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Generalized Mean-Square Amplitudes of Vibration, Mean Amplitudes of Vibration, and Shrinkage Effects of Some Trigonal Bipyramidal XY_5 and XY_3Z_2 Molecules

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Numerical values for the generalized mean-square amplitudes of vibration, mean amplitudes of vibration, and Bastiansen-Morino shrinkage effects are given for the trigonal bipyramidal molecules PF_5, PCl_3F_2, PCl_5, SbF_5, SbF_3Cl_2, $SbCl_5$, $NbCl_5$, and $TaCl_5$.

These molecules have been studied by many investigators who have given vibrational spectra consistent with D_{3h} symmetry. Force constants have also been determined.[1–7] Mean amplitudes of vibration have been calculated by Nagarajan [3,4,8] and Krishna Pillai *et al.*[7] Van Der Voorn *et al.*[6] have pointed out errors in Nagarajan's G matrix. These errors also give incorrect results for the mean amplitudes of vibration. In this work, therefore, the mean amplitudes of vibration have been recalculated.

For PF_5, PCl_3F_2, and PCl_5 the frequencies and force constants given by Van Der Voorn *et al.*[6] have been used. The fundamentals given by Carlson [9] were used for $SbCl_5$, and for the remaining compounds one applied vibrational frequencies quoted by Nagarajan.[4]

For the compounds SbF_5, SbF_3Cl_2, $SbCl_5$, $NbCl_5$, and $TaCl_5$ force constants were calculated assuming that all off-diagonal symmetry force constants are zero. Some authors assign a lower frequency of species E' to the YXY bending than to the YXZ bending, while others use the opposite assignment. In the tables, values consistent with the latter assumption are given in parentheses. All the numerical calculations were carried out on the UNIVAC computer at Norges tekniske högskole.

GENERALIZED MEAN-SQUARE AMPLITUDES

Morino and Hirota [10] have defined the concept of generalized mean-square amplitudes. They are based on the generalized interatomic displacements Δz, Δx, and Δy.

For an atom pair, ij, Δz_{ij} gives the displacement along a line through the equilibrium position of atoms i and j in the direction from j to i. The mean-square amplitude $\langle \Delta z_{ij}^2 \rangle$ may be identified with the mean-square amplitude of vibration for the ij distance. There is an ambiguity concerning the directions of Δx_{ij} and Δy_{ij}. The presently chosen directions of Δy are given below for the actual distances of the XY_3Z_2 molecules.

Distance XY: Δy parallel to the XY_3 plane.
Distance XZ: Δy parallel to the plane through atoms ZXY_1.
Distance Y··Y: Δy perpendicular to the XY_3 plane.
Distance Y··Z: Δy parallel to the XY_3 plane.
Distance Z··Z: Δy parallel to the plane through atoms ZXY_1.

The individual mean-square perpendicular amplitudes, $\langle \Delta x_{ij}^2 \rangle$ and $\langle \Delta y_{ij}^2 \rangle$, may change by a rotation around an axis in the Δz_{ij} direction, but the sum of the mean-square perpendicular amplitudes, *viz.* $\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_i^2 \rangle$, which is used in the calculation of Bastiansen-Morino shrinkage effect, is invariant. The mean cross products are given as $\langle \Delta x \Delta y \rangle$, $\langle \Delta y \Delta z \rangle$, and $\langle \Delta z \Delta x \rangle$. All the mean cross products but one are zero for trigonal bipyramidal XY_3Z_2 molecules. The exception is the $\langle \Delta z \Delta x \rangle$ type for the Y··Z distance.

Calculated values of the generalized mean-square amplitudes are given in Tables 1 and 2.

MEAN AMPLITUDES OF VIBRATION AND BASTIANSEN-MORINO SHRINKAGE EFFECTS

The mean amplitudes of vibration are given in Table 3. They are the square roots of the mean-square parallel amplitudes.

Because of the geometry of the XY_3Z_2 molecules, the resultant contribution to the shrinkage effect from the anharmonicity terms is zero. The shrinkage may then be found when the perpendicular mean-square amplitudes of vibration and the equilibrium distances of the molecule are known.[11,12] Table 4 gives the calculated shrinkage effects.

CONCLUSION

As mentioned above, some authors disagree in their assignments of the bending frequencies of species E'. When the lower frequency is assigned to the YXY bending, this leads to higher values (at 298°K) of the mean amplitudes of vibration for the Y··Y distance than for the Y··Z distance. The other assignment gives the opposite result. The assignment also influences the shrinkage effect.

Following the first assignment, *i.e.* YXY bending assigned to the lower frequency, the mean amplitude of vibration for the Y··Y distance of several molecules seems rather high. On the other hand, when the opposite assignment is used the mean amplitude for the Y··Z distance is higher than expected. It is possible that the assumption of making the off-diagonal symmetry force constants as small as possible is not valid, but at the moment there are not sufficient data to determine these force constants with better confidence.

Table 1. Parallel and perpendicular mean-square amplitudes (Å²) at 0°K and 298.16°K.*

PF_5						
Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
P—F_{eq}	0.0016 (0.0016)	0.0016 (0.0016)	0.0017 (0.0017)	0.0019 (0.0019)	0.0027 (0.0017)	0.0041 (0.0019)
P—F_{ax}	0.0019 (0.0019)	0.0020 (0.0020)	0.0017 (0.0026)	0.0020 (0.0038)	0.0017 (0.0026)	0.0020 (0.0038)
F_{eq}·$\cdot F_{eq}$	0.0035 (0.0027)	0.0047 (0.0030)	0.0024 (0.0016)	0.0036 (0.0019)	0.0020 (0.0020)	0.0023 (0.0023)
F_{eq}·$\cdot F_{ax}$	0.0031 (0.0035)	0.0036 (0.0045)	0.0021 (0.0025)	0.0024 (0.0033)	0.0035 (0.0034)	0.0054 (0.0050)
F_{ax}·$\cdot F_{ax}$	0.0028 (0.0028)	0.0030 (0.0030)	0.0015 (0.0015)	0.0018 (0.0018)	0.0015 (0.0015)	0.0018 (0.0018)

* Values in parentheses are calculated assigning the higher bending frequency of species E' to the YXY bending. An atom having the subscript *eq* is one of the Y atoms of XY_3Z_2, and an atom with subscript *ax* is one of the Z atoms.

PCl_3F_2						
Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
P—Cl	0.0019 (0.0019)	0.0023 (0.0022)	0.0016 (0.0016)	0.0022 (0.0022)	0.0042 (0.0016)	0.0130 (0.0019)
P—F	0.0019 (0.0019)	0.0020 (0.0020)	0.0027 (0.0060)	0.0035 (0.0173)	0.0027 (0.0060)	0.0035 (0.0173)
Cl·$\cdot$Cl	0.0044 (0.0024)	0.0120 (0.0032)	0.0031 (0.0012)	0.0103 (0.0016)	0.0008 (0.0008)	0.0011 (0.0011)
Cl·$\cdot$F	0.0034 (0.0055)	0.0047 (0.0139)	0.0023 (0.0035)	0.0031 (0.0085)	0.0054 (0.0061)	0.0156 (0.0184)
F·$\cdot$F	0.0028 (0.0028)	0.0031 (0.0031)	0.0035 (0.0035)	0.0051 (0.0051)	0.0035 (0.0035)	0.0051 (0.0051)

PCl_5						
Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
P—Cl_{eq}	0.0020 (0.0021)	0.0025 (0.0027)	0.0024 (0.0025)	0.0037 (0.0037)	0.0048 (0.0018)	0.0176 (0.0026)

$P-Cl_{ax}$	0.0025 (0.0025)	0.0033 (0.0033)	0.0021 (0.0047)	0.0031 (0.0167)	0.0021 (0.0047)	0.0031 (0.0167)
$Cl_{eq}\cdot\cdot Cl_{eq}$	0.0049 (0.0029)	0.0158 (0.0046)	0.0036 (0.0017)	0.0141 (0.0030)	0.0022 (0.0022)	0.0040 (0.0040)
$Cl_{eq}\cdot\cdot Cl_{ax}$	0.0032 (0.0041)	0.0053 (0.0105)	0.0022 (0.0032)	0.0035 (0.0094)	0.0052 (0.0049)	0.0200 (0.0185)
$Cl_{ax}\cdot\cdot Cl_{ax}$	0.0026 (0.0026)	0.0036 (0.0036)	0.0014 (0.0014)	0.0026 (0.0026)	0.0014 (0.0014)	0.0026 (0.0026)

SbF_5

Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
$Sb-F_{eq}$	0.0014 (0.0014)	0.0014 (0.0015)	0.0034 (0.0034)	0.0071 (0.0071)	0.0074 (0.0027)	0.0331 (0.0047)
$Sb-F_{ax}$	0.0015 (0.0015)	0.0016 (0.0016)	0.0030 (0.0067)	0.0054 (0.0278)	0.0030 (0.0067)	0.0054 (0.0278)
$F_{eq}\cdot\cdot F_{eq}$	0.0073 (0.0038)	0.0276 (0.0055)	0.0060 (0.0025)	0.0254 (0.0042)	0.0045 (0.0045)	0.0092 (0.0092)
$F_{eq}\cdot\cdot F_{ax}$	0.0055 (0.0073)	0.0099 (0.0211)	0.0032 (0.0050)	0.0053 (0.0165)	0.0097 (0.0087)	0.0383 (0.0323)
$F_{ax}\cdot\cdot F_{ax}$	0.0026 (0.0026)	0.0029 (0.0029)	0.0034 (0.0034)	0.0069 (0.0069)	0.0034 (0.0034)	0.0069 (0.0069)

SbF_3Cl_2

Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta x^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
Sb—F	(0.0016)	(0.0018)	(0.0036)	(0.0073)	(0.0016)	(0.0020)
Sb—Cl	(0.0016)	(0.0021)	(0.0025)	(0.0069)	(0.0025)	(0.0069)
F··F	(0.0033)	(0.0039)	(0.0018)	(0.0023)	(0.0047)	(0.0077)
F··Cl	(0.0048)	(0.0098)	(0.0037)	(0.0079)	(0.0037)	(0.0087)
Cl··Cl	(0.0024)	(0.0033)	(0.0008)	(0.0013)	(0.0008)	(0.0013)

$SbCl_5$

Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
$Sb-Cl_{eq}$	0.0016 (0.0016)	0.0022 (0.0020)	0.0028 (0.0028)	0.0074 (0.0073)	0.0055 (0.0024)	0.0307 (0.0061)

$Sb-Cl_{ax}$	0.0018 (0.0018)	0.0027 (0.0027)	0.0026 (0.0050)	0.0064 (0.0264)	0.0026 (0.0050)	0.0064 (0.0264)
$Cl_{eq}\cdot\cdot Cl_{eq}$	0.0059 (0.0037)	0.0260 (0.0075)	0.0046 (0.0023)	0.0241 (0.0056)	0.0034 (0.0034)	0.0091 (0.0089)
$Cl_{eq}\cdot\cdot Cl_{ax}$	0.0047 (0.0059)	0.0114 (0.0211)	0.0031 (0.0043)	0.0070 (0.0171)	0.0071 (0.0066)	0.0369 (0.0322)
$Cl_{ax}\cdot\cdot Cl_{ax}$	0.0031 (0.0031)	0.0049 (0.0049)	0.0024 (0.0024)	0.0064 (0.0064)	0.0024 (0.0024)	0.0064 (0.0064)

$NbCl_5$

Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
$Nb-Cl_{eq}$	0.0018 (0.0018)	0.0025 (0.0025)	0.0027 (0.0027)	0.0067 (0.0067)	0.0038 (0.0026)	0.0140 (0.0066)
$Nb-Cl_{ax}$	0.0016 (0.0016)	0.0021 (0.0021)	0.0027 (0.0037)	0.0065 (0.0126)	0.0027 (0.0037)	0.0065 (0.0126)
$Cl_{eq}\cdot\cdot Cl_{eq}$	0.0043 (0.0035)	0.0131 (0.0075)	0.0034 (0.0025)	0.0119 (0.0063)	0.0027 (0.0027)	0.0061 (0.0061)
$Cl_{eq}\cdot\cdot Cl_{ax}$	0.0044 (0.0048)	0.0101 (0.0132)	0.0030 (0.0035)	0.0071 (0.0102)	0.0055 (0.0052)	0.0202 (0.0188)
$Cl_{ax}\cdot\cdot Cl_{ax}$	0.0023 (0.0023)	0.0030 (0.0030)	0.0020 (0.0020)	0.0045 (0.0045)	0.0020 (0.0020)	0.0045 (0.0045)

$TaCl_5$

Atom pair	Parallel $\langle \Delta z^2 \rangle$		Perpendicular $\langle \Delta x^2 \rangle$		$\langle \Delta y^2 \rangle$	
	0°	298.16°	0°	298.16°	0°	298.16°
$Ta-Cl_{eq}$	0.0015 (0.0015)	0.0020 (0.0020)	0.0025 (0.0025)	0.0066 (0.0066)	0.0035 (0.0023)	0.0131 (0.0060)
$Ta-Cl_{ax}$	0.0014 (0.0014)	0.0019 (0.0019)	0.0024 (0.0033)	0.0059 (0.0117)	0.0024 (0.0033)	0.0059 (0.0117)
$Cl_{eq}\cdot\cdot Cl_{eq}$	0.0041 (0.0033)	0.0121 (0.0068)	0.0032 (0.0023)	0.0110 (0.0056)	0.0028 (0.0028)	0.0064 (0.0064)
$Cl_{eq}\cdot\cdot Cl_{ax}$	0.0042 (0.0047)	0.0097 (0.0126)	0.0028 (0.0033)	0.0065 (0.0093)	0.0053 (0.0050)	0.0189 (0.0175)
$Cl_{ax}\cdot\cdot Cl_{ax}$	0.0023 (0.0023)	0.0031 (0.0031)	0.0021 (0.0021)	0.0048 (0.0048)	0.0021 (0.0021)	0.0048 (0.0048)

Table 2. Mean cross product, $\langle \Delta z \Delta x \rangle$, for the Y··Z distance (Å²) at 0°K and 298.16°K.

Molecule	0°	298.16°
PF_5	0.0000 (0.0004)	0.0000 (0.0009)
PCl_3F_2	0.0002 (0.0017)	0.0002 (0.0072)
PCl_5	0.0000 (0.0010)	0.0001 (0.0060)
SbF_5	−0.0003 (0.0016)	−0.0009 (0.0103)
SbF_3Cl_2 $SbCl_5$	(−0.0004) −0.0001 (0.0010)	(−0.0002) −0.0006 (0.0094)
$NbCl_5$	0.0000 (0.0006)	0.0001 (0.0031)
$TaCl_5$	0.0000 (0.0004)	−0.0003 (0.0026)

Table 3. Mean amplitudes of vibration (Å) at 0°K and 298.16°K.

Atom pair	PF_5		PCl_3F_2		PCl_5	
	0°	298.16°	0°	298.16°	0°	298.16°
$P-F_{eq}$	0.0397 (0.0394)	0.0406 (0.0402)				
$P-F_{ax}$	0.0431 (0.0431)	0.0445 (0.0445)	0.0436 (0.0436)	0.0452 (0.0452)		
$P-Cl_{eq}$			0.0434 (0.0433)	0.0475 (0.0473)	0.0449 (0.0458)	0.0502 (0.0523)
$P-Cl_{ax}$					0.0499 (0.0499)	0.0577 (0.0577)
Y··Y	0.0588 (0.0520)	0.0685 (0.0549)	0.0660 (0.0490)	0.1095 (0.0569)	0.0697 (0.0540)	0.1255 (0.0681)
Y··Z	0.0559 (0.0593)	0.0599 (0.0670)	0.0585 (0.0740)	0.0686 (0.1177)	0.0566 (0.0641)	0.0729 (0.1024)
Z··Z	0.0527 (0.0527)	0.0551 (0.0551)	0.0530 (0.0530)	0.0555 (0.0555)	0.0507 (0.0507)	0.0601 (0.0601)

Atom pair	SbF_5 0°	SbF_5 298.16°	SbF_3Cl_2 0°	SbF_3Cl_2 298.16°	$SbCl_5$ 0°	$SbCl_5$ 298.16°
Sb—F_{eq}	0.0371 (0.0371)	0.0382 (0.0382)	(0.0402)	(0.0422)		
Sb—F_{ax}	0.0383 (0.0383)	0.0397 (0.0397)				
Sb—Cl_{eq}					0.0401 (0.0401)	0.0473 (0.0473)
Sb—Cl_{ax}			(0.0395)	(0.0461)	0.0425 (0.0425)	0.0520 (0.0520)
Y··Y	0.0852 (0.0613)	0.1635 (0.0740)	(0.0575)	(0.0625)	0.0768 (0.0607)	0.1612 (0.0867)
Y··Z	0.0739 (0.0855)	0.0994 (0.1452)	(0.0697)	(0.0990)	0.0686 (0.0766)	0.1065 (0.1451)
Z··Z	0.0514 (0.0514)	0.0534 (0.0534)	(0.0493)	(0.0573)	0.0557 (0.0557)	0.0702 (0.0702)

Atom pair	$NbCl_5$ 0°	$NbCl_5$ 298.16°	$TaCl_5$ 0°	$TaCl_5$ 298.16°
X—Y	0.0419 (0.0419)	0.0504 (0.0503)	0.0382 (0.0382)	0.0449 (0.0448)
X—Z	0.0399 (0.0399)	0.0460 (0.0460)	0.0375 (0.0375)	0.0434 (0.0434)
Y··Y	0.0659 (0.0591)	0.1144 (0.0864)	0.0644 (0.0575)	0.1101 (0.0822)
Y··Z	0.0661 (0.0695)	0.1007 (0.1148)	0.0651 (0.0684)	0.0985 (0.1120)
Z··Z	0.0480 (0.0480)	0.0551 (0.0551)	0.0482 (0.0482)	0.0554 (0.0554)

Table 4. Bastiansen-Morino shrinkage effect (Å) at 0°K and 298.16°K.

Atom pair	PF_5 0°	PF_5 298.16°	PCl_3F_2 0°	PCl_3F_2 298.16°	PCl_5 0°	PCl_5 298.16°
Y··Y	0.0016 (0.0012)	0.0022 (0.0013)	0.0019 (0.0011)	0.0048 (0.0014)	0.0022 (0.0013)	0.0065 (0.0017)
Y··Z	0.0005 (0.0006)	0.0005 (0.0007)	0.0007 (0.0011)	0.0007 (0.0023)	0.0007 (0.0009)	0.0007 (0.0020)
Z··Z	0.0018 (0.0029)	0.0020 (0.0044)	0.0024 (0.0066)	0.0029 (0.0207)	0.0016 (0.0040)	0.0023 (0.0147)

Atom pair	SbF_5		SbF_3Cl_2		$SbCl_5$	
	0°	298.16°	0°	298.16°	0°	298.16°
Y··Y	0.0032	0.0126			0.0021	0.0101
	(0.0016)	(0.0032)	(0.0013)	(0.0026)	(0.0012)	(0.0032)
Y··Z	0.0007	0.0013			0.0005	0.0011
	(0.0010)	(0.0033)	(0.0005)	(0.0011)	(0.0007)	(0.0026)
Z··Z	0.0021	0.0038			0.0016	0.0040
	(0.0059)	(0.0265)	(0.0020)	(0.0057)	(0.0038)	(0.0212)

Atom pair	$NbCl_5$		$TaCl_5$	
	0°	298.16°	0°	298.16°
Y··Y	0.0017	0.0056	0.0015	0.0053
	(0.0013)	(0.0035)	(0.0012)	(0.0032)
Y··Z	0.0005	0.0010	0.0004	0.0010
	(0.0006)	(0.0014)	(0.0005)	(0.0014)
Z··Z	0.0019	0.0046	0.0016	0.0041
	(0.0027)	(0.0100)	(0.0024)	(0.0091)

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