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Approximate Calculations of Mean Amplitudes of Vibration

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The mean amplitudes of vibration for the interatomic distances in several four-atomic molecules are calculated by an approximate method, and the results are compared to the rigorously calculated values. The method is based on a four-constant approximation for the hyperbolic cotangent and gives the mean amplitudes with about 1/2 percent accuracy.

Morino *et al.*[1] have developed an approximate formula for calculating mean square amplitudes of vibration, assuming $\coth t = 1/t + t/4$. This approximation is applicable only for frequencies below 1 200 cm^{-1} and may give as much as 4 % error in the mean amplitude. In the present investigation, a four-constant approximation, *viz.*

$$\coth t = -\Theta_{-3}t^{-3} + \Theta_{-1}t^{-1} + \Theta_1 t - \Theta_3 t^3$$

has been applied. The resulting formula for the mean square amplitude may be written

$$\overline{R_i^2} = -\delta\ (\mathrm{FGF})^{-1}_{ii} + \gamma\ \mathrm{F}^{-1}_{ii} + \alpha\ \mathrm{G}_{ii} - \beta\ (\mathrm{GFG})_{ii}$$

where F and G denote the energy matrices introduced by Wilson [2], and

$$\alpha = h^2\Theta_1/16\pi^2 kT;\quad \beta = h^4\Theta_3/256\pi^4(kT)^3$$

$$\gamma = \Theta_{-1}kT\ :\quad \delta = 16\Theta_{-3}\pi^2(kT)^3/h^2$$

The contants Θ may be adjusted by a least-squares technique for a given interval of t. It has been possible to construct functions with at the most about 1 % deviation from the hyperbolic cotangent in the following intervals:

I	$t = 0.5$—4.0	(207—1 658 cm^{-1})
II	$t = 1.0$—5.5	(414—2 279 cm^{-1})
III	$t = 1.5$—6.5	(622—2 694 cm^{-1})
IV	$t = 2.0$—7.5	(829—3 108 cm^{-1})

Table 1. Calculated mean square amplitudes.

Molecule	Distance	Mean square amplitude ($Å^2$) *	Range of frequencies (cm^{-1})	Ref.
P_4	P–P	$0.06457a - 0.009531\beta + 0.4961\gamma - 4.3079\delta$	363 – 606	3
ND_3	N–D	$0.5679a - 2.1116\beta + 0.1536\gamma - 0.04243\delta$	749 – 2 555	3
	D–D	$0.9930a - 2.3322\beta + 0.8355\gamma - 1.3597\delta$		
NH_3	N–H	$1.0636a - 7.1948\beta + 0.1575\gamma - 0.02344\delta$	950 – 3 337	3
	H–H	$1.9844a - 9.1025\beta + 0.8699\gamma - 0.8296\delta$		
PH_3	P–H	$1.0243a - 3.2640\beta + 0.3215\gamma - 0.1010\delta$	992 – 2 328	4; 5
	H–H	$1.9841a - 3.8743\beta + 1.7552\gamma - 2.2467\delta$		
AsH_3	As–H	$1.0054a - 2.6630\beta + 0.3796\gamma - 0.1434\delta$	906 – 2 123	6; 5
	H–H	$1.9841a - 3.2054\beta + 2.1525\gamma - 3.3872\delta$		
SbH_3	Sb–H	$1.0003a - 2.1112\beta + 0.4739\gamma - 0.2246\delta$	782 – 1 894	7; 5
	H–H	$1.9841a - 2.5041\beta + 2.9850\gamma - 6.5533\delta$		
CH_2O	C–H	$1.0753a - 5.1578\beta + 0.2253\gamma - 0.04783\delta$	1 280 – 2 874	
	C–O	$0.1458a - 0.2705\beta + 0.08365\gamma - 0.04955\delta$	1 503 – 2 780	3
	H–H	$1.9841a - 7.5236\beta + 0.6839\gamma - 0.3247\delta$	1 503 – 2 780	
	O–H	$1.0546a - 3.4850\beta + 0.5137\gamma - 0.3781\delta$	1 280 – 2 874	

* Based upon the atomic weight units for masses and mdyne/Å for force constants.

The proper one of the alternatives I to IV should be selected according to the magnitude of the fundamentals contributing to the desired mean amplitude. The corresponding intervals of frequencies, referring to the temperature 298 °K, are included above. Thus the present formula will give not more than

Table 2. Mean amplitudes of vibration in Å units at 298 °K.

Molecule	Distance	Approximation I	II	III	IV	Rigorous
P_4	P–P	0.0534				0.0533 [8]
ND_3	N–D			0.0619		0.0618
	D–D			0.1042		0.1040
PH_3	P–H			0.0866	0.0862	0.0862 [8]
	H–H			0.1512	0.1514	0.1521 [8]
AsH_3	As–H		0.0896	0.0899	0.0893	0.0894 [8]
	H–H		0.1587	0.1598	0.1596	0.1597 [8]
SbH_3	Sb–H		0.0950	0.0946		0.0944 [8]
	H–H		0.1734	0.1745		0.1736 [8]
CH_3O	C–H				0.0798	0.0801 [8]
	C–O				0.0375	0.0372 [8]
	H–H				0.1201	0.1170 [8]
	O–H				0.0944	0.0912 [8]

about 0.5 % error in the mean amplitude for vibrational frequencies within the indicated intervals.

The method has been applied to several molecules with the results given in Table 1, which also includes the actual intervals of frequencies with references to the experimental data. The mean amplitudes calculated by the approximate method are given in Table 2. In accordance with the prediction, it is seen that most of the present results deviate less than 0.5 % from the rigorously calculated values. The mean amplitudes for NH_3 are not included in Table 2, because the extremely high frequency 3 337 cm^{-1} falls outside the chosen intervals. The approximation IV gives 0.0715 Å for N—H and 0.1227 Å for the H—H mean amplitude. When compared with the rigorously calculated values 0.0727 and 0.1236 Å, the errors 1.7 and 0.7 % are found for the N—H and H—H amplitudes, respectively.

Further details concerning the method and development of the formula is to be published later.

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