Mean Amplitudes of Vibration for the C—H Stretching

S. J. CYVIN

Institutt for Teoretisk Kjemi, Norges Tekniske Høgskole, Trondheim, Norway

Approximate formulae for mean square amplitudes of vibration for the C—H stretching are evaluated. Characteristic numerical values are tabulated.

Calculations of mean amplitudes of vibration from spectroscopic data have proved to be of great interest in molecular structure studies [1]. In the present work the C—H bond distances are studied, and explicit formulae for the mean square amplitudes are given.

When small harmonic vibrations are assumed, the formula to be used is [2]

$$u^2 = \langle r^2 \rangle_{\text{Av}} = \sum_i (hC_i^2/4\pi)\lambda_i^{-\frac{1}{2}} \tag{1}$$

where $\langle \rangle_{\text{Av}}$ denotes the time average, $\lambda_i = 4\pi^2\nu_i^2$, ν_i being a fundamental frequency, h is Planck's constant, and C_i are the coefficients in

$$r = \sum_i C_i Q_i \tag{2}$$

where Q_i is a normal coordinate, and r denotes the deviations from the equilibrium C—H distance. The dependence on temperature could be omitted in this case, because the C—H stretching frequencies are comparatively high. The coefficients in eqn. (2) can be computed by means of a normal coordinate analysis. Wilson's GF matrix method [3,4] is very useful for this purpose.

As pointed out by Wilson [4], it is a good approximation to separate the extreme high C—H stretching frequencies in a molecule from the remaining fundamentals. This is very useful in the problem of mean amplitudes of vibration, as explicit formulae for u can be evaluated by applying the method. As a first example, the allene molecule shall be considered, and the formula is going to be worked out in details in the next section.

THE ALLENE MOLECULE

The allene molecule model is of symmetry V_d. If the four C—H distances are taken as a reducible representation of the group, the symmetric structure

$$\Gamma = A_1 + B_2 + E \tag{3}$$

is obtained. Following Wilson's method [3,4], the three symmetry coordinates

$$
\begin{aligned}
s^{(A_1)} &= (1/2)\ (r_1 + r_2 + r_3 + r_4) \\
s^{(B_2)} &= (1/2)\ (r_1 + r_2 - r_3 - r_4) \\
s^{(E)} &= 2^{-\frac{1}{2}}(r_1 - r_2)
\end{aligned}
\tag{4}
$$

Table 1. Characteristic expressions by calculating mean amplitudes for C—H stretching in certain molecules.

Molecule	Symm. group	Symm. species	F	G	ν/c (cm^{-1})
Acetylene	$D_{\infty h}$	A_{1g}	$k + k''$	$\mu_H + \mu_C$	3 373.7 [5]
		A_{1u}	$k - k''$	$\mu_H + \mu_C$	3 287 [5]
Benzene	D_{6h}	A_{1g}	$K_1 = (k + 2k_p) + (k_m + 2k_0)$	$\mu_H + \mu_C$	3 073 [6]
		B_{1u}	$K_2 = (k + 2k_p) - (k_m + 2k_0)$	$\mu_H + \mu_C$	3 057 [6]
		E_{2g}	$K_3 = (k - k_p) + (k_m - k_0)$	$\mu_H + \mu_C$	3 056 [6]
		E_{1u}	$K_4 = (k - k_p) - (k_m - k_0)$	$\mu_H + \mu_C$	3 064 [6]
Formaldehyde	C_{2v}	A_1	$k + k'$	$\mu_H + 2\mu_C\cos^2a$	2 780 [5]
		B_1	$k - k'$	$\mu_H + 2\mu_C\sin^2a$	2 874 [5]
Ethylene	V_h	A_g	$K_1 = (k + k') + (k'' + k''')$	$\mu_H + 2\mu_C\cos^2a$	3 019.3 [5,7]
		B_{3u}	$K_2 = (k + k') - (k'' + k''')$	$\mu_H + 2\mu_C\cos^2a$	2 989.5 [5,7]
		B_{1g}	$K_3 = (k - k') + (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	3 075 [7]
		B_{2u}	$K_4 = (k - k') - (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	3 105.5 [5,7]
Allene	V_d	A_1	$K_1 = k + k' + 2k''$	$\mu_H + 2\mu_C\cos^2a$	2 996 [8]
		B_2	$K_2 = k + k' - 2k''$	$\mu_H + 2\mu_C\cos^2a$	3 005 [8]
		E	$K_3 = k - k'$	$\mu_H + 2\mu_C\sin^2a$	3 085 [8]
*Cyclo*propane	D_{3h}	A_1'	$K_1 = (k + k') + 2(k'' + k''')$	$\mu_H + 2\mu_C\cos^2a$	3 029 [5]
		E'	$K_2 = (k + k') - (k'' + k''')$	$\mu_H + 2\mu_C\cos^2a$	3 024.4 [5]
		A_2''	$K_3 = (k - k') + 2(k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	3 103.0 [5]
		E''	$K_4 = (k - k') - (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	3 080 [5]
Chloromethane	C_{3v}	A_1	$k + 2k'$	$\mu_H + \mu_C (1 + 2\cos2a)$	2 966.2 [5]
		E	$k - k'$	$\mu_H + 2\mu_C\sin^2a$	3 041.8 [5]
Ethane (eclipsed)	D_{3h}	A_1'	$K_1 = (k + 2k') + (k'' + 2k''')$	$\mu_H + \mu_C (1 + 2\cos2a)$	2 899.2 [5]
		A_2''	$K_2 = (k + 2k') - (k'' + 2k''')$	$\mu_H + \mu_C (1 + 2\cos2a)$	2 954 [5]
		E'	$K_3 = (k - k') + (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	2 994.3 [5]
		E''	$K_4 = (k - k') - (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	2 963 [5]
Ethane (staggered)	D_{3d}	A_{1g}	$K_1 = (k + 2k') + (k'' + 2k''')$	$\mu_H + \mu_C (1 + 2\cos2a)$	2 899.2 [5]
		A_{2u}	$K_2 = (k + 2k') - (k'' + 2k''')$	$\mu_H + \mu_C (1 + 2\cos2a)$	2 954 [5]
		E_g	$K_3 = (k - k') + (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	2 963 [5]
		E_u	$K_4 = (k - k') - (k'' - k''')$	$\mu_H + 2\mu_C\sin^2a$	2 994.3 [5]
Methane	T_d	A_1	$k + 3k'$	μ_H	2 914.2 [5]
		F_1	$k - k'$	$\mu_H + (4/3)\mu_C$	3 020.3 [5]

are formed. r_1 and r_2 are the deviations from equilibrium C—H distances at the atom C_1, r_3 and r_4 at the atom C_3. The corresponding elements on the principal diagonal of the symmetrized F and G matrix are shown in Table 1. k is the principal force constant for C—H stretching, k' is the interaction force constant between the C—H stretchings at the same carbon atom, and k'' at different carbon atoms. μ_H and μ_C are the inverse masses of H and C atoms, and the equilibriun H—C—H angle is denoted by 2α. From the transformation (4) we obtain

$$r_1 = (1/2)s^{(A_1)} + (1/2)s^{(B_2)} + 2^{-\frac{1}{2}}s^{(E)} \tag{5}$$

Wilson's approximation of separating the extreme high C—H stretching frequencies is equivalent to assuming the symmetry coordinates in eqn. (5) to be proportional with the normal coordinates,

$$\begin{aligned} s^{(A_1)} &= (\mu_H + 2\,\mu_C \cos^2\alpha)^{\frac{1}{2}}\, Q^{(A_1)} \\ s^{(B_2)} &= (\mu_H + 2\,\mu_C \cos^2\alpha)^{\frac{1}{2}}\, Q^{(B_2)} \\ s^{(E)} &= (\mu_H + 2\,\mu_C \sin^2\alpha)^{\frac{1}{2}}\, Q^{(E)} \end{aligned} \tag{6}$$

Then the coefficients C of eqn. (2) can easily be computed, their squares being

$$\begin{aligned} A_1: & \quad C^2 = (1/4)\,(\mu_H + 2\,\mu_C \cos^2\alpha) \\ B_2: & \quad C^2 = (1/4)\,(\mu_H + 2\,\mu_C \cos^2\alpha) \\ E: & \quad C^2 = (1/2)\,(\mu_H + 2\,\mu_C \sin^2\alpha) \end{aligned} \tag{7}$$

Hence eqn. (1) gives the explicit formula for the mean square amplitude of C—H as

$$u^2 = (h/16\pi)\,(K_1^{-\frac{1}{2}} + K_2^{-\frac{1}{2}})\,(\mu_H + \mu_C \cos^2\alpha)^{\frac{1}{2}} + (h/8\pi)\,K_3^{-\frac{1}{2}}\,(\mu_H + 2\mu_C \sin^2\alpha)^{\frac{1}{2}} \tag{8}$$

where the force constants from Table 1 have been introduced according to

$$\begin{aligned} A_1: & \quad \lambda_1 = K_1(\mu_H + 2\mu_C \cos^2\alpha) \\ B_2: & \quad \lambda_2 = K_2(\mu_H + 2\mu_C \cos^2\alpha) \\ E: & \quad \lambda_3 = K_3(\mu_H + 2\mu_C \sin^2\alpha) \end{aligned} \tag{9}$$

The formula (8) is based on following approximations: 1) Small harmonic vibrations are assumed, 2) the temperature dependence is omitted, 3) the high C—H stretching frequencies are separated from the remaining fundamentals. This will be referred to as the first approximation.

FURTHER APPLICATIONS

The method has been applied to several representative molecules containing the C—H bond and are listed in Table 1. The principal diagcnal elements of the symmetrized F and G matrices are included in the table, as well as the experimental fundamentals. Troughout the table, the principal force constant for C—H stretching is denoted by k and the interaction constants for pairs of adjacent C—H bonds by k'. The remaining force constants are

Table 2. Mean square amplitude for C—H by the first approximation for certain molecules.

Molecule	First approximation for u^2
Acetylene	$(h/8\pi)[(k + k'')^{-\frac{1}{2}} + (k - k'')^{-\frac{1}{2}}](\mu_H + \mu_C)^{\frac{1}{2}}$
Benzene	$(h/12\pi)[(1/2)K_1^{-\frac{1}{2}} + (1/2)K_2^{-\frac{1}{2}} + K_3^{-\frac{1}{2}} + K_4^{-\frac{1}{2}}](\mu_H + \mu_C)^{\frac{1}{2}}$
Formaldehyde	$(h/8\pi)(k + k')^{-\frac{1}{2}}(\mu_H + 2\mu_C\cos^2 a)^{-\frac{1}{2}} + (h/8\pi)(k-k')^{-\frac{1}{2}}(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
Ethylene	$(h/16\pi)(K_1^{-\frac{1}{2}} + K_2^{-\frac{1}{2}})(\mu_H + 2\mu_C\cos^2 a)^{\frac{1}{2}} + (h/16\pi)(K_3^{-\frac{1}{2}} + K_4^{-\frac{1}{2}})$ $(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
Allene	$(h/16\pi)(K_1^{-\frac{1}{2}} + K_2^{-\frac{1}{2}})(\mu_H + 2\mu_C\cos^2 a)^{\frac{1}{2}} + (h/8\pi)K_3^{-\frac{1}{2}}(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
*Cyclo*propane	$(h/12\pi)[(1/2)K_1^{-\frac{1}{2}} + K_2^{-\frac{1}{2}}](\mu_H + 2\mu_C\cos^2 a)^{\frac{1}{2}} + (h/12\pi)[(1/2)K_3^{-\frac{1}{2}} + K_4^{-\frac{1}{2}}]$ $(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
Chloromethane	$(h/12\pi)(k + 2k')^{-\frac{1}{2}}[\mu_H + \mu_C(1 + 2\cos 2a)]^{\frac{1}{2}} + (h/6\pi)(k - k')^{-\frac{1}{2}}$ $(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
Ethane	$(h/24\pi)(K_1^{-\frac{1}{2}} + K_2^{-\frac{1}{2}})[\mu_H + \mu_C(1 + 2\cos 2a)]^{\frac{1}{2}} + (h/12\pi)(K_3^{-\frac{1}{2}} + K_4^{-\frac{1}{2}})$ $(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
Methane	$(h/16\pi)(k + 3k')^{-\frac{1}{2}}\mu_H^{\frac{1}{2}} + (3h/16\pi)(k-k')^{-\frac{1}{2}}[\mu_H + (4/3)\mu_C]^{\frac{1}{2}}$

due to interaction between C—H stretchings at different carbon atoms. In the case of benzene, *o*, *m* and *p* refer to *ortho*, *meta* and *para*. The final formulae for the mean square amplitudes for C—H by the first approximation are listed in Table 2.

Table 3. General formulae for the mean square amplitude of C—H.

Type	Second approximation for u^2
≡CH	$(h/4\pi)k^{-\frac{1}{2}}(\mu_H + \mu_C)^{\frac{1}{2}}$
=CH$_2$	$(h/8\pi)(k + k')^{-\frac{1}{2}}(\mu_H + 2\mu_C\cos^2 a)^{\frac{1}{2}} + (h/8\pi)(k-k')^{-\frac{1}{2}}(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
—CH$_3$	$(h/12\pi)(k + 2k')^{-\frac{1}{2}}[\mu_H + \mu_C(1 + 2\cos 2a)]^{\frac{1}{2}} + (h/6\pi)(k - k')^{-\frac{1}{2}}(\mu_H + 2\mu_C\sin^2 a)^{\frac{1}{2}}$
CH$_4$	$(h/16\pi)(k + 3k')^{-\frac{1}{2}}\mu_H^{\frac{1}{2}} + (3h/16\pi)(k - k')^{-\frac{1}{2}}[\mu_H + (4/3)\mu_C]^{\frac{1}{2}}$

Type	Third approximation for u^2
≡CH	$(h/4\pi)k^{-\frac{1}{2}}(\mu_H + \mu_C)^{\frac{1}{2}}$
=CH$_2$	$(h/8\pi)k^{-\frac{1}{2}}\{[\mu_H + (1/2)\mu_C]^{\frac{1}{2}} + [\mu_H + (3/2)\mu_C]^{\frac{1}{2}}\}$
—CH$_3$	$(h/12\pi)k^{-\frac{1}{2}}\{[\mu_H + (1/3)\mu_C]^{\frac{1}{2}} + 2[\mu_H + (4/3)\mu_C]^{\frac{1}{2}}\}$
CH$_4$	$(h/16\pi)k^{-\frac{1}{2}}\{\mu_H^{\frac{1}{2}} + 3[\mu_H + (4/3)\mu_C]^{\frac{1}{2}}\}$

Type	Fourth approximation for u^2
General	$(h/4\pi)k^{-\frac{1}{2}}(\mu_H + \mu_C)^{\frac{1}{2}}$

Table 4. Calculated mean amplitudes for C—H stretching (Å units).

Molecule	1. appr.	2. appr.	3. appr.	4. appr.
Acetylene	0.07379	0.07378	0.07378	0.07378
Benzene	0.07696	0.07696	0.07696	0.07696
Formaldehyde	0.08007	0.08007	0.08007	0.08007
Ethylene	0.07713	0.07712	0.07712	0.07713
Allene	0.07718	0.07718	0.07718	0.07719
*Cyclo*propane	0.07701	0.07701	0.07700	0.07701
Chloromethane	0.07752	0.07752	0.07751	0.07751
Ethane	0.07824	0.07824	0.07822	0.07822
Methane	0.07781	0.07781	0.07780	0.07781

GENERAL FORMULAE

As a second approximation for u^2, the interactions between bonds attached to different C atoms may be omitted. By doing this, general formulae are obtained for the four types of C—H distances, depending on the number of H atoms attached directly to the C atom. The formulae are listed in Table 3.

The third approximation for u^2 is obtained by putting the interaction constant k' equal to zero in the second approximation formula. Simultaneously, the numerical values 120° and 109°28' have been inserted for the H—C—H angle in the methylene and methyl groups, respectively.

In the third approximation, only the principal C—H stretching force constant, k, is included. By making the corresponding approximation in the G matrix, the proper element on the principal diagonal to be used is $\mu_H + \mu_C$. Hence a general formula for all types of C—H distances is obtained, which is listed in Table 3 as the fourth approximation. This last formula is naturally identical with the second and third approximation for C—H of the ≡CH type.

NUMERICAL CALCULATIONS

All the approximate formulae have been applied for numerical calculations of u values for the molecules here considered. The calculations were based on individual force constants, as obtained from the experimental fundamentals (see Table 1). The results are summarized in Table 4.

Table 5. Characteristic values of mean amplitudes for C—H stretching.

k (10^5dyn cm^{-1})	4.4	4.6	4.8	5.0	5.2
u (Å)	0.0800	0.0791	0.0783	0.0775	0.0767
k (10^5dyn cm^{-1})	5.4	5.6	5.8	6.0	6.2
u (Å)	0.0760	0.0753	0.0746	0.0740	0.0734

CONCLUSION

It may be concluded that the introduced approximations are very good. It is seen from Table 4 that they do not affect the results appreciably. Hence if the C—H stretching force constant is assumed to have a characteristic value in several different molecules, it is possible to give a characteristic value for the root mean square C—H amplitude as well. In Table 5 the proper u values are enumerated in the actual region of force constant values.

REFERENCES

1. Bastiansen, O. and Cyvin, S. J. *Nature* **180** (1957) 980.
2. Morino, Y., Kuchitsu, K. and Shimanouchi, T. *J. Chem. Phys.* **20** (1952) 726.
3. Wilson, E. B. Jr. *J. Chem. Phys.* **7** (1939) 1047.
4. Wilson, E. B. Jr. *J. Chem. Phys.* **9** (1941) 76.
5. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules,* N. Y. 1945.
6. Brodersen, S. and Langseth, A. *Kgl. Danske Videnskab Selskab, Mat. Fys. Skrifter* **1** (1956) 1.
7. Torkington, P. *Proc. Phys. Soc. London* **A 64** (1951) 32.
8. Lord, R. C. and Venkateswarlu, P. *J. Chem. Phys.* **20** (1952) 1237.