

Mean Amplitudes of Vibration and Shrinkage Effects of Acetylene from Spectroscopic Data

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Force constants, mean-square amplitude matrix elements, mean amplitudes of vibration and shrinkage effects for the acetylene molecule have been calculated from spectroscopic data. Small harmonic vibrations have been assumed. The shrinkage effects at the temperature of 298°K came out with the values 0.019 Å and 0.041 Å for the C··H and H··H distances, respectively. In particular some studies have been made on certain approximation methods. By transferring the CC stretching frequency from acetylene to the simple two-particle model CH·CH, a very good approximation for the CC mean amplitude of vibration was produced.

The theory of vibrational mean-square amplitudes for linear symmetrical X_2Y_2 molecules¹ has been applied to acetylene. It would have been interesting to compare the presently calculated mean amplitudes of vibration and shrinkage effects with those from electron-diffraction, but the latter ones are unfortunately not available at present. Anyhow the spectroscopic calculations for acetylene (H—C≡C—H) along with those of cyanogen² (N≡C—C≡N) are believed to be of great interest in connection with some recent electron-diffraction experiments on the H—C≡C—C≡N molecule.

An additional reason for undertaking this work was the desire of making a study of the effect of certain approximation methods. In this connection the acetylene molecule has been treated tentatively as a two-particle structure CH·CH.

RIGOROUS TREATMENT

The adopted values for the equilibrium interatomic distances are²⁻⁴ $R = 1.058_5$ Å for C—H and $D = 1.204_7$ Å for C≡C. The fundamental frequencies from Herzberg⁵ were applied and are not much different from some later observations⁶. The normal frequencies (ω) were computed from the fundamentals (ν) by means of approximately estimated anharmonicity constants (x), following the method of Dennison^{7,8}. The anharmonicity constants are defined by

$$\nu_i = (1 - x_i)\omega_i$$

and the assumption

$$x_i/x_i^* = \nu_i/\nu_i^*$$

is made. Here the asterisk is used to identify the appropriate quantities of acetylene- d_2 . The resulting numerical values are presented in Table 1.* The

Table 1. Fundamentals (ν), anharmonicity constants (x), and normal frequencies (ω) for acetylene and acetylene- d_2 .

C ₂ H ₂	No.	$\nu(\text{cm}^{-1})$	x^a	$\omega(\text{cm}^{-1})$
Σ_g^+	1	3373.7	0.03939	3512.0
	2	1973.8	0.02 ^b	2014.1
Σ_u^+	3	3287	0.02107	3357.7
Π_g	4	611.8	0.01 ^b	618.0
Π_u	5	729.1	0.02634	748.8
C ₂ D ₂	No.	$\nu(\text{cm}^{-1})$	x^a	$\omega(\text{cm}^{-1})$
Σ_g^+	1	2700.5	0.03153	2788.4
	2	1762.4	0.01786	1794.5
Σ_u^+	3	2427	0.01555	2465.3
Π_g	4	510.9 ^c	0.00835	515.2
Π_u	5	539.1	0.01947	549.7

^a Approximate computations. All of the reported decimals are not significant.

^b Assumed.

^c Calculated.

value of $x_2 = 0.02$ has been chosen within the limited range making $x_1 > x_2$ and both of these constants positive. The calculated value of $\nu_4^* = 510.9 \text{ cm}^{-1}$ is well compatible with the corresponding value of 505 cm^{-1} obtained from a combination band, as quoted by Herzberg⁵.

Table 2. Force constants and mean-square amplitude matrix elements for acetylene.

Symbol ^a	Force constant (mdyne/Å)	Symbol ^a	Mean-square amplitude (Å ²) ^b $T = 0 \quad 298^\circ\text{K}$	
F_1	6.412	Σ_1	0.006860	
F_2	29.561	Σ_2	0.001285	
F_{12}	9.194	Σ_{12}	-0.001473	
F_3	6.175	Σ_3	0.005400	
F_4	0.1216	Σ_4	0.05046	0.05586
F_5	0.2699	Σ_5	0.02756	0.02908

^a For explanation of symbols, see Ref.¹

^b For the figures in the middle column the temperature dependence is insignificant.

* Similar corrections for anharmonicity in acetylene have been performed previously by many workers; cf. Refs. ^{5,6} and references cited therein. Special reference is made to a paper of Wu and Kiang.⁹ From their reported values the calculated anharmonicity constants x_1 , x_2 , x_3 and x_4 for C₂H₂ (in the present notation) are 0.0404, 0.0159, 0.0295, and 0.0322, respectively. The agreement is satisfactory.

The force constants (which reproduce the normal frequencies for acetylene and acetylene- d_2 given in Table 1) are shown in Table 2, along with the mean-square amplitude matrix elements at $T = 0$ and 298°K for C_2H_2 . The calculated mean amplitudes of vibration and shrinkage effects are presented in Table 3.

Table 3. Mean amplitudes of vibration and shrinkage effects for acetylene.

Distance	Symbol ^a	Mean amplitude of vibration (Å) ^{b,c}	
		$T = 0$	298°K
CH	u_r		0.0783
CC	u_d		0.0358
C·H	u_{r+d}		0.0730
H·H	u_{2r+d}		0.1041
Distance	Symbol ^a	Shrinkage effect (Å)	
		$T = 0$	298°K
C·H	δ_{r+d}^g	0.017	0.019
H·H	δ_{2r+d}^g	0.038	0.041

^{a,b} See footnotes to Table 2.

^c The values show good correspondence with those of Bakken.¹⁰

APPROXIMATE TREATMENTS

Separation of frequencies. The approximate method of separating high and low frequencies developed by Wilson¹¹ may be applied to the Σ_g^+ species of acetylene. The corresponding simplified F and G matrices read

$$F^\circ = \begin{bmatrix} F_1^\circ & 0 \\ 0 & F_2^\circ \end{bmatrix}; \quad G^\circ = \begin{bmatrix} (m_C + m_H)/m_C m_H & 0 \\ 0 & 2/(m_C + m_H) \end{bmatrix}$$

Hence the following equations are obtained for the force constants of the F° matrix:

$$F_1^\circ = 4\pi^2 c^2 \omega_1^2 m_C m_H / (m_C + m_H) \quad (1)$$

$$F_2^\circ = 2\pi^2 c^2 \omega_2^2 (m_C + m_H) \quad (2)$$

$$F_{12}^\circ = 0 \quad (3)$$

The resulting equations for the mean-square amplitudes of vibration according to this approximation are given in the following.

$$(u_r^\circ)^2 = (\hbar/16\pi^2 c) [(m_C + m_H)/m_C m_H] [(1/\omega_1) \coth(\hbar c \omega_1 / 2kT) + (1/\omega_3) \coth(\hbar c \omega_3 / 2kT)] \quad (4)$$

$$(u_d^\circ)^2 = (\hbar/4\pi^2 c \omega_2) [1/(m_C + m_H)] \coth(\hbar c \omega_2 / 2kT) \quad (5)$$

$$(u_{r+d}^\circ)^2 = (u_r^\circ)^2 + (u_d^\circ)^2 \quad (6)$$

$$(u_{2r+d}^\circ)^2 = (\hbar/4\pi^2 c \omega_1) [(m_C + m_H)/m_C m_H] \coth(\hbar c \omega_1 / 2kT) + (u_d^\circ)^2 \quad (7)$$

Symbols:

- m_C = mass of the C atom,
 m_H = mass of the H atom,
 c = velocity of light,
 h = Planck's constant,
 k = Boltzmann's constant,
 T = absolute temperature.

For the numerical results, see Table 4.

Table 4. Approximate mean amplitudes of vibration for acetylene after separation of frequencies.

Distance	Symbol	Value	Difference ^a
CH	u_r	0.0727	-0.0056
CC	u_d	0.0359	+0.0001
C·H	u_{r+d}	0.0810	+0.0080
H·H	u_{2r+d}	0.0178	+0.0037

^a Compared with the values in Table 3.

Table 5. Approximate results for some quantities related to the CC bond of acetylene.

Approximation	ω_2 (cm^{-1})	H_2^a ($\text{\AA}/\text{mdyne}$)	F_2 ($\text{mdyne}/\text{\AA}$)	u_d (\AA)
1. alternative $\omega = \omega_2$	2014.1	0.06434	15.543	0.0359
2. alternative $1/F = H_2$	2067.4	0.06106	16.376	0.0354
3. alternative $F = F_2$	2777.6	0.03383	29.561	0.0305

^a From the rigorous calculation: $H_2 = 0.06106 \text{ \AA}/\text{mdyne}$.

Simplified model. The approximate treatment based on simplified molecular models has been discussed elsewhere.¹² The method has been applied previously to allene¹³, benzene¹⁴, cyclopropane¹², and other molecules. In the present case of acetylene the simplified treatment turns out to be extremely simple, as the molecule may be regarded as a two-particle structure and treated as a diatomic molecule $(\text{CH})_2$. Hence the following equations apply to the force constant and the mean-square amplitude of vibration:

$$F = 2\pi^2 c^2 \omega^2 (m_C + m_H) \quad (8)$$

$$u^2 = (h/4\pi^2 c \omega) [1/(m_C + m_H)] \coth(hc\omega/2kT) \quad (9)$$

It may be assumed that if the CC normal frequency from acetylene (*viz.* ω_2) is inserted as ω in eqn. (9), the resulting u^2 value will represent an approximation for the mean-square amplitude of vibration for the CC distance (*viz.* u_d^2). This approximation will be referred to as the first alternative and is seen to be coincident with the result from the separation of frequencies (*cf.* eqn. 5).

It is interesting to notice that the force constant F from the first-alternative approximation, being identical with F_2° of eqn. (2), deviates largely from the rigorously calculated F_2 (cf. Tables 2 and 5). This feature may be attributed to the fact that F_2 is not a pure CC stretching force constant, as is apparent from the comparatively high value of the interaction constant F_{12} (see Table 2). However, the *inverse* force constant H_2 , i.e. the appropriate element of the matrix $H = F^{-1}$, is seen to be not so much affected by the approximation in question. As pointed out by Cyvin and Slater¹⁵ the inverse force constants do possess the property of being pure constants for defined coordinates.

The above considerations give a clue to another approximation, namely that obtained by putting the inverse of F in eqn. (8) equal to H_2 , i.e.

$$1/F = F_1/(F_1F_2 - F_{12}^2) \quad (10)$$

The numerical results from this approximation, referred to as the second alternative, are included in Table 5. The approximation is seen to be very good.

For the sake of completeness the calculations with

$$F = F_2 \quad (11)$$

have also been carried through, the results being found in Table 5 as the third alternative. These calculations are seen to give a much poorer approximation for the CC mean amplitude of vibration, compared to the results from the first and second alternatives.

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