

Mean Amplitudes of Vibration in Molecules with Internal Rotation: Hexafluorobutyne

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A force field is constructed and the mean amplitudes of vibration are calculated for hexafluorobutyne. Framework mean amplitudes are calculated for various equilibrium configurations with differing angles of torsion. At 298°K the framework mean amplitudes for the long F...F distances vary from 0.2349 Å in the *cis* position to 0.1155 Å in the *trans* position.

In the electron diffraction study of molecules with internal rotation, the framework mean amplitudes of vibration as a function of the torsional angle are of great interest. With the intention to obtain the framework mean amplitudes for various molecules with internal rotation from spectroscopic data, halogenated ethanes were chosen as the first compounds to be studied.¹ In this paper framework mean amplitudes are calculated for hexafluorobutyne, which is an equally simple and convenient molecule for the spectroscopic study.

SYMMETRY COORDINATES

Symmetry coordinates are constructed on the basis of D_3 symmetry, which is the molecular symmetry of the equilibrium configuration for an arbitrary angle of torsion. When varying the torsional angle, two special structures appear, the eclipsed configuration of D_{3h} symmetry and the staggered of D_{3d} symmetry. The symmetry coordinates together with algebraic expressions for some of the elements of the symmetrized G matrix and Coriolis C^{α} matrix can be found in another paper.²

As for the ethanes the coupling terms in the G matrix with the torsional coordinate are all zero. The torsional mode of vibration is then easily separated.

FORCE FIELD

A force field is constructed by means of the fundamental frequencies given by Miller and Bauman,³ who used the D_{3d} symmetry in the interpretation of

the vibrational spectrum. Some interaction force constants are rather arbitrarily transferred from dimethylacetylene⁴ and hexafluoroethane.⁵

In calculating the framework mean amplitudes, the same force field is assumed for all angles of torsion. With this restriction on the force field, the symmetry conditions require that the set of force constants should be the same for the E_g block and the E_u block. Because of the doubtiness of the

Table 1. Symmetrized force constants in mdyne/Å.

A_{1g}	F_{11}	8.47	A_{2u}	F_{66}	7.99
	F_{12}	0.92		F_{67}	0.68
	F_{13}	0.94		F_{68}	0.81
	F_{14}	0.63		F_{77}	5.73
	F_{22}	6.03		F_{78}	-0.71
	F_{23}	0.41		F_{88}	1.55
	F_{24}	-0.53			
	F_{33}	15.85			
	F_{34}	0			
	F_{44}	1.34			
E_g	F_{99}	6.64	E_u	F_{1313}	5.78
	F_{910}	-0.53		F_{1314}	-0.53
	F_{911}	0.85		F_{1315}	0.85
	F_{912}	0		F_{1316}	0
	F_{1010}	1.23		F_{1414}	2.12
	F_{1011}	0		F_{1415}	0
	F_{1012}	0		F_{1416}	0
	F_{1111}	0.56		F_{1515}	0.25
	F_{1112}	0		F_{1516}	0
	F_{1212}	0.26		F_{1616}	0.25

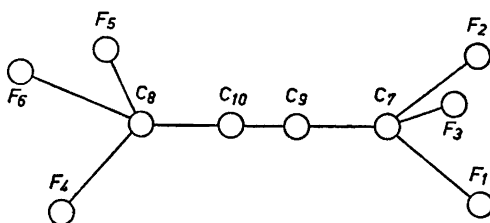


Fig. 1. Hexafluorobutyne. Numbering of the atoms.

ω_{14} and the ω_{15} frequencies,³ and because of some difficulties in obtaining a suitable set of constants for the E_u vibrations, the force constants of the E_g species were used in the calculation of the mean amplitudes of vibration.

In Table 1 the set of force constants can be found, while the fundamental frequencies, observed and calculated, are given in Table 2.

Table 2. Fundamental frequencies in cm^{-1} .

Notation	Type of vibration	Freq. obs. by Miller and Bauman	Calc. freq.
A_{1g}	ω_1	C-F stretch	1181
	ω_2	C-C stretch	771
	ω_3	C \equiv C stretch	2300
	ω_4	CF ₃ deformation	291
A_{1u}	ω_5	Torsion	[90]
A_{1u}	ω_6	C-F stretch	1294
	ω_7	C-C stretch	900
	ω_8	CF ₃ deformation	642
E_g	ω_9	C-F stretch	1245
	ω_{10}	CF ₃ deformation	624
	ω_{11}	C-CF ₃ rocking	464
	ω_{12}	C-C \equiv C bending	186
E_u	ω_{13}	C-F stretch	1195
	ω_{14}	CF ₃ deformation	605
	ω_{15}	C-CF ₃ rocking	[234]
	ω_{16}	C-C \equiv C bending	[65]
The E_u frequencies obtained by using the set of force constants from the E_g species:			
	ω_{13}		1246
	ω_{14}		490
	ω_{15}		350
	ω_{16}		79

Table 3. Mean amplitudes of vibration (with torsion included) for hexafluorobutyne with staggered configuration, in Å units. Also included are the framework mean amplitudes for the F₁F₅ (gauche) distance. For all the other distances the mean amplitudes are independent of the torsional mode for this equilibrium configuration.

Atomic distance	$T=0^\circ\text{K}$	$T=298^\circ\text{K}$
C ₇ ...C ₈	0.0543	0.0576
C ₇ -C ₉	0.0453	0.0461
C ₇ ...C ₁₀	0.0484	0.0497
C ₅ \equiv C ₁₀	0.0356	0.0358
F ₁ -C ₇	0.0439	0.0444
F ₁ ...C ₈	0.0774	0.1284
F ₁ ...C ₉	0.0603	0.0729
F ₁ ...C ₁₀	0.0685	0.0989
F ₁ ...F ₂	0.0536	0.0580
F ₁ ...F ₄ (<i>trans</i>)	0.0797	0.1155
F ₁ ...F ₅ (<i>gauche</i>)	0.1048	0.2105
F ₁ ...F ₆ (frame)	0.1035	0.2074

MEAN AMPLITUDES OF VIBRATION

Table 3 shows the mean amplitudes of vibration for all different distances in the case of staggered configuration. For this configuration only the mean amplitude of the F_1F_5 distance is dependent on the torsional frequency, and for this distance the framework mean amplitude is also cited.

The numbering of the atoms follows the notation in Fig. 1.

FRAMEWORK MEAN AMPLITUDES

The basic assumptions made in calculating framework mean amplitudes, are the neglecting of the torsional vibrations, and the assumption of the same set of force constants for all the molecular configurations throughout the variation of the angle of torsion. For a more thorough and detailed discussion of the general principles, one refers to the paper on halogenated ethanes.¹

In this paper¹ also an approximate formula for the angle dependence of the framework mean-square amplitudes was derived:

$$\rho^2 \langle \Delta \rho^2 \rangle_{fr.} = \alpha + \beta \cos \theta + \gamma \cos^2 \theta \quad (1)$$

Here ρ is the distance between the end atoms in a 1-7-8-4 chain, and θ the angle of torsion between the 1-7-8 and the 4-8-7 planes.

Table 4. Framework mean amplitudes of vibration for the F_1F_4 distance in hexafluorobutylene with various equilibrium structures, in Å units. θ is the equilibrium angle of torsion. $T = 298^\circ \text{K}$.

θ (degrees)	$\langle \Delta \rho^2 \rangle^{\frac{1}{2}}$ frame	θ (degrees)	$\langle \Delta \rho^2 \rangle^{\frac{1}{2}}$ frame
0 (<i>cis</i>)	0.2349	100	0.1690
10	0.2341	110	0.1590
20	0.2316	120	0.1492
30	0.2276	130	0.1401
40	0.2221	140	0.1319
50	0.2153	150	0.1251
60 (<i>gauche</i>)	0.2074	160	0.1198
70	0.1986	170	0.1166
80	0.1891	180 (<i>trans</i>)	0.1155
90	0.1792		

As for the hexafluoroethane¹ the variations of the framework mean amplitudes with the angle of torsion are negligible for all distances except for the long $F \cdots F$ distances. The variation is shown in Table 4 and in Fig. 2.

On applying the approximate formula (1) on the framework mean amplitudes of the $F_1 \cdots F_4$ distances, the following values for the empirical constants are obtained:

$\alpha = 0.89362$, $\beta = 0.47034$, and $\gamma = -0.00882$; all in Å⁴ units. The framework mean amplitudes calculated from this formula agree with the rigorously calculated ones in all the decimals quoted.

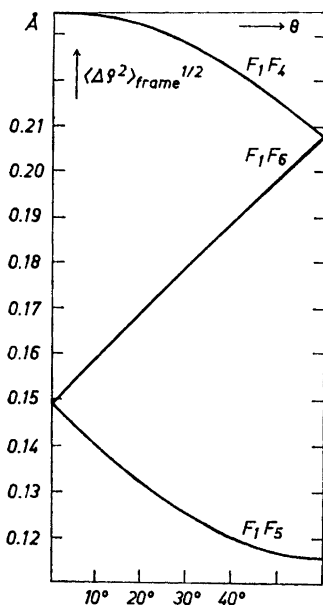


Fig. 2. Framework F...F mean amplitudes of vibration for hexafluorobutyne at 298 °K in equilibrium configurations with different angles of torsion θ . The torsional angle θ is defined as the angle between the $F_1-C_7-C_8$ plane and the $C_7-C_8-F_4$ plane.

EQUILIBRIUM PARAMETERS

The equilibrium distances and bond angles used throughout the calculations, are all taken from an investigation by Sheehan and Schomaker:⁶

$C-F = 1.34$ Å, $C-C = 1.465$ Å, $C \equiv C = 1.22$ Å and the angle $\angle FCF = 107.5^\circ$.

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