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The Non-Degenerate Vibrations of Dimethylacetylene, Diacetylene, and Dimethyldiacetylene

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By using force constants obtained from the observed non-degenerate frequencies of dimethylacetylene and diacetylene, the non-degenerate frequencies of dimethyldiacetylene were calculated. It was found that when several of these force constants were modified, agreement to within 2 percent of the observed values of the frequencies was possible. In order to check the values of the modified force constants the non-degenerate frequencies of diacetylene were recalculated. The central C—C stretching force constant was found to have a value of $3.234_2 \times 10^5$ dynes/cm which is much less than the normal value (5×10^5 dynes/cm) for a C—C stretching force constant. Finally, the previous tentative assignment of the observed Raman frequencies of dimethyldiacetylene has been revised as a result of the calculations.

INTRODUCTION

IN their analysis of the vibrational spectrum of diacetylene, Wu and Shen¹ found that the value of the stretching force constant for the carbon-carbon single bond was much lower than the value usually obtained for a C—C stretching frequency. They obtained a value of 3.58×10^5 dynes/cm which seems low when compared with a normal value of about 5×10^5 dynes/cm. Since Meister and Cleveland² have obtained the Raman spectrum of dimethyldiacetylene, and because a calculation of the fundamental frequencies of this molecule was necessary in order to check the tentative assignments of the observed frequencies made by the same investigators, it seemed possible that such a calculation should indicate whether this lowering of the value of the C—C stretching force constant also occurs for dimethyldiacetylene.

In order to calculate the non-degenerate fundamental frequencies for dimethyldiacetylene, it was necessary to obtain force constants for the potential energy function. These were obtained from molecules having a structure similar to that of dimethyldiacetylene. For the carbon chain force constants the diacetylene molecule was used, while the methyl group force constants were obtained from the dimethylacetylene molecule.

* This paper is a report on an investigation carried out by Mr. Arnold G. Meister in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Illinois Institute of Technology.

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¹ T. Y. Wu and S. T. Shen, *Chin. J. Phys.* **2**, 128 (1936).

² Arnold G. Meister and Forrest F. Cleveland, *J. Chem. Phys.* **12**, 393 (1944).

It was hoped that a similar method could be used for the doubly degenerate vibrations of dimethyldiacetylene but, unfortunately, this was not the case. The assignments of the doubly degenerate vibrations of diacetylene are still uncertain and no meaningful set of force constants could be obtained with the present assignments.³ Either selection rules had to be violated in order to obtain reasonable force constants or if the selection rules were obeyed meaningless force constants resulted. It seems that it will be necessary to obtain the Raman spectrum of gaseous diacetylene since the Raman data now available is for the liquid state. Also, an investigation of the infra-red spectrum of dimethyldiacetylene would be very helpful in determining the doubly degenerate vibrations of both dimethyldiacetylene and diacetylene. So, for these reasons, no treatment will be made of the doubly degenerate vibrations of dimethylacetylene, diacetylene, or dimethyldiacetylene.

The Wilson *FG* matrix method⁴ was used in all the calculations. It was very convenient because certain sections of the matrices involved were identical for some of the molecules being considered. As a further simplification, the C—H stretching frequencies for the methyl group (*ca.* 3000 cm^{-1}) were "split out" from the rest of the frequencies by making the appropriate force constants become infinite.⁴ This procedure reduced considerably the number of determinants

³ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 325.

⁴ E. B. Wilson, Jr., *J. Chem. Phys.* **7**, 1047 (1939); **9**, 76 (1941).

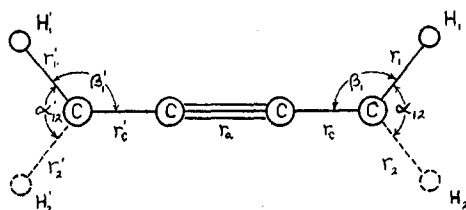


FIG. 1. Bond distances and interbond angles for dimethylacetylene. (Atoms H_3 and H_3' are omitted for clarity and simplicity.)

which had to be evaluated since each secular equation of the n th degree was reduced to one of the $(n-1)$ th degree.

NORMAL COORDINATE TREATMENT

Dimethylacetylene Molecule

Although Crawford⁵ has calculated the fundamental frequencies for dimethylacetylene, it was

felt that the force constants should be recalculated since Crawford used the old value of Avogadro's number (6.06×10^{23}) in his work. Furthermore, he did not calculate all the force constants from the observed frequencies, since he was interested only in establishing the frequencies using calculations involving force constants most of which were transferred from ethane and acetylene. Following Crawford,⁵ the dimethylacetylene molecule was assumed to have the symmetry D_{3h} . Such a symmetry permits only four type A_1 non-degenerate vibrations and three type \bar{A}_2 non-degenerate vibrations. The various bond distances and interbond angles used to determine the internal coordinates are shown in Fig. 1, except those associated with H_3 and H_3' which are omitted for clarity and simplicity.

From the internal coordinates the following symmetry coordinates were formed: for the A_1 vibrations

$$R_1 = \Delta r_a,$$

$$R_2 = \frac{1}{\sqrt{2}}(\Delta r_c + \Delta r_c'),$$

$$R_3 = \frac{1}{(6)^{\frac{1}{2}}}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_1' + \Delta r_2' + \Delta r_3'),$$

$$R_4 = \frac{1}{(12)^{\frac{1}{2}}}(\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{31} + \Delta \alpha_{12}' + \Delta \alpha_{23}' + \Delta \alpha_{31}' - \Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 - \Delta \beta_1' - \Delta \beta_2' - \Delta \beta_3');$$

and for the \bar{A}_2 vibrations

$$R_1 = \frac{1}{\sqrt{2}}(\Delta r_c - \Delta r_c'),$$

$$R_2 = \frac{1}{(6)^{\frac{1}{2}}}(\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_1' - \Delta r_2' - \Delta r_3'),$$

$$R_3 = \frac{1}{(12)^{\frac{1}{2}}}(-\Delta \alpha_{12} - \Delta \alpha_{23} - \Delta \alpha_{31} + \Delta \alpha_{12}' + \Delta \alpha_{23}' + \Delta \alpha_{31}' + \Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_1' - \Delta \beta_2' - \Delta \beta_3').$$

The potential energy function for the non-degenerate vibrations was the same as the one used by Crawford.⁵ It was

$$2V = k_H \sum_6 (\Delta r_i)^2 + k_a r_1^2 \sum_6 (\Delta \alpha_{ij})^2 + k_\beta r_1^2 \sum_6 (\Delta \beta_i)^2 + 2k_{a\beta} r_1^2 \sum_{12} (\Delta \beta_i)(\Delta \alpha_{i, i\pm 1}) \\ + 2k_{ca} r_1 \sum_6 (\Delta r_c)(\Delta \alpha_{ij}) + 2k_{c\beta} r_1 \sum_6 (\Delta r_c)(\Delta \beta_i) + k_c [(\Delta r_c)^2 + (\Delta r_c')^2] + k_a (\Delta r_a)^2 \\ + 2k_{cc} (\Delta r_c)(\Delta r_c') + 2k_{ca} (\Delta r_a)(\Delta r_c + \Delta r_c'),$$

⁵ B. L. Crawford, Jr., J. Chem. Phys. 7, 555 (1939).

where $r_1 = 1.093\text{\AA}$ (the equilibrium value of the C-H bond distance⁵), $i = 1, 2$, or 3 , the subscript to the summation sign indicates the number of terms in the summation, and the summations are taken over primed and unprimed variables.

From the potential energy matrix and the matrix formed from the coefficients of the internal coordinates as obtained from the symmetry coordinates, one gets the following F matrices: for the A_1 vibrations

$$F = \begin{vmatrix} A_1 & & & \\ k_a & \sqrt{2}k_{ca} & 0 & 0 \\ \sqrt{2}k_{ca} & k_c + k_{cc} & 0 & \frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} \\ 0 & 0 & k_H & 0 \\ 0 & \frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} & 0 & \frac{1}{2}r_1^2K_{\alpha\beta} \end{vmatrix};$$

and for the \bar{A}_2 vibrations

$$F = \begin{vmatrix} \bar{A}_2 & & & \\ k_c - k_{cc} & 0 & -\frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} \\ 0 & k_H & 0 \\ -\frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} & 0 & \frac{1}{2}r_1^2K_{\alpha\beta} \end{vmatrix},$$

where $k_{c\gamma} = k_{c\alpha} - k_{c\beta}$ and $K_{\alpha\beta} = k_{\alpha} + k_{\beta} - 4k_{\alpha\beta}$.

The G matrices were obtained from relations given by Wilson.⁴ They were the following, assuming tetrahedral angles for the methyl groups: for the A_1 vibrations

$$G = \begin{vmatrix} A_1 & & & \\ 2\mu_c & -\sqrt{2}\mu_c & 0 & 0 \\ -\sqrt{2}\mu_c & 2\mu_c & -\frac{\sqrt{3}}{3}\mu_c & \frac{4}{3}\sqrt{3}a\mu_c \\ 0 & -\frac{\sqrt{3}}{3}\mu_c & \mu_H + \frac{\mu_c}{3} & -\frac{4}{3}a\mu_c \\ 0 & \frac{4}{3}\sqrt{3}a\mu_c & -\frac{4}{3}a\mu_c & 2a^2\left(\mu_H + \frac{8}{3}\mu_c\right) \end{vmatrix};$$

TABLE I. Force constants for the non-degenerate vibrations of dimethylacetylene.

Type	Present value (10 ⁶ dynes/cm)	Crawford's value ⁵ (10 ⁶ dynes/cm)
k_a	16.31 ₂	15.587
k_c	5.129 ₆	5.183
k_H	5.014 ₁	4.79
k_{ca}	0.4705 ₉	0.22
k_{cc}	0.1153	0.193
$k_{c\gamma}$	-0.2618 ₆	-0.235
$K_{\alpha\beta}$	0.9640 ₉	0.97

and for the \bar{A}_2 vibrations

$$G = \begin{vmatrix} \bar{A}_2 & & & \\ 2\mu_c & -\frac{\sqrt{3}}{3}\mu_c & -\frac{4}{3}\sqrt{3}a\mu_c \\ -\frac{\sqrt{3}}{3}\mu_c & \mu_H + \frac{\mu_c}{3} & \frac{4}{3}a\mu_c \\ -\frac{4}{3}\sqrt{3}a\mu_c & \frac{4}{3}a\mu_c & 2a^2\left(\mu_H + \frac{8}{3}\mu_c\right) \end{vmatrix},$$

where $a = 1/r_1$.

When the observed frequencies, as given by Crawford,⁵ were used with the F and G matrices, the force constants given in Table I were obtained with $\mu_c = 5.0183 \times 10^{22} \text{ g}^{-1}$ and $\mu_H = 5.9742 \times 10^{23} \text{ g}^{-1}$. The value of $k_{c\gamma}$ is a mean value obtained from the observed frequencies of methyl deuteride and ethane as determined by the authors in an unpublished investigation. It is to be noted that most of the force constants are given to five significant figures. While the experimental data do not warrant this accuracy, since most of the data were given to only four significant figures, such a procedure was followed in order to be consistent in the calculations and in order to establish four significant figure frequency values. Frequency values obtained from such force constants were always rounded off to four significant figures.

Diacetylene Molecule

Although Wu and Shen¹ obtained force constants for the non-degenerate vibrations of diacetylene, a different type of potential energy function was used in their work so that it was necessary to redetermine the force constants. The symmetry of the diacetylene molecule is

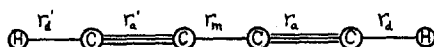


FIG. 2. Bond distances and interbond angles for diacetylene.

$D_{\infty h}$. For this symmetry, one finds that diacetylene has three non-degenerate type A_g vibrations and two non-degenerate type A_u vibrations. The various bond distances and interbond angles used to determine the internal coordinates are given in Fig. 2.

From the internal coordinates the following symmetry coordinates were formed: for the A_g vibrations

$$R_1 = \Delta r_m,$$

$$R_2 = \frac{1}{\sqrt{2}}(\Delta r_d + \Delta r_d'),$$

$$R_3 = \frac{1}{\sqrt{2}}(\Delta r_a + \Delta r_a');$$

and for the A_u vibrations

$$R_1 = \frac{1}{\sqrt{2}}(\Delta r_d - \Delta r_d'),$$

$$R_2 = \frac{1}{\sqrt{2}}(\Delta r_a - \Delta r_a').$$

The potential energy function used was of the following form:

$$2V = k_m(\Delta r_m)^2 + k_d[(\Delta r_d)^2 + (\Delta r_d')^2] + k_a[(\Delta r_a)^2 + (\Delta r_a')^2] + 2k_{ac}[(\Delta r_a)(\Delta d + \Delta r_m) + (\Delta r_a')(\Delta d' + \Delta r_m)] + 2k_{aa}(\Delta r_a)(\Delta r_a').$$

This expression for the potential energy leads to the following F matrices: for the A_g vibrations

$$F = \begin{matrix} A_g \\ \begin{vmatrix} k_m & 0 & \sqrt{2}k_{ac} \\ 0 & k_d & k_{ac} \\ \sqrt{2}k_{ac} & k_{ac} & k_a + k_{aa} \end{vmatrix} \end{matrix},$$

and for the A_u vibrations

$$F = \begin{matrix} A_u \\ \begin{vmatrix} k_d & k_{ac} \\ k_{ac} & k_a - k_{aa} \end{vmatrix} \end{matrix}.$$

The G matrices obtained from the relations

given by Wilson⁴ were the following: for the A_g vibrations

$$G = \begin{matrix} A_g \\ \begin{vmatrix} 2\mu_c & 0 & -\sqrt{2}\mu_c \\ 0 & \mu_H + \mu_c & -\mu_c \\ -\sqrt{2}\mu_c & -\mu_c & 2\mu_c \end{vmatrix} \end{matrix},$$

and for the A_u vibrations

$$G = \begin{matrix} A_u \\ \begin{vmatrix} \mu_H + \mu_c & -\mu_c \\ -\mu_c & 2\mu_c \end{vmatrix} \end{matrix}.$$

When the values of the observed frequencies for the type A_u vibrations as given by Herzberg,³ and the values of k_a and k_{ac} as obtained from dimethylacetylene are used with the F and G matrices and the values of μ_c and μ_H already given, one obtains the following values for k_d and k_{aa} :

$$k_d = 6.110_5 \times 10^5 \text{ dynes/cm},$$

$$k_{aa} = 1.136 \times 10^5 \text{ dynes/cm}.$$

The value of k_m was obtained by using the 644 cm^{-1} type A_g fundamental frequency and the F and G matrices for the A_g vibrations. The value of k_m obtained was

$$k_m = 3.234_2 \times 10^5 \text{ dynes/cm}.$$

Since only one type A_g frequency was used in obtaining the force constants, the remaining A_g frequencies were calculated. The results of this calculation are given in Table II as well as the observed values³ for comparison purposes. The observed value of ν_1 is enclosed in parentheses, since this frequency was not actually observed but, according to Herzberg,³ is believed to be very close to this value.

Dimethyldiacetylene Molecule

Since the dimethyldiacetylene molecule is very similar to the dimethylacetylene molecule and

TABLE II. Calculated and observed values of the A_g fundamental frequencies of diacetylene.

Designation	Calculated (cm ⁻¹)	Observed ³ (cm ⁻¹)
ν_1	3357	(3350)
ν_2	2219	2183
ν_3	644	644

because the methyl groups are much farther apart in dimethyldiacetylene, one would suspect that for dimethyldiacetylene very little hindered rotation occurs. So the symmetry of the dimethyldiacetylene molecule was assumed to be D_{3h}' . For this symmetry the molecule will have five type A_1 non-degenerate fundamental vibrations and four type \bar{A}_2 non-degenerate vibrations. The various bond distances and interbond angles used to determine the internal coordinates are shown in Fig. 3, except those associated with H_3 and H_3' which, as in Fig. 1, are omitted for clarity and simplicity.

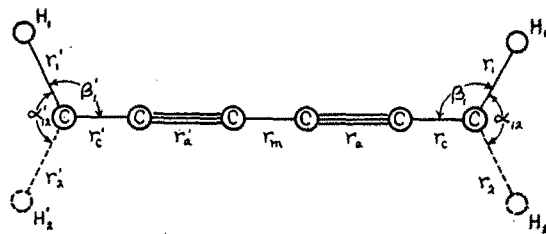


FIG. 3. Bond distances and interbond angles for dimethyldiacetylene. (Atoms H_3 and H_3' are omitted for clarity and simplicity.)

From the internal coordinates the following symmetry coordinates were formed: for the A_1 vibrations

$$R_1 = \Delta r_m,$$

$$R_2 = \frac{1}{\sqrt{2}}(\Delta r_a + \Delta r_a'),$$

$$R_3 = \frac{1}{\sqrt{2}}(\Delta r_c + \Delta r_c'),$$

$$R_4 = \frac{1}{(6)^{\frac{1}{2}}}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_1' + \Delta r_2' + \Delta r_3'),$$

$$R_5 = \frac{1}{(12)^{\frac{1}{2}}}(\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{31} + \Delta \alpha_{12}' + \Delta \alpha_{23}' + \Delta \alpha_{31}' - \Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 - \Delta \beta_1' - \Delta \beta_2' - \Delta \beta_3');$$

and for the type \bar{A}_2 vibrations

$$R_1 = \frac{1}{\sqrt{2}}(\Delta r_a - \Delta r_a'),$$

$$R_2 = \frac{1}{\sqrt{2}}(\Delta r_c - \Delta r_c'),$$

$$R_3 = \frac{1}{(6)^{\frac{1}{2}}}(\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_1' - \Delta r_2' - \Delta r_3'),$$

$$R_4 = \frac{1}{(12)^{\frac{1}{2}}}(-\Delta \alpha_{12} - \Delta \alpha_{23} - \Delta \alpha_{31} + \Delta \alpha_{12}' + \Delta \alpha_{23}' + \Delta \alpha_{31}' + \Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_1' - \Delta \beta_2' - \Delta \beta_3').$$

The potential energy function used was a combination of those already given for dimethylacetylene and diacetylene. It was

$$\begin{aligned} 2V = & k_H \sum_6 (\Delta r_i)^2 + k_a r_1^2 \sum_6 (\Delta \alpha_{ij})^2 + k_\beta r_1^2 \sum_6 (\Delta \beta_i)^2 + 2k_{a\beta} r_1^2 \sum_{12} (\Delta \beta_i)(\Delta \alpha_{i, i \pm 1}) \\ & + 2k_{ca} r_1 \sum_6 (\Delta r_c)(\Delta \alpha_{ij}) + 2k_{c\beta} r_1 \sum_6 (\Delta r_c)(\Delta \beta_i) + k_c [(\Delta r_c)^2 + (\Delta r_c')^2] + k_a [(\Delta r_a)^2 + (\Delta r_a')^2] \\ & + k_m (\Delta r_m)^2 + 2k_{aa} (\Delta r_a)(\Delta r_a') + 2k_{mc} (\Delta r_m)(\Delta r_c + \Delta r_c') \\ & + 2k_{ac} [(\Delta r_a)(\Delta r_c + \Delta r_m) + (\Delta r_a')(\Delta r_c' + \Delta r_m)]. \end{aligned}$$

This expression for the potential energy leads to the following F matrices: for the A_1 vibrations

$$F = \begin{array}{c|ccccc} A_1 & & & & & \\ \hline & k_m & \sqrt{2}k_{ac} & \sqrt{2}k_{mc} & 0 & 0 \\ & \sqrt{2}k_{ac} & k_a + k_{aa} & k_{ac} & 0 & 0 \\ & \sqrt{2}k_{mc} & k_{ac} & k_c & 0 & \frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} \\ & 0 & 0 & 0 & k_H & 0 \\ & 0 & 0 & \frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} & 0 & \frac{1}{2}r_1^2K_{\alpha\beta} \end{array};$$

and for the \bar{A}_2 vibrations

$$F = \begin{array}{c|cccc} \bar{A}_2 & & & & \\ \hline & k_a - k_{aa} & k_{ac} & 0 & 0 \\ & k_{ac} & k_c & 0 & -\frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} \\ & 0 & 0 & k_H & 0 \\ & 0 & \frac{(6)^{\frac{1}{2}}}{2}r_1k_{c\gamma} & 0 & \frac{1}{2}r_1^2K_{\alpha\beta} \end{array}$$

Assuming tetrahedral angles for the methyl groups, the G matrices obtained were the following: for the A_1 vibrations

$$G = \begin{array}{c|ccccc} A_1 & & & & & \\ \hline & 2\mu_c & -\sqrt{2}\mu_c & 0 & 0 & 0 \\ & -\sqrt{2}\mu_c & 2\mu_c & -\mu_c & 0 & 0 \\ & 0 & -\mu_c & 2\mu_c & -\frac{\sqrt{3}}{3}\mu_c & \frac{4}{3}\sqrt{3}a\mu_c \\ & 0 & 0 & -\frac{\sqrt{3}}{3}\mu_c & \mu_H + \frac{\mu_c}{3} & -\frac{4}{3}a\mu_c \\ & 0 & 0 & \frac{4}{3}\sqrt{3}a\mu_c & -\frac{4}{3}a\mu_c & 2a^2\mu_H + \frac{16}{3}a^2\mu_c \end{array};$$

and for the \bar{A}_2 vibrations

$$G = \begin{array}{c|cccc} \bar{A}_2 & & & & \\ \hline & 2\mu_c & -\mu_c & 0 & 0 \\ & -\mu_c & 2\mu_c & -\frac{\sqrt{3}}{3}\mu_c & -\frac{4}{3}\sqrt{3}a\mu_c \\ & 0 & -\frac{\sqrt{3}}{3}\mu_c & \mu_H + \frac{\mu_c}{3} & \frac{4}{3}a\mu_c \\ & 0 & -\frac{4}{3}\sqrt{3}a\mu_c & \frac{4}{3}a\mu_c & 2a^2\left(\mu_H + \frac{8}{3}\mu_c\right) \end{array}$$

TABLE III. Calculated and observed values of the A_1 fundamental frequencies of dimethyldiacetylene.

Designation	Calculated value (cm ⁻¹) Using original force constants	Calculated value (cm ⁻¹) Using modified force constants	Observed value ² (cm ⁻¹)
ν_1	2946	2946	2914
ν_2	2329	2265	2264
ν_3	1379	1375	1381
ν_4	1058	965	957
ν_5	461	473	475

Using the F and G matrices for the A_1 vibrations, the necessary force constants transferred from the dimethylacetylene and diacetylene molecules and the values of μ_H and μ_C already given, one obtains the calculated values of the frequencies as given in column two of Table III. For comparison purposes, the observed values as obtained by Meister and Cleveland² also are given in column four.

A glance at Table III indicates that for ν_2 and ν_4 the agreement between the observed and calculated values is not so good. However, it was found that if the values of k_a , k_{aa} , k_C , and k_{mC} were modified better agreement could be obtained. The modified force constants used are given in Table IV as well as the original values of the same constants. When these modified force constants are used with the F and G matrices for the type A_1 vibrations, one obtains the frequencies given in the third column of Table III. In all cases the agreement is very good and well within the 2 percent limit set by Crawford and Brinkley.⁶

In order to test the modified force constants given in Table IV, the \bar{A}_2 fundamental frequencies were calculated. These frequencies are given in Table V as well as the expected values for the same frequencies. It was necessary to use the expected values for comparison purposes, since the \bar{A}_2 frequencies are allowed only in the infra-red and the infra-red absorption spectrum of dimethyldiacetylene has not been obtained as yet.

The expected values of the \bar{A}_2 frequencies were obtained in the following manner. One would expect the methyl group frequencies to lie close to the values for the same frequencies for the \bar{A}_2 vibrations of dimethylacetylene, since

⁶ B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. 9, 72 (1941).

TABLE IV. Force constants for the non-degenerate vibrations of dimethyldiacetylene.

Type	Original value (10 ⁵ dynes/cm)	Modified value (10 ⁵ dynes/cm)
k_a	16.31 ₂	15.60 ₈
k_m	3.234 ₂	unchanged
k_C	5.129 ₆	4.705 ₀
k_H	5.014 ₁	unchanged
k_{aa}	1.136	0.555 ₀
k_{mC}	0.1153	0.4505
k_{am}	0.4705 ₉	unchanged
$k_{C\gamma}$	-0.2618 ₆	unchanged
$K_{\alpha\beta}$	0.9640 ₉	unchanged

there is even less chance for interaction between the methyl groups in the case of dimethyldiacetylene. For dimethylacetylene these frequencies lie at 2976 and 1380 cm⁻¹, respectively, so that for dimethyldiacetylene it was assumed that ν_1 would lie in the 2950–3000 cm⁻¹ region and ν_3 in the 1350–1400 cm⁻¹ region. In going from diacetylene to dimethyldiacetylene the C≡C symmetrical stretching frequency is changed from 2183 to 2264 cm⁻¹, an increase of 81 cm⁻¹. If one assumes that the \bar{A}_2 antisymmetrical C≡C stretching frequency changes by the same amount, one would expect to find this frequency at 2023+81=2104 cm⁻¹. For this reason ν_2 for dimethyldiacetylene was assumed to lie in the 2100–2150 cm⁻¹ region. The expected value of ν_4 could not be determined so easily. However, it was assumed to lie in the 900–1100 cm⁻¹ region where C–C stretching frequencies usually are found.

As a further check on the set of modified force constants given in Table IV the frequencies of the non-degenerate vibrations of diacetylene were again calculated using these force constants. A modified value of k_d was used, that is, instead of the value 6.110₅×10⁵ dynes/cm as obtained previously from the diacetylene calculations, a value of 6.160₈×10⁵ dynes/cm was used. The results of these calculations are given in Table VI and, for comparison purposes, the observed

TABLE V. Calculated and expected values of the \bar{A}_2 fundamental frequencies for dimethyldiacetylene.

Designation	Calculated value (cm ⁻¹)	Expected value (cm ⁻¹)
ν_1	2946	2950–3000
ν_2	2131	2100–2150
ν_3	1368	1350–1400
ν_4	903	900–1100

TABLE VI. Calculated and observed values of the non-degenerate vibrational frequencies of diacetylene.

Type	Designation	Calculated value (cm ⁻¹)	Observed value ^a (cm ⁻¹)
A_g	ν_1	3366	(3350)
	ν_2	2142	2183
	ν_3	644	644
A_u	ν_1	3350	3350
	ν_2	2023	2023

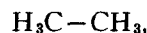
values³ are also given. The agreement between the calculated and observed values is good with the exception of ν_2 of the type A_g vibrations which is about 2 percent below the observed value.

DISCUSSION

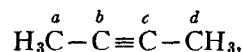
Probably the most significant result of this investigation is the fact that the value of the central C—C stretching force constant (k_m) was found to be the same for dimethyldiacetylene as for diacetylene. It seems difficult to account for such a behavior of this force constant since, if resonance between double and triple bond structures were to occur, one would expect this force constant to have a value greater than the normal value of about 5×10^5 dynes/cm. Furthermore, as Herzberg⁷ has pointed out, electron diffraction data shows that the C—C bond distance for diacetylene is smaller than for ethane, which should indicate a tighter C—C bond for diacetylene than for ethane. For ethane the C—C stretching force constant is 4.50×10^5 dynes/cm.⁸ Also, Pauling, Springall, and Palmer⁹ found that the central C—C bond distance for dimethyldiacetylene was about the same as for diacetylene. However, despite all these reasons for expecting a value for k_m larger than the normal value, the calculations seem to indicate that the value of k_m for both diacetylene and dimethyldiacetylene is $3.234_2 \times 10^5$ dynes/cm which is considerably lower than the normal value of 5×10^5 dynes/cm.

According to the quantum theory of valence, the force of attraction between two atoms is caused by a concentration of negative electrical

charge between the two atoms. Thus in ethane,

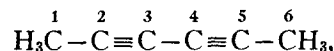


the attraction between the two carbon atoms is caused by a large charge density in the region between the two atoms. In dimethylacetylene,



the charge density between carbon atoms a and b and between carbon atoms c and d is still greater than in ethane, as is shown by the greater value of the carbon-carbon single bond force constant and the decreased value of the bond length obtained by electron diffraction investigations. This must be caused by electrostatic repulsion between electrons forming the triple bond between carbon atoms b and c , causing these electrons to spend part of their time in the regions between carbon atoms a and b or c and d , thus increasing the charge density between these atoms and accordingly increasing the strength of the two carbon single bonds.

For dimethyldiacetylene,



the unusually small value of the carbon-carbon single bond force constant, between carbon atoms 3 and 4, can be understood by supposing that the strong electrostatic repulsion of the negative charge concentrated between carbon atoms 2 and 3 and 4 and 5 prevents a normal concentration of charge between carbon atoms 3 and 4 of the central single bond. This would decrease the strength of this single bond.

The smaller than normal bond distance for this central carbon-carbon single bond may be explained by noting that there is an extraordinarily large charge concentration in the region between carbon atoms 2 and 5. It is thus probable that there are considerable attractive forces between carbon atoms 2 and 4, 3 and 5, and perhaps even between 2 and 5. This force of compression

TABLE VII. Comparison of the carbon-carbon force constants for dimethylacetylene and dimethyldiacetylene.

Bond	Dimethylacetylene (10^5 dynes/cm)	Dimethyldiacetylene (10^5 dynes/cm)
$\text{C}\equiv\text{C}$	16.31 ₂	15.60 ₂
End C—C	5.129 ₆	4.705 ₀

⁷ See reference 3, p. 324.

⁸ See reference 3, p. 193.

⁹ L. Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939).

might well operate to shorten the distance between atoms 3 and 4, even though the strength of the bond between atoms 3 and 4 is itself less than normal.

One may notice also that the triple bond force constants and the end single bond force constants in dimethyldiacetylene are less than the corresponding values for dimethylacetylene (see Table VII). This is the result that would be expected if the unusually large concentration of charge along the axis of the molecule results, as seems probable, in strong electrostatic repulsions that force much of the charge off the axis and prevent the maximum concentration of charge in the space between the atoms.

Another result of this investigation was the disclosure that the tentative assignments of the observed Raman frequencies of dimethyldiacetylene, as made by Meister and Cleveland,² had to be revised. In their analysis they assigned the 475 cm^{-1} frequency as an \bar{E} fundamental and the 686 cm^{-1} frequency as an A_1 fundamental. These assignments were based on a comparison with the diacetylene molecule. As a result of the calculations in this investigation, it appears that the 475 cm^{-1} frequency is an A_1 fundamental, and the 686 cm^{-1} frequency is assumed to be an E or \bar{E} fundamental. Other minor changes in assignments were found to be necessary, so in Table VIII the revised assignment of the observed Raman frequencies of dimethyldiacetylene is given. It will be noticed that some frequencies have been given two possible assignments. In all such cases it will be seen that doubly degenerate frequencies are involved and the ambiguity cannot be removed until the doubly degenerate frequencies are calculated or otherwise determined.

In conclusion, one might point out the similarities which exist between the F and G matrices

TABLE VIII. Revised assignment of the Raman frequencies of dimethyldiacetylene.*

$\Delta\nu$	I	ρ	Assignment and symmetry
247	80	0.64	Fundamental E or \bar{E}
475	220	0.64	Fundamental A_1
686	vw		Fundamental E or \bar{E}
957	vw		Fundamental A_1
1020	vw		Fundamental \bar{E}
1151	vw		$686 + 475 = 1161$, E or \bar{E}
1185	vw		$1426 - 247 = 1179$, $A_1 + A_2 + E$ or $A_1 + A_2 + \bar{E}$
1228	vw		$957 + 247 = 1204$, E or \bar{E}
1253	17		$1020 + 247 = 1267$, $A_1 + A_2 + E$ or $A_1 + A_2 + \bar{E}$
1381	115	0.62	Fundamental A_1
1426	5		Fundamental \bar{E}
1458	vw		Fundamental E
2225	vw		C^{13} isotope
2264	1000	0.40	Fundamental A_1
2309	9		$\{957 + 1381 = 2338$, A_1
2502	vw		$2264 + 247 = 2511$, E or \bar{E}
2821	vw		$1381 + 1426 = 2807$, \bar{E}
2848	21		$1426^2 = 2852$, $A_1 + E$
2914	400	0.17	Fundamental A_1
2954	39		Fundamental \bar{E}

* $\Delta\nu$ =Raman displacement in cm^{-1} , I is the relative intensity measured with a microdensitometer, vw =lines that were too weak to measure with the microdensitometer, ρ =depolarization factor, and the braces indicate a probable case of Fermi resonance.

for the molecules considered. For example, the upper 3×3 matrix, formed from the F matrix for the type A_1 vibrations of dimethyldiacetylene, is much the same as the F matrix for the A_g vibrations of diacetylene. The lower 3×3 matrix, formed from the same type A_1 F matrix is almost the same as the lower 3×3 matrix formed from the F matrix for the type A_1 vibrations of dimethylacetylene. A similar behavior is exhibited by the G matrices for the A_1 and A_g vibrations for the molecules concerned and also the F and G matrices for the \bar{A}_2 and A_u vibration types. One would expect the F and G matrices to behave in this manner, since dimethyldiacetylene has a number of frequencies which are the same as those of diacetylene and dimethylacetylene.