

A force field study of diacetylene molecule by kinetic constant method

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Abstract. The potential constants of diacetylene molecule has been evaluated using kinetic constants. The other molecular constants such as the generalised vibrational mean amplitudes, shrinkage constants, Coriolis coupling constants and centrifugal distortion constants are also calculated using the vibrational frequencies and the results discussed.

Keywords. Molecular dynamics; molecular constants; force field diacetylene molecule; kinetic constants.

1. Introduction

Wilson's group theoretical method of analysis of vibrational molecules is useful in the study of molecular forces (Wilson *et al* 1955). The kinetic constants introduced earlier (Thirugnanasambandam and Mohan 1974, 1975a, b, 1977; Mohan 1977) are important in the architecture and dynamics of molecular vibrations. The purpose of the present paper is to study the several molecular constants of diacetylene molecule. The molecular potential constants of this molecule was evaluated either by transferring C-H bond potential constant from acetylene or assuming the interaction constants (Ferigle *et al* 1953; Ferigle and Weber 1952; Jones 1952; Venkateswarlu *et al* 1967). The assumption of the interaction constants for the conjugated molecules lead to a high degree of inaccuracy due to the uncertainty in the degree of delocalisation of the π electrons of the C atom on which the potential constants depend. However, a re-examination of all the molecular constants of diacetylene molecule on the basis of kinetic constants attempted in the present study leads to interesting results in molecular vibrations.

2. Theoretical considerations

Diacetylene molecule (X_4Y_2 type) which has a conjugated linear structure belongs to the $D_{\infty h}$ point group. The nine fundamental frequencies are distributed as $3\sigma_g^+$ + $2\sigma_u^+$ + $2\pi_g$ + $2\pi_u$. The orientation of the cartesian co-ordinate axes and the

numbering of atoms are shown in figure 1. The traditional symmetry co-ordinates associated with this type of molecules have been used in the present investigation.

3. Kinetic constants, potential constants and compliance constants

The elements of kinetic energy matrix (Wilson *et al* 1955) are used to calculate the kinetic constants. The general expressions for the kinetic constants of diacetylene molecule are given below:

$$k_D = (\mu_x + 4\mu_y)/A$$

$$k_{DD} = \mu_x/A$$

$$k_a = (\mu_x + \mu_y) (\mu_x + 3\mu_y)/\mu_x$$

$$k_{aa} = (\mu_x + \mu_y)^2/\mu_x$$

$$k_r = (\mu_x + 2\mu_y)^2/A\mu_x$$

$$k_{Da} = (\mu_x + 3\mu_y)/A$$

$$k'_{Da} = (\mu_x + \mu_y)/A$$

$$k_{rD} = (\mu_x + 2\mu_y)/A$$

$$k_{rd} = (\mu_x + \mu_y) (\mu_x + 2\mu_y)/\sqrt{2} A\mu_x$$

$$k_\alpha = (ABdr)^{-1} [A\mu_x(r^2 + 2d^2 + 2dr) + 2drB\mu_y]$$

$$k_{\alpha\alpha} = -(ABdr)^{-1} [A\mu_x(r^2 + 2d^2 + 2dr) - 2drB\mu_y]$$

$$k_\beta = (2Ddr AB\mu_x)^{-1} [d^2\mu_y + \mu_x(2D^2 + d^2 + 2Dd)] [r\mu_x A + 2\mu_y BD]$$

$$k_{\beta\beta} = -(2Ddr AB\mu_x)^{-1} [d^2\mu_y + \mu_x(2D^2 + d^2 + 2Dd)] [r\mu_x A - 2\mu_y BD]$$

$$k_{\alpha\beta} = (d + 2D) (2AB d \sqrt{Dr})^{-1} [\mu_x A (r + 2) + 2\mu_y BD]$$

$$k'_{\alpha\beta} = -(d + 2D) (2AB d \sqrt{Dr})^{-1} [\mu_x A (r + 2) - 2\mu_y BD]$$

$$A = 2\mu_y (\mu_x + 2\mu_y)$$

$$B = (Dd)^{-1} \mu_x [\mu_x (r^2 + 4D^2 + 4d^2 + 8Dd + 4dr + 4Dr) + 2\mu_y (r^2 + 2d^2 + 2dr)]$$

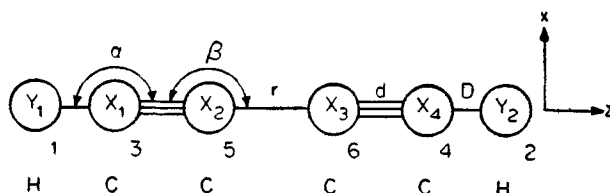


Figure 1. Geometry and the numbering of atoms used for diacetylene molecule.

where μ_x and μ_y are the reciprocal masses of the X and Y atoms respectively. D , d and r represent the equilibrium bond distances of $X - Y$, $X \equiv X$ and $X - X$ bonds respectively.

The F matrix elements are obtained on the basis of most general quadratic potential energy function. They are

σ_r^+ type

$$F_{11} = f_D + f_{DD}$$

$$F_{22} = f_d + f_{dd}$$

$$F_{33} = f_r$$

$$F_{12} = f_{Dd} + f_{Dd}^{\prime}$$

$$F_{13} = \sqrt{2} f_{rD}$$

$$F_{23} = \sqrt{2} f_{rd}$$

σ_d^+ type

$$F_{44} = f_D - f_{DD}$$

$$F_{55} = f_d - f_{dd}$$

$$F_{45} = f_{Dd} - f_{Dd}^{\prime}$$

π_θ type

$$F_{66} = f_\alpha - f_{\alpha\alpha}$$

$$F_{77} = f_\beta - f_{\beta\beta}$$

$$F_{67} = f_{\alpha\beta} - f_{\alpha\beta}^{\prime}$$

π_α type

$$F_{88} = f_\alpha + f_{\alpha\alpha}$$

$$F_{99} = f_\beta + f_{\beta\beta}$$

$$F_{89} = f_{\alpha\beta} + f_{\alpha\beta}^{\prime}$$

The prime relating to the interaction constants indicates the interaction between the bond-distant bond or angle-distant angle.

The secular equations relating to the potential constants have been solved by the method of kinetic constants (Thirugnanasambandam and Mohan 1974, 1975a, 1975b, 1977; Mohan 1977) which provides the required number of additional data through the symmetry kinetic constants and the corresponding symmetry force constants, i.e., $F_{ij}/F_{jj} = K_{ij}/K_{jj}$ ($i < j$). The compliance constants are also evaluated for this molecule by Decius (1963) method.

The structural parameters and the vibrational frequencies employed in the present investigation are taken from Pauling (1939) and Ferigle (1953) respectively. The kinetic constants, potential constants and the compliance constants are given in tables 1-3 respectively.

It may be seen from table 1 that all the kinetic constants assume positive sign for diacetylene molecule. This agrees with the earlier observation on the kinetic constants of carbon suboxide and carbon subsulphide molecules (Mohan 1977).

Table 1. Kinetic constants (10^{-23}).

$K_D(X - Y)$	K_{DD}	K'_{Dd}	K_α	$K_{\beta\beta}$
$K_d(X \equiv Y)$	K_{dd}	K_{rD}	K_β	$K_{\alpha\beta}$
$K_r(X - Y)$	K_{Dd}	K_{rd}	$K_{\alpha\alpha}$	$K'_{\alpha\beta}$
0.1640	0.0017	0.0435	0.1346	0.4540
1.5981	0.5617	0.0837	0.6895	0.1303
2.0762	0.1238	1.0799	0.0085	0.0669

Table 2. Potential constants (10^6 dynes cm^{-1}).

f_D	f_{DD}	f'_{Dd}	f_α	$f_{\beta\beta}$
f_d	f_{dd}	f_{rD}	f_β	$f_{\alpha\beta}$
f_r	f_{Dd}	f_{rd}	$f_{\alpha\alpha}$	$f'_{\alpha\beta}$
6.0885	0.1083	0.2157	0.1683	0.0012
17.7851	2.7803	0.2268	0.1952	0.0430
5.6272	1.3783	2.9270	-0.0205	-0.0092

Table 3. Compliance constants (A/mdyne).

C_D	C_{DD}	C'_{Dd}	C_α	$C_{\beta\beta}$
C_d	C_{dd}	C_{rD}	C_β	$C_{\alpha\beta}$
C_r	C_{Dd}	C_{rd}	$C_{\alpha\alpha}$	$C'_{\alpha\beta}$
0.1673	-0.0025	-0.0002	6.3860	-0.1321
0.0648	-0.0028	0.0000	5.4347	-1.3776
0.2228	-0.0134	-0.0317	0.6629	0.1623

From table 2 the following observations relating to the potential constants may be made:

- (i) The value of acetylenic hydrogen bond force constant (f_D) is reasonable and does not vary much from acetylene.
- (ii) The values obtained for the $\text{C}\equiv\text{C}$ bond stretching force constant (f_d) and the C-C bond stretching force constant (f_r) are reasonable. The present observations agree with those of Ferigle *et al* (1953) and Ferigle and Weber (1952) that the potential constant relating to the middle bond is definitely higher than the single bond C-C stretching potential constant which is about 5 mdyn/A.

- (iii) The values of the bending force constants f_α and f_β appear to have the same magnitude for this molecule.
- (iv) The bond-bond interaction force constants f_{da} , f_{Dd} and f_{rd} assume high values indicating large delocalisation in this molecule.
- (v) The angle-angle interaction force constants $f_{\alpha\alpha}$ and $f'_{\alpha\beta}$ assume negative sign.

On the whole, a systematic set of all the general quadratic potential constants of this molecule is available for the first time.

From table 3 it may be seen that all the interaction compliance constants are negative in sign except $c_{\alpha\alpha}$ and $c'_{\alpha\beta}$. It may also be noticed that the interaction compliance constant c_{rD} assumes zero value. The compliance constants, being the inverse of the force constants, exhibit trends opposite to that of the force constants. The present set of force constants are compared with the results of the earlier authors in table 4. The force constants of diacetylene molecule in the earlier studies were calculated either by transferring the acetylenic bond force constant f_D from the acetylene molecule or by assuming the interaction constants. No such assumptions were made in the present investigation. The force constant relating

Table 4. Comparison of potential constants (10^5 dynes/cm).

f_D	f_{DD}	f'_{Dd}	f_α	$f_{\beta\beta}$	Reference
f_d	f_{da}	f_{rD}	f_β	$f_{\alpha\beta}$	
f_r	f_{Dd}	f_{rd}	$f_{\alpha\alpha}$	$f'_{\alpha\beta}$	
6.0885	0.1083	0.2157	0.1683	0.0012	P.W.
17.7851	2.7803	0.2268	0.1952	0.0430	
5.6272	1.3783	2.9270	-0.0205	-0.0092	a
5.90149	0.206715 to 0.22080	0.0030711 to 0.0028745	
15.5039	0.767722	-0.132044	0.317476 to 0.347455	0.0707 to 0.1269	b
6.63009	
5.6 to 6.1	..	-1.01448 to 0.80129	0.206715 to 0.22081	0.00306702 to 0.00287125	b
16.2134 to 15.1364	-0.250693 to 0.08529	0.597321 to 0.81264	0.317562 to 0.347463	0.0707637 to 0.126828	
6.83743 to 6.59612	b
5.90149	
15.4820	0.03229	0.778701	c
6.63426	-0.081966	
5.82	c
15.12	-0.50	
7.14	-0.50	0.47	

a—Ferigle *et al* (1951); b—Ferigle and Weber (1953); c—Jones (1952).

P.W.—Present work.

to $C\equiv C$ bond in the present study is higher while $C-C$ bond force constant is lower with respect to the earlier studies. The bending force constants f_α and f_β appear to have low values when compared with the previous values. Since all the interaction constants are not available for this molecule, the interaction constants obtained in the present investigation are not compared.

4. Generalised mean square amplitudes

The mean square amplitude matrix elements may be obtained using the normal co-ordinate transformation matrix L from the relation $\Sigma = L \Delta L'$ (Cyvin 1968) and the generalised mean square amplitudes are then calculated following the method of Morino and Hirota (1955). The parallel and perpendicular mean square amplitudes of vibration and the valence mean square amplitudes of vibration at 298.16 K are reported in tables 5a and 5b respectively. These values which are in the expected range could be useful to interpret electron diffraction data of this molecule.

Table 5a. Mean square amplitudes of vibration at 298.16 K (10^{-3} \AA^2).

Vibrations	Parallel	Perpendicular
C-H	5.4464	29.1106
$C\equiv C$	1.3196	35.3115
C-C	2.2578	6.4036
C_3-H_1	6.3440	57.6953
$C_3 \cdots \cdots H_1$	7.5366	52.0079
$C_4 \cdots \cdots H_1$	63.7313	42.7339
$H \cdots \cdots H$	62.8873	55.8822
$C_3 \cdots \cdots C_1$	2.2909	12.0147
$C_4 \cdots \cdots C_1$	0.9039	1.2702

Table 5b. Valence mean square amplitudes (10^{-3} \AA^2).

σ_D (C-H)	σ_{DD}	$\sigma_{D\delta}$	σ_α	$\sigma_{\beta\beta}$
σ_δ ($C\equiv C$)	$\sigma_{\delta\delta}$	σ_{rD}	σ_β	$\sigma_{\alpha\beta}$
σ_r (C-C)	$\sigma_{D\delta}$	$\sigma_{r\delta}$	$\sigma_{\alpha\alpha}$	$\sigma'_{\alpha\beta}$
5.4464	0.0000	0.0000	44.9727	-6.4761
1.3196	-0.0502	0.0000	26.7955	-9.9348
2.2578	-0.4220	-0.6432	-0.1392	2.2037
Mean amplitudes:	l_{C-H}	0.0738 \AA		
	$l_{C\equiv C}$	0.0363 \AA		
	l_{C-C}	0.0475 \AA		

5. Shrinkage constants

The shrinkage effect in linear molecules has been observed from the electron diffraction data by Bastiansen and Tractteberg (1960). These constants may also be theoretically calculated from spectroscopic data (Morino 1960). The shrinkage constants of diacetylene molecule is reported in table 6. The present values are in the expected range.

6. Coriolis coupling constants

The Coriolis coupling constants, useful to interpret vibrational spectra, may be evaluated theoretically from a reliable set of force constants. The Coriolis coupling constants in the present case arises from the coupling

$$\sigma_g^+ \times \pi_g; \sigma_u^+ \times \pi_u; \pi_g \times \pi_g \text{ and } \pi_u \times \pi_u.$$

The Coriolis matrix elements C_{ij}^a ($a = x, y, z$) are obtained by the vector method of Meal and Polo (1956) and the zeta matrix elements may be evaluated from the relation

$$\zeta^a = L^{-1} C^a (L')^{-1}$$

where L is the normal co-ordinate transformation matrix. Table 7 deals with the evaluated Coriolis coupling constants of diacetylene molecule. The high magnitude of $\zeta_{16}^{x,y}$, $\zeta_{27}^{x,y}$, $\zeta_{48}^{x,y}$, $\zeta_{59}^{x,y}$, $\zeta_{6a,6b}^z$, $\zeta_{7a,7b}^z$, $\zeta_{8a,8b}^z$ and $\zeta_{9a,9b}^z$ indicate that the

Table 6. Linear shrinkage effect (10^{-3} A).

$\delta_1 (C_1 \cdots \cdots H_1)$	31.4941	$\delta_4 (H \cdots \cdots H)$	109.4451
$\delta_2 (C_2 \cdots \cdots H_1)$	47.4383	$\delta_5 (C_2 \cdots \cdots C_1)$	29.6705
$\delta_3 (C_4 \cdots \cdots H_1)$	82.6156	$\delta_6 (C_4 \cdots \cdots C_1)$	63.7161

Table 7. Coriolis coupling constants.

$\zeta_{1,6a}^y = -\zeta_{1,6b}^z$	-0.9541	$\zeta_{1,7a}^y = -\zeta_{1,7b}^z$	-0.3015	$\zeta_{4,8a}^y = -\zeta_{4,8b}^z$	-0.9695
$\zeta_{2,6a}^z = -\zeta_{2,6b}^y$	0.2817	$\zeta_{2,7a}^y = -\zeta_{2,7b}^z$	-0.9071	$\zeta_{5,8a}^y = -\zeta_{5,8b}^z$	0.2451
$\zeta_{3,6a}^y = -\zeta_{3,6b}^z$	0.1011	$\zeta_{3,7a}^y = -\zeta_{3,7b}^z$	0.2934	$\zeta_{4,9a}^y = -\zeta_{4,9b}^z$	-0.2133
				$\zeta_{5,9a}^y = -\zeta_{5,9b}^z$	-0.9770
$\zeta_{6a,6b}^z$	1.0000	$\zeta_{7a,7b}^z$	1.0000	$\zeta_{8a,8b}^z$	1.0000
				$\zeta_{8a,9b}^z$	1.0000
$\zeta_{6a,7b}^z$	0.0000	$\zeta_{7a,6b}^z$	0.0000	$\zeta_{8a,9b}^z$	0.0000
				$\zeta_{9a,8b}^z$	0.0000

coupling between the vibrations concerned are significant. The zeta values obey the following quadratic sum rules.

$$\begin{aligned}
 (\zeta_{16}^x, y)^2 + (\zeta_{26}^{x,y})^2 + (\zeta_{36}^x, y)^2 &= 1 \\
 (\zeta_{17}^x, y)^2 + (\zeta_{27}^x, y)^2 + (\zeta_{37}^x, y)^2 &= 1 \\
 (\zeta_{48}^x, y)^2 + (\zeta_{58}^x, y)^2 &= 1 \\
 (\zeta_{49}^x, y)^2 + (\zeta_{59}^x, y)^2 &= 1 \\
 (\zeta_{6a}^z)^2 + (\zeta_{6b, 7a}^z)^2 &= 1 \\
 (\zeta_{7a}^z, 7b)^2 + (\zeta_{7b, 6a}^z)^2 &= 1 \\
 (\zeta_{8a}^z, 8b)^2 + (\zeta_{8b, 9a}^z)^2 &= 1 \\
 (\zeta_{9a}^z, 9b)^2 + (\zeta_{8a, 9b}^z)^2 &= 1
 \end{aligned}$$

7. Centrifugal distortion constants

The determination of the exact rotational levels of a non-rigid molecule requires the knowledge of centrifugal distortion constants. Following Kivelson and Wilson (1952, 1953) the centrifugal distortion constants of this molecule has been calculated using the potential constants obtained in the present investigation and is found to be 0.1674 kHz, which agrees reasonably well with the observed value of 0.09921 kHz by Callomen and Stoicheff (1957).

No experimental data seem to be available for diacetylene molecule for comparing the values of the vibrational mean amplitudes, the shrinkage constants and the Coriolis constants of the present study. The molecular constants obtained by the kinetic constant method are in the expected range and a systematic set of molecular constants are available for this molecule for the first time.

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