

Normal co-ordinates through coriolis coupling constants

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Abstract. Normal co-ordinates, force fields and isotopic frequencies have been calculated for some XY_3 and XY_4 -type molecules using coriolis coupling constants.

Keywords. Coriolis coupling constants; force fields; isotopic frequencies; normal co-ordinates.

1. Introduction

It is well known that coriolis coupling constants strongly depend on the normal co-ordinates of any molecule. Instead of calculating these constants from normal co-ordinates, the reverse procedure is also possible if the constants are accurately determined. This is somewhat difficult because except in a few molecules of high symmetry, the infrared band contour cannot be sufficiently resolved to render an accurate evaluation of these constants. The availability of accurate data enables a reasonable estimate of the normal co-ordinates. Here we present some results in the case of XY_3 pyramidal, planar and XY_4 tetrahedral type molecules.

2. Theory

Meal and Polo (1956) had shown that the coriolis coupling constants about any axis α can be given by

$$\zeta^{\alpha} = l M^{\alpha} \tilde{l}, \quad (1)$$

where $\alpha = x, y, z$; M^{α} is an appropriate skew-symmetric matrix and l is an orthogonal matrix given by

$$Q = l q, \quad (2)$$

where Q s are the normal co-ordinates and q s the mass weighted cartesian co-ordinates of the molecule. The orthogonal transformation matrix l can be constructed as outlined by Wolfram *et al* (1966) for the symmetry types considered in this paper.

Let (S_{1a}^c, S_{1b}^c) and (S_{2a}^c, S_{2b}^c) represent the degenerate pairs of cartesian symmetry

co-ordinates for XY_3 pyramidal molecules. The normal co-ordinates can be written as in

$$\begin{aligned} Q_{1a} &= (a S_{1a}^c + S_{2a}^c)/(1+a^2)^{\frac{1}{2}}, \\ Q_{2a} &= (S_{1a}^c - a S_{2a}^c)/(1+a^2)^{\frac{1}{2}}, \\ Q_{1b} &= (a S_{1b}^c + S_{2b}^c)/(1+a^2)^{\frac{1}{2}}, \\ Q_{2b} &= (S_{1b}^c - a S_{2b}^c)/(1+a^2)^{\frac{1}{2}}. \end{aligned} \quad (3)$$

Similar expressions can be written for XY_3 planar and XY_4 tetrahedral-type molecules. In the above equation, a determines the mixing between the cartesian symmetry co-ordinates. From equation (1) the following expressions can be derived for the coriolis coupling constants.

2.1. XY_3 pyramidal molecules

$$\begin{aligned} \zeta_1 &= \left\{ \left[\frac{(3m_y)^{\frac{1}{2}} s_\beta a}{d_2} + \frac{(3m_x m_y)^{\frac{1}{2}} s_\beta^2}{d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right]^2 \right. \\ &\quad + \left[\frac{1}{\sqrt{3} (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \left[\frac{2 a \sqrt{m_x} s_\beta}{\sqrt{3}} - \frac{(d_2^2 - 2 m_x s_\beta^2)}{\sqrt{3} (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \\ &\quad - 2 \left[\frac{(d_2^2 - 3 m_x s_\beta^2)}{2 \sqrt{3} d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} - \frac{a \sqrt{3 m_x} s_\beta}{2 d_2} \right] \\ &\quad \left[\frac{a \sqrt{m_x} s_\beta}{2 \sqrt{3} d_2} + \frac{(d_2^2 + m_x s_\beta^2)}{2 \sqrt{3} d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \\ &\quad \left. - 2 \left[\frac{a \sqrt{m_x} s_\beta}{2 d_2} - \frac{(d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}}{2 d_2} \right]^2 \right\} \frac{1}{(1+a^2)}, \quad (4) \\ \zeta_2 &= \left\{ \left[\frac{(3m_y)^{\frac{1}{2}} s_\beta}{d_2} - \frac{a(3m_x m_y)^{\frac{1}{2}} s_\beta^2}{d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right]^2 - \left[\frac{a}{\sqrt{3} (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \right. \\ &\quad \left. \left[\frac{2 \sqrt{m_x} s_\beta}{\sqrt{3}} + \frac{a(d_2^2 - 2 m_x s_\beta^2)}{\sqrt{3} (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \right\} \end{aligned}$$

$$\begin{aligned}
& + 2 \left[\frac{(3m_x)^{\frac{1}{2}} s_\beta}{2d_2} + \frac{a(d_2^2 - 3m_x s_\beta^2)}{2\sqrt{3}d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \\
& \left[\frac{\sqrt{m_x} s_\beta}{2\sqrt{3}d_2} - \frac{a(d_2^2 + m_x s_\beta^2)}{2\sqrt{3}d_2 (d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}} \right] \\
& - 2 \left[\frac{\sqrt{m_x} s_\beta}{2d_2} + \frac{a(d_2^2 - m_x s_\beta^2)^{\frac{1}{2}}}{2d_2} \right]^2 \left. \vphantom{\frac{\sqrt{m_x} s_\beta}{2d_2}} \right\} \frac{1}{(1 + a^2)} \quad (5)
\end{aligned}$$

where $s_\beta = 2/\sqrt{3} s_{\alpha/2}$, α being the inter bond angle, m_x , m_y are the masses and $d_2^2 = (2m_x + 3m_y s_\beta^2)$ and a the mixing parameter.

The ζ sum rule from (4) and (5) gives,

$$\zeta_1 + \zeta_2 = - (2m_x c_\beta^2)/(d_2^2 - m_x s_\beta^2). \quad (6)$$

The above sum is also given by,

$$\zeta_1 + \zeta_2 = (I_A/2I_B) - 1, \quad (7)$$

where I_A , I_B being the principal moments of inertia. From table 1, it is seen that the value of ζ in (6) agrees with that in (7) as well as the experimental value. The small discrepancies between the experimental and theoretical values in some cases may be due to the experimental errors. Equations (4) and (5) involve the mixing parameter a , which can be evaluated once the values of ζ_1 and ζ_2 are known. Table 1 also presents the values of the mixing parameters calculated for the molecules and the mean value used in the computations.

Table 1. Coriolis data and mixing parameter for xy_3 pyramidal molecules

Molecule	ζ_1	ζ_2	$\zeta_1 + \zeta_2$	$\zeta_1 + \zeta_2$ values		Mixing parameter from		Mean
				equation (6)	equation (7)	ζ_1	ζ_2	
NH ₃	0.06(M)	-0.26*	-0.20	-0.199	-0.200	0.0146	0.0127	0.0136
PH ₃	0.02(M)	-0.43*	-0.41	-0.429	-0.390	0.0156	0.0221	0.0189
SbH ₃	0.01(M)	-0.48*	-0.47	-0.474	-0.474	0.00109	0.00167	0.00138
PF ₃	—	-0.629	—	—	—	—	-0.01996	-0.01996
PBr ₃	0.76(R)	-0.81†	-0.05	-0.056	-0.056	-0.729	-0.738	-0.734

*Meal and Polo (1956)

†Clark and Rippon (1974)

2.2. XY_3 planar molecules

$$\zeta_1 = \frac{2}{(1+a^2)} \left\{ \left[\frac{(m_x - 3m_y)}{2\sqrt{3}d_1d_2} - \frac{a(3m_x)^{\frac{1}{2}}}{2d_2} \right] \left[\frac{\sqrt{3}(m_x + m_y)}{2d_1d_2} - \frac{a\sqrt{m_x}}{2\sqrt{3}d_2} \right] \right. \\ \left. - \left[\frac{a\sqrt{m_x + d_1}}{2d_2} \right]^2 - \frac{1}{2} \left[\frac{d_2}{\sqrt{3}d_1} \right] \left[\frac{2a\sqrt{m_x}}{\sqrt{3}d_2} + \frac{\sqrt{3}m_y}{d_1d_2} \right] \right. \\ \left. + \frac{1}{2} \left[\frac{a(3m_y)^{\frac{1}{2}}}{d_2} - \frac{(3m_xm_y)^{1/2}}{d_1d_2} \right]^2 \right\} \quad (8)$$

$$\zeta_2 = \frac{2}{(1+a^2)} \left\{ \left[\frac{\sqrt{3}m_x}{2d_2} + \frac{a(m_x - 3m_y)}{2\sqrt{3}d_1d_2} \right] \left[\frac{\sqrt{m_x}}{2\sqrt{3}d_2} + \frac{\sqrt{3}a(m_x + m_y)}{2d_1d_2} \right] \right. \\ \left. - \left[\frac{m_x - ad_1}{2d_2} \right]^2 + \frac{1}{2} \left[\frac{ad_2}{\sqrt{3}d_1} \right] \left[\frac{2\sqrt{m_x}}{\sqrt{3}d_2} - \frac{a\sqrt{3}m_y}{d_1d_2} \right] \right. \\ \left. + \frac{1}{2} \left[\frac{\sqrt{3}m_y}{d_2} + \frac{a\sqrt{3m_xm_y}}{d_1d_2} \right]^2 \right\} \quad (9)$$

where $d_1^2 = (m_x + 3m_y)$, $d_2^2 = (2m_x + 3m_y)$.

The coriolis data of molecules belonging to this symmetry are meagre and are accurate only for the boron trihalides. Table 2 gives the mixing parameter values obtained by using the above relations. Here the ζ sum rule is $\zeta_1 + \zeta_2 = 0$, which can be easily verified from (8) and (9). Table 2 also shows that the sum rule is not obeyed for $^{11}\text{BCl}_3$ and hence the mixing parameter is slightly different as calculated from ζ_1 and ζ_2 .

2.3. XY_4 tetrahedral type molecules

$$\zeta_1 = (a^2 - \frac{1}{2}) / (1 + a^2), \quad (10)$$

$$\zeta_2 = \frac{[1 - (a^2/2)]}{(1 + a^2)}, \quad (11)$$

Table 2. Coriolis data and mixing parameter for xy_3 planar molecules

Molecule	ζ_1	ζ_2	Mixing parameter		Mean
			ζ_1	ζ_2	
$^{10}\text{BF}_3$	0.70*	—	-0.985	—	-0.985
$^{11}\text{BCl}_3$	0.78*	-0.73*	-0.865	-1.254	-1.06
$^{11}\text{BBr}_3$	—	-0.95*	—	-2.165	-2.165
$^{10}\text{BI}_3$	0.95*	—	-3.044	—	-3.044

*Levin and Abramowitz (1965)

and the ζ sum rule is given by

$$\zeta_1 + \zeta_2 = \frac{1}{2}, \quad (12)$$

which can be easily seen from (10) and (11). Table 3 gives the ζ values and the mixing parameters for some molecules of this symmetry.

3. Force field calculations

The mixing parameter a from the coriolis coupling constants gives the symmetry force constants.

The normal co-ordinate transformation matrix L between the internal symmetry and normal co-ordinates can be given by

$$[L] = [B] [\tilde{A}], \quad (13)$$

where $[A]$ is the mixing parameter matrix given by

$$\begin{bmatrix} a & 1 \\ 1 & -a \end{bmatrix} \frac{1}{(1+a^2)^{1/2}}, \quad (14)$$

B is the matrix relating internal symmetry and mass-weighted cartesian co-ordinates, (Wolfram *et al* 1966).

From the L matrix, the force constant matrix can be evaluated from

$$F = \tilde{L}^{-1} \Lambda L^{-1}. \quad (15)$$

The force constants calculated for XY_3 pyramidal and planar type molecules are shown in table 4 along with literature values calculated by independent methods. As our entire calculation is based on the coriolis constants, even a slight inaccuracy causes variation in the final force constant values. If the coriolis constants are

Table 3. Coriolis data and mixing parameter for xy_4 tetrahedral molecules.

Molecule	ζ_1	ζ_2	Mixing parameter from	
			ζ_1	ζ_2
$^{28}\text{SiF}_4$	0.66*	-0.06*	± 1.147	± 1.552
CH_4	0.056*	+0.45*	± 0.767	± 0.761
SnH_4	-0.06**	+0.571**	± 0.644	± 0.639
SiH_4	0.008†	+0.492†	± 0.716	± 0.716
GeH_4	-0.031††	+0.53††	± 0.674	± 0.674

*Shimanouchi *et al* (1966)

**Barraclough (1975)

†Kattenberg and Oskam (1974)

††Straley *et al* 1942

Table 4. Force constants of xy_3 pyramidal and planar molecules.

Molecule	Force constant values ($\text{m} \cdot \text{dy} / \text{\AA}$)					
	Calculated			Literature values		
	F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}
XY ₃ pyramidal type molecule						
NH ₃	6.468	-0.1155	0.6049	6.473*	-0.162*	-0.616*
PH ₃	3.117	-0.0442	0.3667	3.109*	-0.039*	0.355*
PF ₃	4.959	-0.1644	0.501	4.7**	-0.05**	-0.57**
SbH ₃	2.017	-0.0071	0.2014	—	—	—
PbBr ₃	0.5628	-0.0759	1.2993	1.8**	-0.18**	0.32**
XY ₃ planar type molecule						
BF ₃	8.14	-0.934	0.512	7.82†	-0.81†	0.50†
BCl ₃	5.29	-0.971	0.332	4.19†	-0.51†	0.25†
BBr ₃	2.59	-0.140	0.199	2.60†	-0.20†	0.19†
BI ₃	2.38	-0.100	0.029	2.25†	-0.17†	0.13†

*Shimanouchi *et al* (1966)

**Clark and Rippon (1974)

†Levin and Abramowitz (1965)

Table 5. Isotopic frequencies predicted in cm^{-1}

Molecule	Calculated		Literature values*	
	ω_1	ω_2	ω_1	ω_2
XY ₃ pyramidal				
ND ₃	2531	1180.6	2556	1191
NT ₃	2148	967.5	2163	1000
PD ₃	1661.7	805.6	1687	806
PT ₃	1371.7	669.5	1401	668
SbD ₃	1366.7	579.5	1362	592.5
SbT ₃	1108.4	475.4	1125	486
XY ₃ planar				
¹¹ BF ₃	1445.3	482.0	1453.6	480.4
¹⁰ BCl ₃	986.0	257.0	994.0	255.0
¹⁰ BBr ₃	855.0	151.2	856.0	151.0
¹¹ BI ₃	704.5	100.0	704	100
XY ₄ tetrahedral				
²⁸ SiF ₄	1022.65	388.46	1022.9 ^a	387.8 ^a
³⁰ SiF ₄	1013.95	386.4	1014.4 ^a	386.4 ^a
CD ₄	2235.00	987.00	2259.0 ^a	996.0 ^a
CT ₄	1907.30	844.23		
SnD ₄	1352.70	485.45		
SnT ₄	1108.90	400.97		
BiD ₄	1581.20	671.10	1598.5 ^b	674.2 ^b
BiT ₄	1319.75	566.13		
GeH ₄	2135.58	823.78	2113.6 ^c	819.3 ^c
GeT ₄	1254.64	492.16		
CH ₃ D	2998.01	1449.4	3021 ^a	1471 ^a
		(1143.54)†		(1155)† ^a
SiH ₃ D	2167.85	952.3		
		(793.11)†		

*The literature values for XY₃ pyramidal molecules are from Sundaram (1961); XY₃ planar values are from Levin and Abramowitz (1966); XY₄ tetrahedral values are from ^aShimanouchi *et al* (1966), ^bKattenberg and Oskam (1974) and Straley *et al* (1942).

†Values in paranthesis give the corresponding ω_2 values.

accurate, the force field calculated agrees well with the standard values. In the case of PBr_3 , our values show a large variation in the reported values of the ζ constants.

4. Isotopic frequencies

The mixing parameter a also helps in determining the isotopically perturbed frequencies of any molecule (De Wames and Wolfram 1964). From the isotopic rules frequencies of some isotopes of XY_3 planar and XY_4 tetrahedral type molecules were calculated (table 5). The agreement between predicted and observed values is satisfactory.

Our results demonstrate the usefulness of accurate determination of the coriolis coupling constants for the determination of normal co-ordinates.

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