ON THE FORCE CONSTANTS AND FUNDAMENTAL VIBRATIONS OF DIACETYLENE

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ABSTRACT

The assignment of the fundamental frequencies of C_4H_2 given by Timm and Mecke is discussed and a new assignment in accord with the selection rules is suggested. Nine force constants for the molecule are calculated according to Timm and Mecke's assignment, while the new assignment gives no reasonable constants for the deformation vibrations. Further study of the Raman spectrum and the infrared absorption is necessary for a final classification of the deformation frequencies.

THE diacetylene C_4H_2 molecule, on the assumption of a linear model, possesses nine modes of vibrations, five along the axis, and four doubly degenerate ones perpendicular to the axis. An assignment of these fundamental frequencies has been made by Timm and Mecke[1] from their Raman spectrum data and from the infrared absorption bands of Bartholomé[2]. There is little doubt concerning the parallel vibrations; for the perpendicular vibrations, however, their assignment, though very plausible from consideration of similar vibrations in molecules such as C_2N_2, seems to be incompatible with the selection rules in the infrared and the Raman effect for a linear molecule. A new assignment is here attempted which seems to account for all the observed Raman lines and the infrared bands in accord with the selection rules. A comparison of the two schemes is given in tables 1 and 2, the notation of Mecke being used.

(1) Timm and Mecke, Z. f. Phys. **94**, 1, (1935)

R. Mecke, Hand. und Jahrbuch d. chem.-Physik, Bd. 9/II, 392 (1934)

(2) E. Bartholome, Z. f. Phys. Chem. B, **23**, 152 (1932)

TABLE 1

Fundament vibrations of C_4H_2. * assumed value, region not covored in Bartholome's work, ** assumed value but not observed by Timm and Mecke (1) in the Raman spectrum.

Vibrations	Mecke	Here suggested
ν_{CH} (a)	3350 Inf.	3350
$\nu_{C \equiv C}$(a)	2085 Inf.	2085
ν_{CH} (s)	3310 Ra. **	3350 **
$\nu_{C \equiv C}$(s)	2183 Ra.	2183
ν_{C-C} (s)	644 Ra.	644
δ_{CH}(a)	730 Inf.	730 Inf.
δ_{C}(a)	230 Ra.	~470 *
δ_{CH}(s)	720 **	488 Ra.
δ_{C}(s)	488 Ra.	230 Ra.

This assignment, satisfactory as it seems on considerations of selection rules, confronts another difficulty when one calculates the force constants of the molecule, as is shown below.

From the nine fundamental frequencies, we may determine nine force constants, five for the parallel vibrations and four for the perpendicular vibrations. For the parallel vibrations, let the coordinates of the atoms taken in the order $H - C \equiv C - C \equiv C - H$ be x_1, x_2, x_3, x_4, x_5, x_6, and let the relative displacements be $X_1 = x_2 - x_1$, $X_2 = x_3 - x_2$, $X_3 = x_4 - x_3$, $X_4 = x_5 - x_4$, $X_5 = x_6 - x_5$. The kinetic energy and the potential energy are then

$$2\,T = m(\dot{x}_1^2 + \dot{x}_6^2) + M(\dot{x}_2^2 + \dot{x}_3^2 + \dot{x}_4^2 + \dot{x}_5^2)$$

$$2V = k_1 X_3^2 + k_2(X_2^2 + X_4^2) + k_3(X_1^2 + X_5^2) + 2k_4(X_1 X_2 + X_3 X_4)$$
$$+ 2k_5(X_2 X_3 + X_3 X_4)$$

Here interactions between atoms more than two bonds apart are neglected. The determinant factorizes into a product of two determinants, one of the second and one of the third order. For the two asymmetric and hence infrared active frequencies, the quadratic equation gives

TABLE 2.

Classification of Raman lines and infrared absorption band of C_4H_2. The classification of the combination frequencies here suggested is, except for the 705, 730, 1440, cm^{-1} bands, the same as that tentatively given by Bartholomé who assumed $\delta_{CH}(s) \sim 530$, $\delta_C(a) \sim 500$, $\delta_C(s) \sim 250$.

	cm^{-1} Intensity		Classification	
			Timm & Mecke	here suggested
Raman lines	231	(0)	$\delta_C(a)$	$\delta_C(s)$
	411	(1)	$\nu_{C-C}(s) - \delta_C(a)$	$\nu_{C-C}(s) - \delta_C(s)$
	488	(2)	$\delta_C(s)$	$\delta_{CH}(s)$
	644	(2)	$\nu_{C-C}(s)$	$\nu_{C-C}(s)$
	2183	(10)	$\nu_{C\equiv C}(s)$	$\nu_{C\equiv C}(s)$
Infrared bands	705	(7)	$\delta_C(a) + \delta_C(s)$	$\delta_C(a) + \delta_C(s)$
	730	(2)	$\delta_{CH}(a)$	$\delta_{CH}(a)$
	1235	(10)	$\delta_{CH}(a) + \delta_C(s)$	$\delta_{CH}(a) + \delta_{CH}(s)$
	1440	(2)	$\delta_{CH}(a) + \delta_C(s)$	$\nu_{C\equiv C}(s) - \delta_{CH}(a)$
	2085	(3)	$\nu_{C\equiv C}(a)$	$\nu_{C\equiv C}(a)$
	2950	(0.7)		$\nu_{C\equiv C}(s) + \delta_{CH}(a)$
	2980	(0.8)		
	3030	(1)		
	3120	(1)		$\nu_{CH}(a) - \delta_C(s)$
	3350	(3)	$\nu_{CH}(a)$	$\nu_{CH}(a)$
	3550	(0.3)		$\nu_{CH}(a) + \delta_C(s)$
	3920	(1)		$\nu_{CH}(a) + \nu_{C-C}(s)$
	6500	(0.3)	$\nu_{CH}(a) + \nu_{CH}(s)$	$\nu_{CH}(a) + \nu_{CH}(s)$
	8950?	(0.1)		
Assumed			$\delta_{CH}(s)$ 720?	$\delta_C(a)$ 470?
			$\nu_{CH}(s)$ 3310?	$\nu_{CH}(s)$ 3350?

$$5.76 \; \lambda_1 \lambda_2 = k_2 k_3 - k_4^2$$

$$5.76 \, (\lambda_1 + \lambda_2) = 0.96 \, k_2 + 6.24 \, k_3 - 0.96 \, k_4$$

For the three symmetric and Raman active frequencies, the cubic equation gives

$$59.5 \, \lambda_3 \lambda_4 \lambda_5 = k_1 k_2 k_3 - k_1 k_4^2 - k_3 k_5^2$$

$$59.5 \left(\lambda_3 \lambda_4 + \lambda_4 \lambda_5 + \lambda_5 \lambda_3 \right) = k_1 k_2 + 13 k_1 k_3 + 12.5 k_2 k_3 + 2 k_4 k_5$$

$$- 2 k_1 k_4 - 12.5 k_4^2 - 28 k_3 k_5 - 2 k_5^2$$

$$59.5 \left(\lambda_3 + \lambda_4 + \lambda_5 \right) = 12 k_1 + 12 k_2 + 64.5 k_3 - 11 k_4 - 26 k_5$$

where $\qquad \lambda_i = 4 \pi_2 \nu_i^2 \cdot 9.10^{20}/6.06 \times 10^{23}$

By substituting into these equations $\nu_1 = \nu_{CH}(a) = 3350$, $\nu_2 = \nu_{C \equiv C}(a) = 2085$, $\nu_3 = \nu_{CH}(s) = 3350$, $\nu_4 = \nu_{C \equiv C}(s) = 2185$, $\nu_5 = \nu_{C-C}(s) = 644$, one obtains five equations for the five constants k_1, k_2, k_3, k_4, k_5. Their values are found by so adjusting them that the two sides of each equation are as close to each other as possible. The force constants so determined are given in table 3.

TABLE 3.

Force constants of $C_4 H_2$ in dynes/cm.

	$C_4 H_2$	$C_2 H_6$	$C_2 H_2$
$k_1 (c - c)$	2.85×10^5	4.96×10^5	
$k_2 (c \equiv c)$	16.3×10^5		15.7×10^5
$k_3 (c = H)$	5.95×10^5		5.88×10^5
k_4	0.75×10^5		
k_5	1.38×10^5		

The constant k_2 for the triple bond carbons and k_3 for the CH bond are quite close to the values obtained[5, 6] for acetylene. The constant k_1 for the single bond carbons, however, is considerably smaller than that calculated from ethane $C_2 H_6$. The rather low value of the frequency $\nu_5 = \nu_{C-C}(s) = 644$ is is responsible for the low value of k_1 obtained here. The difference between the values of k_1 in $C_4 H_2$ and $C_2 H_6$ may be partly understood when one considers the rather large interaction between the second and the fourth carbon atoms as indicated by the rather high value of the constant k_5, and when one remembers the fact that in obtaining the value 4.96×10^5 for $C_2 H_6$, the interaction between the hydrogen atoms in one CH_3 group and the carbon atom in the other CH_3 group

is neglected[3].   However, the difference is so great that it seems desirable to reexamine the Raman spectrum of C_4H_2 in the neighbourhood of 700 cm^{-1}.

For the perpendicular vibrations, we choose the angles between two neighbouring bonds as the variables.   Let y_1, y_2, y_3, y_4, y_5, y_6, be the displacements of the atoms in the order
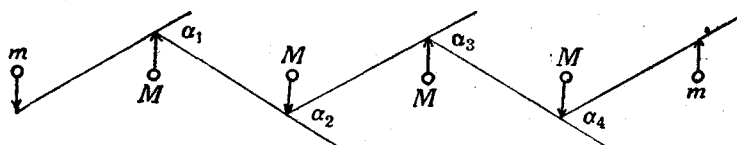

Fig. 1

$H - C \equiv C - C \equiv C - H$ from their equilibrium positions in directions perpendicular to the axis.   If the distances $C = H$, $C \equiv C$, $C - C$ be a, b, c respectively, then

(3) Sutherland and Dennison, Proc. Roy. Soc. A. **148**, 250 (1935).

By taking into account only interactions between neighbouring atoms, they introduced for the five parallel vibrations of C_2H_6 (or C_2H_4) a potential function containing only four constants. On eliminating the four constants from the five equations giving the five frequencies, there results one relation between the five frequencies. That the observed frequencies are consistent with this relation justifies the negligence of the interection hetween the hydrogen atoms in one CH_3 (or CH_2) group and the C atom in the other CH_3 (or CH_2) group. That this, however, may not be done in molecules where the hydrogen atoms are replaced by other atoms is shown by C_2Cl_4. In this molecule, there is little doubt that the three parallel symmetric vibrations $v_{2\pi}(s)$, $v_\pi(s)$, $\delta_\pi(s)$ are the strong and partially depolarized Raman lines 1570, 447, 234 (Wu, Jour. Chinese Chem. Soc. 4, 402, (1936) and $v_\pi(a)$ is probably of the order 400 cm^{-1} so that $v_\pi(s) + v_\alpha(a)$ is probably one of the infrared bands at 912, 802, 782, 755 cm^{-1} (Wu, Phys. Rev. 46, 495 (1934)), $\delta_\pi(a)$ is probably of the order 350 cm^{-1}. Using these frequencies and the equations similar to those for C_2H_4 given by Sutherland and Dennison, one obtains a force constant for the $C = C$ bond which differs greatly from the value calculated from ethylene C_2H_4. It seems that here the interaction between the Cl atoms of one CCl_2 group and the C atom in the other CCl_2 group is great enough so that it is no longer justified to neglect it. Calculation of the five constants for C_2Cl_4, however, can be made only when the asymmetric parallel vibrations, especially $\delta_\pi(a)$, have been determined with certainty.

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

$$\alpha_1 = \frac{y_2 - y_1}{a} + \frac{y_2 - y_3}{b}, \qquad \alpha_2 = \frac{y_3 - y_2}{b} + \frac{y_3 - y_4}{c}$$

$$\alpha_3 = \frac{y_4 - y_3}{c} + \frac{y_4 - y_5}{b}, \qquad \alpha_4 = \frac{y_5 - y_4}{b} + \frac{y_5 - y_6}{a}$$

The kinetic and the potential energies are

$$2\,T = m\,(\dot{y}_1^2 + \dot{y}_6^2) + M\,(\dot{y}_2^2 + \dot{y}_3^2 + \dot{y}_4^2 + \dot{y}_5^2)$$

$$2\,V = k_6\,(\alpha_1^2 + \alpha_4^2) + k_7\,(\alpha_2^2 + \alpha_3^2) + 2k_8\,(\alpha_1\,\alpha_2 + \alpha_3\,\alpha_4) + 2k_9\,\alpha_2\,\alpha_3$$

Without great error, we assume that the distances $C - H$, $C \equiv C$, $C - C$ are the same as in C_2H_2 and C_2H_6, i.e., $a = 1.08 \times 10^{-8}$, $b = 1.20 \times 10^{-8}$, $c = 1.40 \times 10^{-8}$. The determinantal equation decomposes into two quadratic equations. For the asymmetric vibrations $\delta_{CH}(a)$, $\delta_C(a)$,

$$9.4\ \lambda_6\,\lambda_7 = k_6\,k_7 + k_6\,k_9 - k_8^2$$

$$9.4\,(\lambda_6 + \lambda_7) = 11.2\,k_6\ 1.11\,k_7 - 3.48\,k_8 + 1.11\,k_9$$

For the symmetric vibrations $\delta_{CH}(s)$ $\delta_C(s)$,

$$2.1\ \lambda_8\,\lambda_9 = k_6\,k_7 - k_6\,k_9 - k_8^2$$

$$2.1\,(\lambda_8 + \lambda_9) = 2.44\,k_6 - 0.982\,k_7 - 1.09\,k_8 - 0.982\,k_9.$$

Here $\qquad \lambda_i = 4\pi^2\,\nu_i^2\ 9.10^{20}(10^{-8})^2/6.06 \times 10^{23}$.

If we assume $\delta_{CH}(a) = 750$, $\delta_C(a) = 470$, $\delta_{CH}(s) = 488$, $\delta_C(s) = 231$ so as to be in accord with the selection rules, it is impossible to get any set of reasonable values for the constants k_6, k_7, k_8, k_9. If however one assumes with Timm and Mecke $\delta_{CH}(a) = 750$, $\delta_C(a) = 230$, $\delta_{CH}(s) = 720$, $\delta_C(s) = 388$, then one gets the following values

TABLE 4

Force Constants in C_4H_2 in dynes cm/radian.

$C - H$ and $C \equiv C$	$k_6 = 2.6 \times 10^{-12}$
$C \equiv C$ and $C - C$	$k_7 = 3.6 \times 10^{-12}$
	$k_8 = 0.14 \times 10^{-12}$
	$k_9 = 0.15 \times 10^{-12}$

As there are no known constants in other molecules with which these can be compared, all one can say is that these values seem quite reasonable, and that the assignment of Timm and Mecke is to .be preferred on consideration of the force constants.[5] But then one is again comfronted with the difficulty with the selection rules. The assignment of the Raman line 230 to $\delta_C(a)$ may not be a serious difficulty, as one may assume that $\delta_C(a)$ is of the order of 230. But $\delta_{CH}(s)$ if equal to 720 cm^{-1} should be present in the Raman spectrum. This again suggests a reexamination of the Raman spectrum of C_4H_2, and a study of the degrees of depolarizations of the lines if possible. A study of the infrared absorption bands under higher dispersion and beyond 15μ is desirable. Until more data are available, we may regard any assignment of the perpendicular vibrations as tentative.

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(5) We are indebted to Dr. S. C. Woo for comments concerning this point.