

Generalised Mean-square Amplitudes of Vibration and Coriolis Coupling Coefficients for C_3H_6 and C_3D_6

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Generalised vibrational mean-square amplitudes for cyclopropane and cyclopropane- d_6 are calculated using spectroscopic data, and the values at 300 °K are reported. A complete set of the Coriolis coupling coefficients for these molecules has been evaluated.

These molecules have been subjected to spectroscopic investigations previously. GÜNTARD, LORD and McCUBBIN¹ have given the potential constants for these molecules along with the approximate zeta values for the $E' \times E'$ species. CYVIN² has worked out both the force constants and vibrational parallel mean-square amplitudes for these molecules. But no attempt has been made so far to obtain the generalised mean square amplitudes and a complete set of the zeta values for cyclopropane and cyclopropane- d_6 . Hence both these aspects have been taken up in this investigation. Fig. 1 shows the

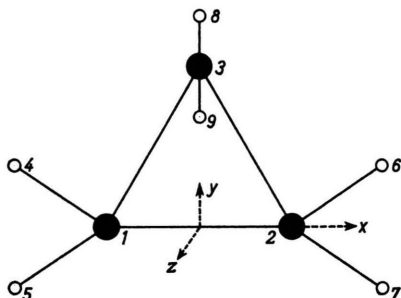


Fig. 1.

numbering of atoms and the orientation of axes. Frequencies and symmetry coordinates used here are the same as those given by CYVIN² and the parameters are taken from BASTIANSEN et al.³

Generalised Mean-square amplitudes

The concept of generalised mean-square amplitudes comprising $(\Delta z)^2$, the mean square parallel amplitudes, $(\Delta x)^2$ and $(\Delta y)^2$ the mean-square perpendicular amplitudes and $(\Delta z \Delta x)$, $(\Delta x \Delta y)$ and

$(\Delta y \Delta z)$, the mean cross products and the method of their evaluation have been put forward by MORINO and HIROTA⁴.

The Σ values, required in the calculation of generalised mean-square amplitudes are obtained by CYVIN's² secular equation method. Expressions have been derived for the generalised mean-square amplitudes of different atom pairs. Starting from the S vectors, the B matrix is formed and the A-matrix which is the basis for the calculation of generalised mean square amplitudes is obtained by the matrix relation

$$A = M^{-1} B' G^{-1} \text{ where } M^{-1}$$

is the matrix containing the reciprocal masses of the atoms and G^{-1} is the inverse kinetic energy matrix. The generalised meansquare amplitudes may be obtained in terms of the Σ matrix according to

$$\langle (\xi_i - \xi_j) (\eta_i - \eta_j) \rangle = \tilde{A}_{ij}^{\xi} \Sigma A_{ij}^{\eta}$$

where $\xi, \eta = x, y$ or z and ij refer to an arbitrary atom pair.

Coriolis coupling coefficients

The molecules under investigation belong to the D_{3h} point group and have $3 A_1' + A_2' + 4 E' + A_1'' + 2 A_2'' + 3 E''$ vibrations. According to JAHN's rule⁵, two vibrational states will couple through a Coriolis interaction if the direct product of two vibrational states contains a rotational species.

For molecules in the D_{3h} point group vibrations under the E'' species possess rotation about the X and Y axes and the vibrations under the A_2' species possess rotation about the Z-axis. Hence the following types of interactions among the vibrational

¹ H. GÜNTARD, R. C. LORD, and McCUBBIN, JR., J. chem. Physics **25**, 768 [1956].

² S. J. CYVIN, Acta polytechn. [Stockholm] Ph. 6 1960, 279.

³ O. BASTIANSEN, F. N. FRITSCH, and KENNETH HEDBERG, Acta crystallogr. [Copenhagen] **17**, 538 [1964].

⁴ Y. MORINO and E. HIROTA, J. chem. Physics **23**, 737 [1955].

⁵ H. A. JAHN, Physic. Rev. **56**, 680 [1939].

species produce non-vanishing Coriolis coupling coefficients.

- (1) $A_1' \times A_2'$; (2) $A_1'' \times A_2''$; (3) $E' \times E'$
 (4) $E'' \times E''$; (5) $A_1' \times E''$; (6) $A_2' \times E''$
 (7) $A_1'' \times E'$; (8) $A_2'' \times E'$ and (9) $E' \times E''$

where the first four types possess rotation about the Z axis and the next five about the X and Y axes.

The $\zeta^{\alpha's}$ ($\alpha = x, y, z$) are calculated using the following matrix relation,

$$\text{where} \quad \zeta^{\alpha} = \tilde{L} \bar{C}^{\alpha} L \\ \bar{C}^{\alpha} = G^{-1} C^{\alpha} G^{-1}.$$

In the above relations L is the normal coordinate transformation matrix and C^{α} is a matrix introduced by MEAL and POLO⁶, the elements of which may be obtained by the well known vector method first suggested by them. Elements of the F matrices obtained from the general valence force field are used to get the L matrix elements.

Results and Discussion

To get the solution of the secular equation, it is assumed that the Σ elements contain all the possible interaction mean-square amplitudes also. Table I contains the expressions for generalised mean-square amplitudes for the different bonded and nonbonded distances in the molecule. The numerical values for the generalised mean-square amplitudes and the mean cross products are given in Table II. Table III shows a comparison between the mean amplitude values obtained in this investigation and from the electron diffraction data³. From Table II it can be seen that, in general, the out of plane perpendicular mean amplitudes have large values which implies that the corresponding force is rather small. Again for the atom pairs 4...6 and 7...4 we have larger mean amplitudes for the smaller distance. The 5...4 atom pair has nearly the same mean amplitude as for 7...4 though the distance is consider-

M. S. A. Quantity Atom pair.	$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$
$C_1 - C_2$	$(x_1 - x_2)^2$	$\langle(y_1 - y_2)^2\rangle$	$\langle(z_1 - z_2)^2\rangle$
$C_1 \dots H_4$	$\langle\{-\cos \varphi_1(x_1 - x_4) - \cos \varphi_2(y_1 - y_4) + \cos \varphi_3(z_1 - z_4)\}^2\rangle$	$\langle\{-\cos \psi_1(x_1 - x_4) - \cos \psi_2(y_1 - y_4) + \cos \psi_3(z_1 - z_4)\}^2\rangle$	$\langle\{-\cos \eta_1(x_1 - x_4) - \cos \eta_2(y_1 - y_4)\}^2\rangle$
$C_1 \dots H_6$	$\langle\{\cos \varphi_1'(x_1 - x_6) + \cos \varphi_2'(y_1 - y_6) + \cos \varphi_3'(z_1 - z_6)\}^2\rangle$	$\langle\{\cos \psi_1'(x_1 - x_6) + \cos \psi_2'(y_1 - y_6) + \cos \psi_3'(z_1 - z_6)\}^2\rangle$	$\langle\{\cos \eta_1'(x_1 - x_6) + \cos \eta_2'(y_1 - y_6)\}^2\rangle$
$H_5 \dots H_4$	$\langle(z_5 - z_4)^2\rangle$	$\langle(x_5 - x_4)^2\rangle$	$\langle(y_5 - y_4)^2\rangle$
$H_4 \dots H_6$	$\langle(x_4 - x_6)^2\rangle$	$\langle(y_4 - y_6)^2\rangle$	$\langle(z_4 - z_6)^2\rangle$
$H_7 \dots H_4$	$\langle\{-\cos \varphi_1''(x_7 - x_4) + \cos \varphi_3''(z_1 - z_4)\}^2\rangle$	$\langle\{\cos \psi_1''(x_7 - x_4) + \cos \psi_3''(z_7 - z_4)\}^2\rangle$	$\langle(y_7 - y_4)^2\rangle$

Table I. Expressions for Generalised mean square amplitudes of vibration of C_3H_6 and C_3D_6 . $\varphi_1, \varphi_2; \psi_1, \psi_2$; and η_1, η_2 are the angles made by (Δz) , (Δx) and (Δy) components of bond 1-4 with negative direction X and Y axes, φ_3, ψ_3 and η_3 ($=90^\circ$) with positive direction of the Z axis. $\varphi_1', \varphi_2', \varphi_3'; \psi_1', \psi_2', \psi_3'$; and $\eta_1', \eta_2', \eta_3'$ ($=90^\circ$) are the angles made by (Δz) , (Δx) and (Δy) components of bond 1...6 with positive directions of X, Y and Z axes respectively. φ_1'' and φ_3'' are the angles made by (Δz) component of 7...4 with negative X axis and positive Z axis respectively. ψ_1'' and ψ_3'' are the angles made by (Δx) component of 7...4 with positive X and Z axes respectively.

Molecule	M. S. A. Quantity Atom Pair	$[\Delta z]^2$	$[\Delta x]^2$	$[\Delta y]^2$	$[\Delta x \Delta z]$	$[\Delta x \Delta y]$	$[\Delta y \Delta z]$
C_3H_6	$C_1 - C_2$	(1.510)*	0.002241	0.001869	0.000970	-0.000001	—
	$C_1 - H_4$	(1.089)*	0.006059	0.014383	0.020093	-0.000035	+0.000002
	$C_1 - H_6$	(2.234)*	0.011630	0.010727	0.016380	-0.004200	+0.000552
	$H_5 - H_4$	(1.838)*	0.015807	0.030171	0.033661	—	-0.003351
	$H_4 \dots H_6$	(2.521)*	0.030959	0.030262	0.012997	+0.000008	+0.004181
	$H_7 \dots H_4$	(3.120)*	0.017550	0.021874	0.029978	-0.007208	+0.000061
C_3D_6	$C_1 - C_2$		0.002240	0.002245	0.001734	-0.000002	—
	$C_1 - D_4$		0.004400	0.013310	0.014340	-0.000086	+0.000004
	$C_1 \dots D_6$		0.009419	0.008145	0.010979	-0.003661	+0.000708
	$D_5 \dots D_4$		0.012583	0.022357	0.024142	—	-0.001545
	$D_4 \dots D_6$		0.022813	0.021935	0.009467	+0.000007	+0.002498
	$D_7 \dots D_4$		0.013110	0.014334	0.021438	-0.004365	+0.000025

Table II. Generalized mean square amplitudes of vibration ($\text{\AA}^2$). * distances of the corresponding bonds in $\text{\AA}$.

Molecule	Atom pair	Mean Amplitudes of vibration [Å]	
		Spectroscopic	Electron diffraction
C ₃ H ₆	C ₁ —C ₂	0.047350	0.04800
	C ₁ —H ₄	0.077840	0.08400
	C ₁ ...H ₆	0.107800	0.11400
	H ₅ ...H ₄	0.125700	0.05100
	H ₄ ...H ₆	0.176000	0.21400
	H ₇ ...H ₄	0.132100	0.08700

ably smaller which shows that the nonbonded force between 7 and 4 is comparable to that between 5 and 4.

From Table III, it can be seen that the values obtained by spectroscopic method are in general agreement with those of electron diffraction studies,

Table III. Comparison of the mean amplitudes of vibration by Spectroscopic and Electron diffraction methods.

Species	ϱ_{ij}^a	Molecule		Species	ϱ_{ij}^a	Molecule	
		C ₃ H ₆	C ₃ D ₆			C ₃ H ₆	C ₃ D ₆
A ₁ ' × A ₂ '	$\zeta_{14}^{z_{14}}$	0.5541	0.4854	E'' × E''	$\zeta_{12a,12b}^{z_{12a,12b}}$	— 0.0295	— 0.0251
	$\zeta_{24}^{z_{24}}$	— 0.0421	— 0.6304		$\zeta_{12a,13b}^{z_{12a,13b}}$	— 0.3313	— 0.3922
	$\zeta_{34}^{z_{34}}$	0.8314	0.6070		$\zeta_{12a,14b}^{z_{12a,14b}}$	— 0.3301	— 0.1597
A ₁ '' × A ₂ ''	$\zeta_{9,10}^{z_{9,10}}$	— 0.5100	— 0.1806		$\zeta_{13a,13b}^{z_{13a,13b}}$	0.6638	0.2342
	$\zeta_{9,11}^{z_{9,11}}$	— 0.8608	— 0.9835		$\zeta_{13a,14b}^{z_{13a,14b}}$	— 0.1687	— 0.6598
	$\zeta_{5a,5b}^{z_{5a,5b}}$	— 0.0100	— 0.0461		$\zeta_{14a,14b}^{z_{14a,14b}}$	— 0.8370	— 0.4879
	$\zeta_{5a,6b}^{z_{5a,6b}}$	0.2216	— 0.4760	A ₁ ' × E''	$\zeta_{12a,1}^{z_{12a,1}}$	0.0406	0.0417
	$\zeta_{5a,7b}^{z_{5a,7b}}$	0.0406	— 0.2541		$\zeta_{12a,2}^{z_{12a,2}}$	0.0633	— 0.1625
E' × E'	$\zeta_{5a,8b}^{z_{5a,8b}}$	— 0.7722	— 0.6891		$\zeta_{12a,3}^{z_{12a,3}}$	0.3400	0.3060
	$\zeta_{6a,6b}^{z_{6a,6b}}$	— 0.8631	— 0.1812		$\zeta_{13a,1}^{z_{13a,1}}$	0.3889	0.2803
	$\zeta_{6a,7b}^{z_{6a,7b}}$	0.3884	— 0.4615		$\zeta_{13a,2}^{z_{13a,2}}$	— 0.1994	— 0.1056
	$\zeta_{6a,8b}^{z_{6a,8b}}$	— 0.3105	0.7718		$\zeta_{13a,3}^{z_{13a,3}}$	— 0.1310	— 0.2546
	$\zeta_{7a,7b}^{z_{7a,7b}}$	0.0450	— 0.4094		$\zeta_{14a,1}^{z_{14a,1}}$	— 0.0869	— 0.2062
A ₁ ' × E''	$\zeta_{7a,8b}^{z_{7a,8b}}$	— 0.6392	— 0.3765		$\zeta_{14a,2}^{z_{14a,2}}$	0.0108	0.1414
	$\zeta_{8a,8b}^{z_{8a,8b}}$	— 0.1821	— 0.4094		$\zeta_{14a,3}^{z_{14a,3}}$	— 0.1129	0.0382
	$\zeta_{12b,1}^{z_{12b,1}}$	0.0703	0.0722	A ₁ '' × E'	$\zeta_{9,5a}^{z_{9,5a}}$	— 0.4617	— 0.4818
	$\zeta_{12b,2}^{z_{12b,2}}$	— 0.1096	— 0.2814		$\zeta_{9,6a}^{z_{9,6a}}$	0.0870	— 0.0817
	$\zeta_{12b,3}^{z_{12b,3}}$	0.5888	0.5300		$\zeta_{9,7a}^{z_{9,7a}}$	0.3895	0.3660
	$\zeta_{13b,1}^{z_{13b,1}}$	0.6735	0.4855		$\zeta_{9,8a}^{z_{9,8a}}$	0.0532	— 0.0466
	$\zeta_{13b,2}^{z_{13b,2}}$	— 0.3454	— 0.1829		$\zeta_{9,5b}^{z_{9,5b}}$	0.2667	0.2783
	$\zeta_{13b,3}^{z_{13b,3}}$	— 0.2269	— 0.4409		$\zeta_{9,6b}^{z_{9,6b}}$	— 0.0502	0.0472
	$\zeta_{14b,1}^{z_{14b,1}}$	— 0.1505	— 0.3572		$\zeta_{9,7b}^{z_{9,7b}}$	— 0.2250	— 0.2113
	$\zeta_{14b,2}^{z_{14b,2}}$	0.0187	0.2448		$\zeta_{9,8b}^{z_{9,8b}}$	— 0.0307	0.0269
A ₂ ' × E''	$\zeta_{14b,3}^{z_{14b,3}}$	— 0.1955	0.0662	A ₂ '' × E'	$\zeta_{10,5a}^{z_{10,5a}}$	0.0615	0.1506
	$\zeta_{4,12a}^{z_{4,12a}}$	— 0.5240	— 0.5342		$\zeta_{10,6a}^{z_{10,6a}}$	0.1430	— 0.3153
	$\zeta_{4,13a}^{z_{4,13a}}$	— 0.1988	— 0.0814		$\zeta_{10,7a}^{z_{10,7a}}$	0.3583	0.1987
	$\zeta_{4,14a}^{z_{4,14a}}$	0.2467	0.2875		$\zeta_{10,8a}^{z_{10,8a}}$	— 0.2549	— 0.2912
	$\zeta_{4,12b}^{z_{4,12b}}$	0.3026	0.3084		$\zeta_{11,5a}^{z_{11,5a}}$	— 0.3465	— 0.3108
A ₂ '' × E'	$\zeta_{4,13b}^{z_{4,13b}}$	0.1148	0.0479		$\zeta_{11,6a}^{z_{11,6a}}$	— 0.0264	0.0100
	$\zeta_{4,14b}^{z_{4,14b}}$	— 0.1424	— 0.1661		$\zeta_{11,7a}^{z_{11,7a}}$	0.0488	0.1784
	$\zeta_{10,5b}^{z_{10,5b}}$	0.1064	0.2608		$\zeta_{11,8a}^{z_{11,8a}}$	0.1871	0.0262
	$\zeta_{10,6b}^{z_{10,6b}}$	0.2477	— 0.5461		$\zeta_{14a,5a}^{z_{14a,5a}}$	— 0.3098	— 0.2912
	$\zeta_{10,7b}^{z_{10,7b}}$	0.6205	0.3442		$\zeta_{14a,6a}^{z_{14a,6a}}$	0.0266	— 0.1509
	$\zeta_{10,8b}^{z_{10,8b}}$	— 0.4414	— 0.5043		$\zeta_{14a,7a}^{z_{14a,7a}}$	0.1466	0.0424
	$\zeta_{11,5b}^{z_{11,5b}}$	— 0.6002	— 0.5383		$\zeta_{14a,8a}^{z_{14a,8a}}$	— 0.0816	— 0.0210
	$\zeta_{11,6b}^{z_{11,6b}}$	— 0.0456	0.0173	E'' × E'	$\zeta_{12b,5a}^{z_{12b,5a}}$	— 0.0809	— 0.0857
	$\zeta_{11,7b}^{z_{11,7b}}$	0.0843	0.3090		$\zeta_{12b,6a}^{z_{12b,6a}}$	0.0041	— 0.0959
	$\zeta_{11,8b}^{z_{11,8b}}$	0.3240	0.0453		$\zeta_{12b,7a}^{z_{12b,7a}}$	— 0.3965	— 0.5134
E'' × E'	$\zeta_{12a,5a}^{z_{12a,5a}}$	0.0467	0.0495		$\zeta_{12b,8a}^{z_{12b,8a}}$	— 0.4148	— 0.2464
	$\zeta_{12a,6a}^{z_{12a,6a}}$	— 0.0023	0.0554		$\zeta_{13b,5a}^{z_{13b,5a}}$	— 0.0764	0.2235
	$\zeta_{12a,7a}^{z_{12a,7a}}$	0.2289	0.2964		$\zeta_{13b,6a}^{z_{13b,6a}}$	— 0.2791	— 0.1713
	$\zeta_{12a,8a}^{z_{12a,8a}}$	0.2394	0.1423		$\zeta_{13b,7a}^{z_{13b,7a}}$	— 0.0693	— 0.2562
	$\zeta_{13a,5a}^{z_{13a,5a}}$	0.0441	— 0.1290		$\zeta_{13b,8a}^{z_{13b,8a}}$	— 0.1815	0.1965
	$\zeta_{13a,6a}^{z_{13a,6a}}$	0.1612	0.0989		$\zeta_{14b,5a}^{z_{14b,5a}}$	0.5367	0.5043
	$\zeta_{13a,7a}^{z_{13a,7a}}$	0.0400	0.1479		$\zeta_{14b,6a}^{z_{14b,6a}}$	— 0.0461	0.2613
	$\zeta_{13a,8a}^{z_{13a,8a}}$	0.1048	— 0.1135		$\zeta_{14b,7a}^{z_{14b,7a}}$	— 0.2539	— 0.0734
					$\zeta_{14b,8a}^{z_{14b,8a}}$	0.1413	0.0364

Table IV. Coriolis coupling constants.

though some differences are noted for the non-bonded mean amplitudes.

The ζ values obtained are given in Table IV.

The individual ζ value for a given vibration depends on the masses of the atoms, the geometry of the molecule, and the vibrational potential function. However, several authors⁷⁻¹⁰ have shown that for harmonic oscillations the sum of the ζ values of the vibrations in a given degenerate symmetry species is independent of the force system chosen to represent the molecule. Several useful relations among the zetas have already been worked out^{6, 10}. The following sum rules are applicable to these molecules.

For the $E' \times E'$ coupling

$$\zeta_5^z + \zeta_6^z + \zeta_7^z + \zeta_8^z = -1.$$

For the $E'' \times E''$ coupling

$$\zeta_{12}^z + \zeta_{13}^z + \zeta_{14}^z = -1 + \frac{I_A}{2 I_B}$$

For the $A_1' \times A_2'$ coupling

$$(\zeta_{14}^z)^2 + (\zeta_{24}^z)^2 + (\zeta_{34}^z)^2 = 1$$

For the $A_1'' \times A_2''$ coupling

$$(\zeta_{9,10}^z)^2 + (\zeta_{9,11}^z)^2 = 1.$$

For $A_2' \times E''$,

$$\begin{aligned} \sum (\zeta_{4,i}^x)^2 &= \sum (\zeta_{4,i}^y)^2 \\ (i=12 a, 12 b, 13 a, 13 b, 14 a, 14 b) \\ \sum (\zeta_{4,i}^x)^2 + \sum (\zeta_{4,i}^y)^2 &= 1 \\ i=12 a \dots 14 b. \end{aligned}$$

For $A_1'' \times E'$,

$$\begin{aligned} \sum (\zeta_{9,i}^x)^2 &= \sum (\zeta_{9,i}^y)^2; \\ (i=5 a, 5 b, 6 a, 6 b, 7 a, 7 b, 8 a, 8 b), \\ \sum (\zeta_{9,i}^x)^2 + \sum (\zeta_{9,i}^y)^2 &= 1, \\ i=5 a \dots 8 b. \end{aligned}$$

The ζ values obtained here satisfy these sum rules quite well.

ζ^y values are not given in Table IV because $\zeta_{i,ja}^x = \zeta_{i,jb}^y$ and $\zeta_{i,jb}^x = -\zeta_{i,ja}^y$ for $A_1' \times E''$, $A_2' \times E''$, $A_1'' \times E'$ and $A_2'' \times E'$ couplings. For $E'' \times E'$ coupling

$$\zeta_{ia,ja}^x = -\zeta_{ib,jb}^x = -\zeta_{ia,jb}^y = -\zeta_{ib,ja}^y$$

and $\zeta_{ib,ja}^x = \zeta_{ia,jb}^x = \zeta_{ia,ja}^y = -\zeta_{ib,jb}^y$

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