ for a parallel vibration, when allowance is made for the effect of the weaker Q branch. It must be remembered, however, that the theoretical curves should be compared only with *gas* phase data of fairly high resolution.

In any case, this explanation is not applicable to the doublet in the 1448 cm^{-1} line, reported by Gredy,⁶ since this line is depolarized and consequently of the perpendicular type.

The moderately strong intensity of the overtone at 2857 cm^{-1} is probably due to some resonance with the fundamental at 2916 cm^{-1} ; this effect is observed in other compounds containing methyl groups.

NORMAL COORDINATE TREATMENT

Approximate factoring

By using the symmetry of the molecule, the secular equation for the internal vibrations can be factored into one cubic and three quartic factors (Table III). Each of these factors contains a $\text{C}-\text{H}$ stretching frequency of $2900-3000\text{ cm}^{-1}$; by an appropriate choice of the symmetry coordinates used to set up the secular equation, these frequencies may be approximately factored off, and the problem reduced to one quadratic and three cubic equations.¹⁵ This approximation was found to be accurate to within 2 cm^{-1} for all frequencies, and the reduction of the order of the factors effected a great saving of labor.

Potential function

A valence-force potential function, including interaction terms, was used. The bond distances

TABLE IV. The fundamental frequencies of dimethyl acetylene, observed and calculated, in cm^{-1} .

	OBS.	CALC.	ERROR %	FORCE CONSTANTS INVOLVED†
A_1 :	725 1380 2270 2916	722* 1402 2273* 2904	-0.4 +1.6 +0.1 -0.4	$(K_C + \frac{1}{2}k_{CC}), k_{CA}, [k_{C\gamma}]$ $[H_\alpha, H_\beta, h_{\alpha\beta}, k_{C\gamma}]$ $[K_A], k_{CA}$ $[K_H]$
\bar{A}_2 :	1126 1380 (2976)	1124* 1402 2904	-0.2 +1.6 (-2.4)	$(K_C - \frac{1}{2}k_{CC}), [k_{C\gamma}]$ $[H_\alpha, H_\beta, h_{\alpha\beta}, k_{C\gamma}]$ $[K_H]$
E :	213 1050 1468 (2976)	214* 1036 1476 3019	+0.5 -1.3 +0.5 (+1.4)	$(H_\phi + \frac{1}{2}h_{\phi\phi})$ $[H_\beta]$ $[H_\alpha, H_\beta, h_{\alpha\beta}]$ $[K_H]$
\bar{E} :	371 1029 1448 2966	370* 1040 1476 3019	-0.3 +1.1 +1.9 +1.8	$(H_\phi - \frac{1}{2}h_{\phi\phi})$ $[H_\beta]$ $[H_\alpha, H_\beta, h_{\alpha\beta}]$ $[K_H]$

* These frequencies were used to adjust the unknown force constants $K_C, k_{CC}, k_{CA}, H_\phi$, and $h_{\phi\phi}$.

† Force constants adopted from C_2H_6 and C_2H_2 are in brackets, [].

¹³ S. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

¹⁴ G. Placzek and E. Teller, Zeits. f. Physik **81**, 209 (1933).

¹⁵ B. L. Crawford, Jr., and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939). The method used to find the appropriate symmetry coordinates was developed in collaboration with Professor E. B. Wilson, Jr.; it will be described in a future publication.

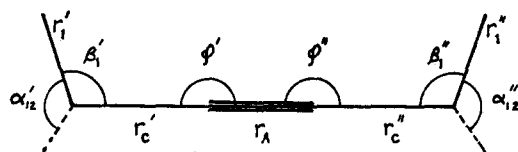


FIG. 4. Potential energy variables for dimethyl acetylene. Dotted lines indicate projections of C-H bonds r_2' , r_3' , r_2'' , r_3'' , on the plane of the paper. Equilibrium values of α_{ij}' , α_{ij}'' , β_i' , β_i'' , are all $109^\circ 28'$, the tetrahedral angle.

and valence angles used are shown in Fig. 4. The equilibrium values were assumed to be the same as the corresponding ones in methyl acetylene;^{16, 17} the values adopted were: C-H, 1.093, C-C, 1.462, C \equiv C, 1.204Å, with tetrahedral angles in the CH₃ groups.

The assumption was made that the part of the potential function pertaining to the CH₃ groups would be the same as in ethane, *except* that interactions between the two CH₃ groups would be negligible in dimethyl acetylene because of their greater separation. Accordingly, the potential function used by Stitt¹⁸ was adopted, the interactions between methyl groups being omitted. This gave the following:

$$2V_1 = K_H \sum_6 (\Delta r_{i'}')^2 + H_\alpha r_1^2 \sum_6 (\Delta \alpha_{ij}')^2 + H_\beta r_1^2 \sum_6 (\Delta \beta_i')^2 + h_{\alpha\beta} r_1^2 \sum_{12} (\Delta \beta_i') (\Delta \alpha_{ij}') + k_{C\alpha} r_1 \sum_6 (\Delta r_{C'}) (\Delta \alpha_{ij}') + k_{C\beta} r_1 \sum_6 (\Delta r_{C'}) (\Delta \beta_i'),$$

where $i = 1, 2, 3$, and the summations are taken over both ' and '' variables. (The number of terms in each summation is indicated.) The force constants $k_{C\alpha}$ and $k_{C\beta}$ always appear as $(k_{C\alpha} - k_{C\beta}) = k_{C\gamma}$. The values of these five "methyl group" constants (Table V), were taken from Stitt's¹⁸ results. Inasmuch as the C-C bond in dimethyl acetylene is not the same as that in ethane, the use of this value for $k_{C\gamma}$ is somewhat arbitrary.

The remaining part of the potential function

¹⁶ G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem. **41**, 123 (1937).

¹⁷ L. Pauling, H. D. Springall and K. J. Palmer, J. Am. Chem. Soc. **61**, 927 (1939).

¹⁸ F. Stitt, J. Chem. Phys. **7**, 297 (1939). Dr. Stitt's notation differs somewhat from ours. His K_H , K_α , K_β , $K_{\alpha\beta}$, $K_{C\alpha}$, and $K_{C\beta}$ correspond to our K_H , H_α , H_β , $h_{\alpha\beta}$, $k_{C\alpha}$, and $k_{C\beta}$, respectively.

TABLE V. Force constants involved in dimethyl acetylene.

CONSTANT	TYPE	VALUES (10 ⁶ DYNES/CM)	COMPARISON VALUE
K_H	C-H stretching	4.79*	
H_α	HCH angle bending	0.46*	
H_β	HCC angle bending	0.55*	
$h_{\alpha\beta}$	angle interaction	+0.02*	
$k_{C\gamma}$	C-C stretching—angle interaction	-0.47*	
K_A	C \equiv C stretching	15.587†	
K_C	C-C stretching	5.18 ₃	4.50*
k_{CC}	C-C bond interaction	+0.38 ₆	
k_{CA}	C-C, C \equiv C interaction	+0.44	
H_φ	C \equiv C-C bending	0.155	0.2096†
$h_{\varphi\varphi}$	angle interaction	+0.134	+0.1567†

* Values from C₂H₆, Stitt (reference 18).

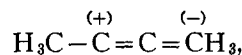
† Values from C₂H₂, Colby (references 19 and 20).

used is similar to that used for acetylene:¹⁹

$$2V_2 = K_A (\Delta r_A)^2 + K_C [(\Delta r_C')^2 + (\Delta r_C'')^2] + k_{CC} (\Delta r_C') (\Delta r_C'') + k_{CA} (\Delta r_A) [(\Delta r_C') + (\Delta r_C'')] + H_\varphi r_C^2 [(\Delta \varphi')^2 + (\Delta \varphi'')^2] + h_{\varphi\varphi} r_C^2 (\Delta \varphi') (\Delta \varphi'').$$

The force constant for the acetylenic bond, K_A , was taken to be the same as in C₂H₂ (Table V). The other constants were regarded as unknowns to be evaluated from the observed frequencies.

The observed shortening of the C-C single bond with respect to that in ethane^{16, 17} has certain implications regarding the force constants K_C and k_{CC} . In qualitative agreement with Badger's rule, we should expect K_C to be greater than in C₂H₆. Moreover, if we regard this shortening as evidence of contributions from allenic structures such as:¹⁷



we should expect k_{CC} to be fairly large, and positive. The sign follows from the fact that contraction of r_C' will favor an allenic structure involving a single bond at r_C'' ; this single-bond character will in turn favor an *extension* of r_C'' . Hence the potential energy should be lower when $\Delta r_C' = -\Delta r_C''$, and this implies that k_{CC} is positive.

¹⁹ W. F. Colby, Phys. Rev. **47**, 388 (1935).

Results of calculations

The force constants finally adopted are given in Table V; the frequencies calculated from them are compared with the observed values in Table IV. The last column in Table IV lists, opposite each frequency, the force constants which have an appreciable effect on that frequency. Thus, in the E factor, the constants H_ϕ and $h_{\phi\phi}$ will control the lowest frequency (213 cm^{-1}), but the three higher frequencies will change by a wave number or two at most, for the maximum range of possible values of these constants.

The agreement of the calculated frequencies with the observed is quite good. In the case of the frequencies marked with an asterisk in Table IV, this agreement is not significant: five force constants are determined from five known frequencies. The other ten frequencies, however, are determined by constants *which were transferred from another molecule* (ethane); the excellent agreement obtained (maximum error 1.9 percent) lends support to the idea that valence-force potential constants have a real physical meaning, and can be transferred from one molecule to another in cases where similar structures are involved. The agreement of the rocking frequencies in the E and \bar{E} factors (1036 and 1040 cm^{-1} , calculated) is especially pleasing. The corresponding frequencies in ethane (830 and 1200 cm^{-1}) are quite different; yet the ethane force constants give the correct frequencies for dimethyl acetylene.

The values of K_C and k_{CC} accord with the *a priori* considerations given above. The comparison between the bending constants H_ϕ and $h_{\phi\phi}$ ($\text{C}\equiv\text{C}-\text{C}$ angles) with the corresponding constants in acetylene ($\text{C}\equiv\text{C}-\text{H}$ angles) is given in Table V in terms of *linear* constants. Alternatively, we may express the potential function for such distortions in terms of *angular* constants; i.e., the terms in V_2 involving $(\Delta\phi')$

and $(\Delta\phi'')$ will be

$$H_\phi'[(\Delta\phi')^2 + (\Delta\phi'')^2] + h_{\phi\phi}'(\Delta\phi')(\Delta\phi''),$$

instead of those given above. The comparison now becomes:

	C_4H_6	C_2H_2
H_ϕ'	0.331	0.234
$h_{\phi\phi}'$	+0.286	+0.175

where H_ϕ' and $h_{\phi\phi}'$ are in units of ($10^{-11}\text{ erg/radian}^2$).²⁰ The two apparently discordant comparisons are of course in agreement when the physical meanings of the two types of bending constant are considered.

The effect of the C^{13} isotope can be calculated from the normal coordinate treatment. The observed effect (see Table II) is complicated by the resonance splitting of the expected 2270 cm^{-1} Raman line. We may calculate²¹ the isotopic shift for each of the unsplit levels separately, however; the mean of these shifts should agree with the mean of the observed isotopic shifts. The A_1 fundamental at 2270 cm^{-1} should be shifted by 46.4 cm^{-1} . The \bar{A}_2 fundamental at 1126 cm^{-1} should be shifted by 12.8 cm^{-1} ; if we neglect anharmonic forces, its overtone should be shifted by 25.6 cm^{-1} . The mean of 46.4 and 25.6 gives us an expected mean shift of 36.0 cm^{-1} ; the mean of the observed shifts is 32.8 cm^{-1} .

In concluding, I wish to express my thanks to Professor G. B. Kistiakowsky for the loan of the material studied, and to Professor E. B. Wilson, Jr., for proposing this research and for contributing many helpful suggestions to its progress.

²⁰ The values given for C_2H_2 , here and in Table V, were recalculated from Colby's formulas (reference 19). Colby used the values 1.08 and 1.19 \AA for the $\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ distances, respectively; we have used 1.057 and 1.204 \AA . This change will not affect the force constants for the linear vibrations of C_2H_2 . It should be noted that in the nonlinear part of the C_2H_2 potential function, our H_ϕ' is equal to Colby's K_1 , while our $h_{\phi\phi}' = 2K_2$ in his notation.

²¹ For the method used in calculating the isotope shifts, see reference 14, page 229.