Theory and Calculation of Centrifugal Distortion Constants for Polyatomic Molecules

Part II. Application to Molecular Models

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The $T^{(i)}_{\alpha\beta,S}$ elements in the theory of centrifugal distotrtion are given for the linear XYZ and a number of four-atomic molecule models. For some of the most important ones of these models (viz. linear XYZ and X_2Y_2, planar and pyramidal XY_3) also the $J^{(i)}_{\alpha\beta,S}$ quantities are given, i. e. the derivatives of inertia tensor components.

1. Introduction

A modification of Kivelson and Wilson's[1] theory of calculating centrifugal distortion constants was presented in Part I[2]. In the present work we wish to show the application of this theory to some molecular models. The bent symmetrical XY_2 model has already been used[2] for exemplification of the theory. In the present paper we mainly wish to tabulate the nonvanishing $T^{(i)}_{\alpha\beta,S}$ elements for most of the molecular models included in our first paper of proposed standardized symmetry coordinates[3]. We omit the models for which the chosen cartesian axes are not coincident or parallel with a set of principal axes. The quantities of $t_{\alpha\beta\gamma\delta}$ in the notation of Kivelson and Wilson[1] are obtained from the mentioned elements by

$$t_{\alpha\beta\gamma\delta} = \sum_i \sum_j T^{(i)}_{\alpha\beta,S}\, T^{(j)}_{\gamma\delta,S}\, \Theta_{ij}\,,$$

which is equivalent to the matrix relation (37) or (38) of Part I[2]. Here Θ_{ij} are certain constants obtainable from the normal-coordinate analysis of harmonic vibrations[4]. In accord with Eq. (40) of Part I they read

$$\Theta_{ij} = \sum_k (L^{-1})_{ki}\, (L^{-1})_{kj}\, \lambda_k^{-1}$$

in terms of the inverse L matrix elements and the familiar frequency parameters $(\lambda_k = 4\,\pi^2\,c^2\,\omega_k^2)$. For some of the most important models we also give the partial derivatives at equilibrium of inertia tensor components, $J^{(i)}_{\alpha\beta,S}$. The centrifugal distortion constants may be obtained from these quantities by[1]

$$t_{\alpha\beta\gamma\delta} = \sum_i \sum_j J^{(i)}_{\alpha\beta,S}\, J^{(j)}_{\gamma\delta,S}\, N_{ij}\,,$$

where N_{ij} are the compliants given by

$$N_{ij} = \sum_k L_{ik}\, L_{jk}\, \lambda_k^{-1}\,.$$

For the connection between the $J^{(i)}_{\alpha\beta,S}$ and $T^{(i)}_{\alpha\beta,S}$ quantities it has been shown

$$J^{(i)}_{\alpha\beta,S} = \sum_j (G^{-1})_{ij}\, T^{(j)}_{\alpha\beta,S}\,,$$

which is equivalent to the matrix relation (51) of Part I[2].

It is hoped that the modified method invoking the $T^{(i)}_{\alpha\beta,S}$ elements, and in particular the expressions derived in the subsequent sections will facilitate the practical computations of centrifugal distortion constants for small molecules.

2. Application to Molecular Models

For standard orientations of the models with respect to the coordinate axes, and the chosen symmetry coordinates, the reader is referred to a previous paper[3]. We also adhere to the notation therein[3] for equilibrium structure parameters.

2.1. Linear XYZ *and linear symmetrical* X_2Y_2

In the considered linear XYZ and X_2Y_2 models the only nonvanishing $T^{(i)}_{\alpha\beta,S}$ and $J^{(i)}_{\alpha\beta,S}$ elements belong to the species Σ^+ and Σ_g^+, respectively. They are given below.

[1] D. Kivelson and E. B. Wilson jr., J. Chem. Phys. **21**, 1229 [1953].
[2] S. J. Cyvin, B. N. Cyvin, and G. Hagen, Z. Naturforsch. **23 a**, 1649 [1968].
[3] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, I. Elvebredd, and G. Hagen, Mol. Phys. **14**, 43 [1968].
[4] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.

Planar rectangular $Z_4(D_{2h})$				
$\boldsymbol{T}_{\alpha\beta,S}$	xx	yy	zz	yz
$S_1(A_g)$	$2R\sqrt{2}$	0	$2R\sqrt{2}$	.
$S_2(A_g)$	$2D\sqrt{2}$	$2D\sqrt{2}$	0	.
$S(B_{2g})$	.	.	.	$4\sqrt{RD}$

Puckered Z_4 ring (D_{2d})			
$\boldsymbol{T}_{\alpha\alpha,S}$	xx	yy	zz
$S_1(A_1)$	$4D\cos^2 A$	$4D\cos^2 A$	$8D\sin^2 A$
$S_2(A_1)$	$-4D(1-2\sin^2 A)\tan A$	$-4D(1-2\sin^2 A)\tan A$	$8D(1-2\sin^2 A)\tan A$
$S(B_1)$	$-4D\sin^2 A$	$4D\sin^2 A$	0
$\boldsymbol{T}_{\alpha\beta,S}$	yz	zx	xy
$S(B_2)$	.	.	$4D\tan A$
$S_a(E)$	k*	0	.
$S_b(E)$	0	k*	.

* $k=-D(1-2\sin^2 A)^{1/2}(1+2\sin^2 A)^{1/2}\tan A$.

Table 1. $T^{(i)}_{\alpha\beta,S}$ elements for two different Z_4 models.

For XYZ $(C_{\infty v})$:

$$T^{(1)}_{xx,S}=T^{(1)}_{yy,S}=2R_1,\quad T^{(2)}_{xx,S}=T^{(2)}_{yy,S}=2R_2,$$
$$J^{(1)}_{xx,S}=J^{(1)}_{yy,S}=2M^{-1}m_Y\times[R_1(m_X+m_Z)+R_2 m_Z],$$
$$J^{(2)}_{xx,S}=J^{(2)}_{yy,S}=2M^{-1}m_Z\times[R_1(m_X+m_Y)+R_1 m_Y].$$

Here as usual the symbols m_X, m_Y and m_Z denote the masses of the appropriate atoms, and M is the total mass of the molecule.

For X_2Y_2 $(D_{\infty h})$:

$$T^{(1)}_{xx,S}=T^{(1)}_{yy,S}=2\sqrt{2}R,\quad T^{(2)}_{xx,S}=T^{(2)}_{yy,S}=2D,$$
$$J^{(1)}_{xx,S}=J^{(1)}_{yy,S}=\sqrt{2}(2R+D)\,m_Y,$$
$$J^{(2)}_{xx,S}=J^{(2)}_{yy,S}=D\,m_X+(2R+D)\,m_Y.$$

2.2. *Planar rectangular Z_4 and puckered Z_4 rings*

The $T^{(i)}_{\alpha\beta,S}$ elements for the planar rectangular Z_4 model (symmetry D_{2h}) and puckered Z_4 ring (D_{2d}) are found in Table 1.

2.3. *Planar XY_3 and pyramidal XY_3 models*

The elements of $\boldsymbol{T}_{\alpha\beta,S}$ for the planar symmetrical XY_3 (D_{3h}) and regular pyramidal XY_3 (C_{3v}) models are found in Table 2 and 3, respectively. Table 2 also contains the $\boldsymbol{J}_{\alpha\beta,S}$ quantities for the planar model. The corresponding quantities of the pyramidal model are considerably more complex. However, they seem worth while being given here because of the great importance of the considered (ammonia-type) model.

$\boldsymbol{T}_{\alpha\beta,S}$	xx	yy	zz	xy
$S(A_1')$	$\sqrt{3}R$	$\sqrt{3}R$	$2\sqrt{3}R$	.
$S_{1a}(E')$	$-\frac{1}{2}\sqrt{6}R$	$\frac{1}{2}\sqrt{6}R$	.	0
$S_{2a}(E')$	$\frac{3}{2}\sqrt{2}R$	$-\frac{3}{2}\sqrt{2}R$	.	0
$S_{1b}(E')$	0	0	.	$\frac{1}{2}\sqrt{6}R$
$S_{2b}(E')$	0	0	.	$-\frac{3}{2}\sqrt{2}R$
$\boldsymbol{J}_{\alpha\beta,S}$	xx	yy	zz	xy
$S(A_1')$	$\sqrt{3}Rm_Y$	$\sqrt{3}Rm_Y$	$2\sqrt{3}Rm_Y$	.
$S_{1a}(E')$	$-\frac{1}{2}\sqrt{6}Rm_Y$	$\frac{1}{2}\sqrt{6}Rm_Y$	.	0
$S_{2a}(E')$	$\frac{1}{2}\sqrt{2}Rm_Y$	$-\frac{1}{2}\sqrt{2}Rm_Y$	.	0
$S_{1b}(E')$	0	0	.	$\frac{1}{2}\sqrt{6}Rm_Y$
$S_{2b}(E')$	0	0	.	$-\frac{1}{2}\sqrt{2}Rm_Y$

Table 2. $T^{(i)}_{\alpha\beta,S}$ and $J^{(i)}_{\alpha\beta,S}$ elements for the planar symmetrical XY_3 model (D_{3h}).

$$J^{(1)}_{xx,S}(A_1)=J^{(1)}_{yy,S}(A_1)=\tfrac{2}{3}\sqrt{3}RM^{-1}m_Y\times[m_X(1+2\cos^2 A)+6m_Y\sin^2 A],$$
$$J^{(2)}_{xx,S}(A_1)=J^{(2)}_{yy,S}(A_1)=\tfrac{1}{3}\sqrt{3}RM^{-1}m_Y\times(3m_Y-m_X)\sin 2A,$$
$$J^{(1)}_{zz,S}(A_1)=\tfrac{8}{3}R\,m_Y\sin^2 A,$$
$$J^{(2)}_{zz,S}(A_1)=\tfrac{2}{3}\sqrt{3}R\,m_Y\sin 2A,$$
$$J^{(1)}_{xx,S}(E_a)=-J^{(1)}_{yy,S}(E_a)=-\tfrac{2}{3}\sqrt{6}R\,m_Y\sin^2 A,$$
$$J^{(2)}_{xx,S}(E_a)=-J^{(2)}_{yy,S}(E_a)=\tfrac{1}{3}\sqrt{6}R\,m_Y\sin 2A,$$
$$J^{(1)}_{yz,S}(E_b)=J^{(1)}_{zx,S}(E_a)=4\sqrt{2}R^3(MI)^{-1}m_X m_Y^2(\cos^2 A+\tfrac{1}{2})\sin A\cos B,$$
$$J^{(2)}_{yz,S}(E_b)=J^{(2)}_{zx,S}(E_a)=2\sqrt{2}R^3(MI)^{-1}m_X m_Y^2\sin A\sin 2A\cos B,$$
$$J^{(1)}_{xy,S}(E_b)=\tfrac{2}{3}\sqrt{6}R\,m_Y\sin^2 A,$$
$$J^{(2)}_{xy,S}(E_b)=-\tfrac{1}{3}\sqrt{6}R\,m_Y\sin 2A.$$

$T_{\alpha\alpha,S}$	xx	yy	zz
$S_1(A_1)$	$\frac{2}{3}\sqrt{3}\,R(1+2\cos^2 A)$	$\frac{2}{3}\sqrt{3}\,R(1+2\cos^2 A)$	$\frac{8}{3}\sqrt{3}\,R\sin^2 A$
$S_2(A_1)$	$-\frac{2}{3}\sqrt{3}\,R(4\cos^2 A-1)\tan A$	$-\frac{2}{3}\sqrt{3}\,R(4\cos^2 A-1)\tan A$	$\frac{4}{3}\sqrt{3}(4\cos^2 A-1)\tan A$
$S_{1a}(E)$	$-\frac{2}{3}\sqrt{6}\,R\sin^2 A$	$\frac{2}{3}\sqrt{6}\,R\sin^2 A$	.
$S_{2a}(E)$	$\frac{1}{3}\sqrt{6}\,R(1+2\cos^2 A)\tan A$	$-\frac{1}{3}\sqrt{6}\,R(1+2\cos^2 A)\tan A$	.
$T_{\alpha\beta,S}$	yz	zx	xy
$S_{1a}(E)$	0	$2\sqrt{2}\,R\sin A\cos B$	0
$S_{2a}(E)$	0	$2\sqrt{2}\,R\sin A\tan A\cos B$	0
$S_{1b}(E)$	$2\sqrt{2}\,R\sin A\cos B$	0	$\frac{2}{3}\sqrt{6}\,R\sin^2 A$
$S_{2b}(E)$	$2\sqrt{2}\,R\sin A\tan A\cos B$	0	$-\frac{1}{3}\sqrt{6}\,R(1+2\cos^2 A)\tan A$

Table 3. $T^{(i)}_{\alpha\beta,S}$ elements for the regular pyramidal XY_3 model (C_{3v}). Notice: $\cos B=3^{-1/2}(4\cos^2 A-1)^{1/2}$.

Here $\cos B=3^{-1/2}(4\cos^2 A-1)^{1/2}$, M is the total mass of the molecule, and I is the moment of inertia; $I=I^e_{xx}=I^e_{yy}$. For further details, see [5].

2.4. Other four-atomic models

Table 4 shows the elements of $\boldsymbol{T}_{\alpha\beta,S}$ for other molecular models treated previously [3]. They are the (i) planar rhombic X_2Y_2, (ii) planar symmetrical cis-X_2Y_2, (iii) planar symmetrical XY_2Z, and (iv) linear WXYZ.

3. Relations Among $t_{\alpha\beta\gamma\delta}$ Constants for Some Models

In Part I the nonvanishing $t_{\alpha\beta\gamma\delta}$ constants for bent symmetrical XY_2 molecules are given, includ-

Planar rhombic $X_2Y_2(D_{2h})$				
$T_{\alpha\beta,S}$	xx	yy	zz	yz
$S_1(A_g)$	$4R$	$4R\cos^2 A$	$4R\sin^2 A$	.
$S_2(A_g)$	0	$-2\sqrt{2}\,R\sin 2A$	$2\sqrt{2}\,R\sin 2A$	.
$S(B_{3g})$	.	.	.	$2R\sin 2A$
Planar cis-$X_2Y_2(C_{2v})$				
$T_{\alpha\beta,S}$	xx	yy	zz	yz
$S_1(A_1)$	$2\sqrt{2}\,R$	$2\sqrt{2}\,R\sin^2 B$	$2\sqrt{2}\,R\cos^2 B$	.
$S_2(A_1)$	$2D$	0	$2D$	.
$S_3(A_1)$	0	$\sqrt{2}\,RD\sin 2B$	$-\sqrt{2}\,RD\sin 2B$	.
$S_1(B_2)$	.	.	.	$-\sqrt{2}\,R\sin 2B$
$S_2(B_2)$	.	.	.	$2\sqrt{2}\,RD\sin^2 B$
Planar symmetrical $XY_2Z(C_{2v})$				
$T_{\alpha\beta,S}$	xx	yy	zz	yz
$S_1(A_1)$	$2\sqrt{2}\,R$	$2\sqrt{2}\,R\cos^2 A$	$2\sqrt{2}\,R\sin^2 A$	.
$S_2(A_1)$	$2D$	$2D$	0	.
$S_3(A_1)$	0	$\sqrt{2}\,RD\sin 2A$	$-\sqrt{2}\,RD\sin 2A$	.
$S_1(B_2)$	.	.	.	$\sqrt{2}\,R\sin 2A$
$S_2(B_2)$	.	.	.	$2\sqrt{2}\,RD\sin^2 A$
Linear WXYZ$(C_{\infty v})$				
$T_{\alpha\alpha,S}$	xx	yy		
$S_1(\Sigma^+)$	$2R_1$	$2R_1$		
$S_2(\Sigma^+)$	$2R_2$	$2R_2$		
$S_3(\Sigma^+)$	$2D$	$2D$		

Table 4. Elements of $\boldsymbol{T}_{\alpha\beta,S}$ for other four-atomic models.

[5] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo 1968.

ing the existing relations between them. Here we shall discuss the similar features for some of the most important models under consideration. All the relations are easily derived from the tabulated $T^{(i)}_{\alpha\beta,S}$ elements.

3.1. *Linear* XYZ *and linear symmetrical* X_2Y_2

The relation $t_{xxxx} = t_{yyyy} = t_{xxyy}$ is typical for a linear molecule, where Z is chosen along the molecular axis. Fo two of the models studied here, viz. the XYZ and symmetrical X_2Y_2, we give here these only nonvanishing $t_{\alpha\beta\gamma\delta}$ constants. They may be evaluated as follows.

For XYZ ($C_{\infty v}$):

$$t_{xxxx} = t_{yyyy} \doteq t_{xxyy} = 4\,R_1^2\,\Theta_{11} + 8\,R_1\,R_2\,\Theta_{12} + 4\,R_2^2\,\Theta_{22}\,,$$

where the Θ_{ij} constants belong to species Σ^+.

For X_2Y_2 ($D_{\infty h}$):

$$t_{xxxx} = t_{yyyy} = t_{xxyy} = 8\,R^2\,\Theta_{11} + 8\sqrt{2}\,R\,D\,\Theta_{12} + 4\,D^2\,\Theta_{22}\,,$$

where Θ_{ij} belong to $\Sigma_g^{\,+}$.

3.2. *Planar symmetrical* XY_3 *model*

For the planar symmetrical XY_3 model an analysis yields the result that all the nonvanishing $t_{\alpha\beta\gamma\delta}$ may be expressed by only two independent constants. Firstly, we have:

$$t_{xxxx} = t_{yyyy} = 3\,R^2\,\Theta + \tfrac{3}{2}\,R^2\,\Theta_{11} - 3\sqrt{3}\,R^2\,\Theta_{12} + \tfrac{9}{2}\,R^2\,\Theta_{22}\,,$$

$$t_{xxyy} = 3\,R_2\,\Theta - \tfrac{3}{2}\,R^2\,\Theta_{11} + 3\sqrt{3}\,R^2\,\Theta_{12} + \tfrac{9}{2}\,R^2\,\Theta_{22}\,.$$

Here the symbol Θ refers to the element belonging to species A_1', and actually $\Theta = m_Y/\lambda_1$. The constants Θ_{11}, Θ_{12} and Θ_{22} belong to the species E'. It is clear that only two of the above three $t_{\alpha\beta\gamma\delta}$ constants are independent. Next we have the following nonvanishing constants expressed in terms of those given above:

$$t_{xyxy} = \tfrac{1}{2}\,(t_{xxxx} - t_{xxyy}) = \tfrac{3}{2}\,R^2\,\Theta_{11} - 3\sqrt{3}\,R^2\,\Theta_{12} + \tfrac{9}{2}\,R^2\,\Theta_{22}\,,$$

$$t_{zzzz} = 2\,(t_{xxxx} + t_{xxyy}) = 12\,R^2\,\Theta\,,$$

$$t_{xxzz} = t_{yyzz} = t_{xxxx} + t_{xxyy} = 6\,R^2\,\Theta\,.$$

3.3. *Regular pyramidal* XY_3 *model*

In the regular pyramidal XY_3 model four of the $t_{\alpha\beta\gamma\delta}$ constants may be expressed in terms of two independent constants (say t_{xxxx} and t_{xxyy}) similarly to the above planar case:

$$t_{xxxx} = t_{yyyy} = K(A_1) + K(E)\,,$$

$$t_{xxyy} = K(A_1) - K(E)\,,$$

$$t_{xyxy} = \tfrac{1}{2}\,(t_{xxxx} - t_{xxyy}) = K(E)\,.$$

Here $K(A_1)$ and $K(E)$ are certain combinations of Θ_{ij} constants from species A_1 and E, respectively. These combinations are easily evaluated from the elements given in Table 3. But we have the additional nonvanishing constants as given below.

$$t_{zzzz}\,,\quad t_{xxzz} = t_{yyzz}\,,\quad t_{yzyz} = t_{zxzx}\,,$$

$$t_{xxzx} = -\,t_{yyzx} = -\,t_{yzxy}\,.$$

3.4. *Planar molecules with X perpendicular to the molecular plane*

For alle the here treated planar molecules except XY_3 (see above) the X axis is chosen perpendicular to the molecular plane. For these molecules certain relations hold between the constants t_{xxxx}, t_{yyyy}, t_{xxyy}, t_{xxzz} and t_{yyzz}, only three of them being independent. These relations have already been given in connection with the bent symmetrical XY_2 model [2], and shall not be repeated here.