Theory and Calculation of Centrifugal Distortion Constants for Polyatomic Molecules

Part II. Application to Molecular Models

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The $T_{ab,s}^{0}$ elements in the theory of centrifugal distortion are given for the linear XYZ and a number of four-atomic molecular models. For some of the most important ones of these models (viz. linear XY and X$_2$Y$_2$, planar and pyramidal X$_Y$$_2$) also the $f_{ab,s}^{0}$ 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 model has already been used 2 for exemplification of the theory. In the present paper we mainly wish to tabulate the nonvanishing $T_{ab,s}^{0}$ 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 $t_{ab;3}$ in the notation of Kivelson and Wilson 1 are obtained from the mentioned elements by

$$t_{ab;3} = \sum_i \sum_s T_{ab,s}^{(0)} N_{ij};$$

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

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

in terms of the inverse L matrix elements and the familiar frequency parameters ($\lambda_k = 4 \pi^2 \omega_k^2$). For some of the most important models we also give the partial derivatives at equilibrium of inertia tensor components, $f_{ab,s}^{(0)}$. The centrifugal distortion constants may be obtained from these quantities by

$$t_{ab;3} = \sum \sum J_{ab,s}^{(0)} J_{ab,s}^{(0)} N_{ij},$$

where $N_{ij}$ are the compliants given by

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

For the connection between the $J_{ab,s}^{(0)}$ and $T_{ab,s}^{(0)}$ quantities it has been shown

$$J_{ab,s}^{(0)} = \sum J_{ab,s}^{(0)} T_{ab,s}^{(0)},$$

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

It is hoped that the modified method invoking the $T_{ab,s}^{(0)}$ 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$_2$Y$_2$

In the considered linear XYZ and X$_2$Y$_2$ models the only nonvanishing $T_{ab,s}^{(0)}$ and $J_{ab,s}^{(0)}$ elements belong to the species $X^s$ and $X^b$, respectively. They are given below.

Planar rectangular \( Z_4(D_{2h}) \)

<table>
<thead>
<tr>
<th>( T_{xx,s} )</th>
<th>( xx )</th>
<th>( yy )</th>
<th>( zz )</th>
<th>( yz )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_1(A_B) )</td>
<td>( 2 R \sqrt[4]{2} )</td>
<td>0</td>
<td>( 2 R \sqrt[4]{2} )</td>
<td>.</td>
</tr>
<tr>
<td>( S_2(A_B) )</td>
<td>2 ( D \sqrt[4]{2} )</td>
<td>.</td>
<td>0</td>
<td>.</td>
</tr>
<tr>
<td>( S(B_{2g}) )</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>( 4 \sqrt{RD} )</td>
</tr>
</tbody>
</table>

Puckered \( Z_4 \) ring \( (D_2d) \)

<table>
<thead>
<tr>
<th>( T_{xx,s} )</th>
<th>( xx )</th>
<th>( yy )</th>
<th>( zz )</th>
<th>( xy )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_1(A_1) )</td>
<td>( 4 D \cos^2 A )</td>
<td>( 4 D \cos^2 A )</td>
<td>( 8 D \sin^2 A )</td>
<td>( 4 D \sin^2 A )</td>
</tr>
<tr>
<td>( S_2(A_1) )</td>
<td>( -4 D(1-2\sin^2 A) \tan A )</td>
<td>( -4 D(1-2\sin^2 A) \tan A )</td>
<td>0</td>
<td>.</td>
</tr>
<tr>
<td>( S(B_1) )</td>
<td>( -4 D\sin^2 A )</td>
<td>( 4 D \sin^2 A )</td>
<td>( 8 D(1-2\sin^2 A) \tan A )</td>
<td>( 4 D \sin^2 A )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( T_{xx,s} )</th>
<th>( yy )</th>
<th>( zz )</th>
<th>( xy )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S(B_2) )</td>
<td>.</td>
<td>k*</td>
<td>0</td>
</tr>
<tr>
<td>( S_a(E) )</td>
<td>k*</td>
<td>0</td>
<td>.</td>
</tr>
<tr>
<td>( S_b(E) )</td>
<td>0</td>
<td>k*</td>
<td>.</td>
</tr>
</tbody>
</table>

\[ k = -D(1-2\sin^2 A)^{1/4}(1+2\sin^2 A)^{1/4} \tan A \]

Table 1. \( T_{xx,s} \) elements for two different \( Z_4 \) models.

2.2. Planar rectangular \( Z_4 \) and puckered \( Z_4 \) rings

The \( T^{(ii)}_{xx,s} \) 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 \( T_{xx,s} \) 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 \( J_{xx,s} \) 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.
Table 3. $T_{33}^{ij}$ elements for the regular pyramidal $XY_2$ model ($C_{3v}$). Notice: $\cos B = 3^{-\frac{1}{2}} (4 \cos^2 A - 1)^{\frac{1}{2}}$. 

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

### 2.4. Other four-atomic models

Table 4 shows the elements of $T_{33}^{ij}$ for other molecular models treated previously. They are the (i) planar rhombic $X_2 Y_2$, (ii) planar symmetrical cis-$X_2 Y_2$, (iii) planar symmetrical $XY_2 Z$, and (iv) linear $WXYZ$. In Part I the nonvanishing $t_{\alpha \beta \gamma \delta}$ constants for bent symmetrical $XY_2$ molecules are given, includ-

<table>
<thead>
<tr>
<th>$T_{33}^{ij}$</th>
<th>$xx$</th>
<th>$yy$</th>
<th>$zz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{1}(iA_1)$</td>
<td>$\frac{2}{3} \sqrt{3} R (1 + 2 \cos^2 A)$</td>
<td>$\frac{2}{3} \sqrt{3} R (1 + 2 \cos^2 A)$</td>
<td>$\frac{2}{3} \sqrt{3} R \sin^2 A$</td>
</tr>
<tr>
<td>$S_{2}(iA_1)$</td>
<td>$-\frac{2}{3} \sqrt{3} R (4 \cos^2 A - 1) \tan A$</td>
<td>$-\frac{2}{3} \sqrt{3} R (4 \cos^2 A - 1) \tan A$</td>
<td>$\frac{2}{3} (4 \cos^2 A - 1) \tan A$</td>
</tr>
<tr>
<td>$S_{1b}(E)$</td>
<td>$-\frac{1}{3} \sqrt{6} R \sin^2 A$</td>
<td>$\frac{1}{3} \sqrt{6} R \sin^2 A$</td>
<td></td>
</tr>
<tr>
<td>$S_{za}(E)$</td>
<td>$\frac{1}{3} \sqrt{6} R (1 + 2 \cos^2 A) \tan A$</td>
<td>$-\frac{1}{3} \sqrt{6} R (1 + 2 \cos^2 A) \tan A$</td>
<td></td>
</tr>
<tr>
<td>$T_{33}^{ij}$</td>
<td>$yz$</td>
<td>$xx$</td>
<td>$xy$</td>
</tr>
<tr>
<td>$S_{1a}(E)$</td>
<td>0</td>
<td>$2 \sqrt{2} R \sin A \cos B$</td>
<td>0</td>
</tr>
<tr>
<td>$S_{2a}(E)$</td>
<td>0</td>
<td>$2 \sqrt{2} R \sin A \tan A \cos B$</td>
<td>0</td>
</tr>
<tr>
<td>$S_{1b}(E)$</td>
<td>$2 \sqrt{2} R \sin A \cos B$</td>
<td>0</td>
<td>$\frac{2}{3} \sqrt{6} R \sin^2 A$</td>
</tr>
<tr>
<td>$S_{2b}(E)$</td>
<td>$2 \sqrt{2} R \sin A \tan A \cos B$</td>
<td>0</td>
<td>$-\frac{1}{3} \sqrt{6} R (1 + 2 \cos^2 A) \tan A$</td>
</tr>
</tbody>
</table>

Table 4. Elements of $T_{33}^{ij}$ for other four-atomic models.

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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 \( T^{(s)}_{ij} \) elements.

### 3.1. Linear XYZ and linear symmetrical \( X_2Y_2 \)

The relation \( t_{xxxx} = t_{yyyy} = t_{zzzz} \) is typical for a linear molecule, where \( Z \) is chosen along the molecular axis. For two of the models studied here, viz. the XYZ and symmetrical \( X_2Y_2 \), we give here these only nonvanishing \( t_{abij} \) constants. They may be evaluated as follows.

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

\[
t_{xxxx} = t_{yyyy} = t_{zzzz} = 4 R_1^2 \Theta_{11} + 8 R_1 R_2 \Theta_{12} + 4 R_2^2 \Theta_{22},
\]

where the \( \Theta_{ij} \) constants belong to species \( \Sigma^+ \).

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

\[
t_{xxxx} = t_{yyyy} = t_{zzzz} = 8 R^2 \Theta_{11} + 8 \sqrt{2} RD \Theta_{12} + 4 D^2 \Theta_{22},
\]

where \( \Theta_{ij} \) belong to \( \Sigma^+ \).

### 3.2. Planar symmetrical \( XY_3 \) model

For the planar symmetrical \( XY_3 \) model an analysis yields the result that all the nonvanishing \( t_{abij} \) may be expressed by only two independent constants. Firstly, we have:

\[
t_{xxxx} = t_{yyyy} = 3 R^2 \Theta + \frac{3}{2} R^2 \Theta_{11} - 3 \sqrt{3} R^2 \Theta_{12} + \frac{3}{2} R^2 \Theta_{22},
\]

\[
t_{zzzz} = 3 R^2 \Theta - \frac{3}{2} R^2 \Theta_{11} + 3 \sqrt{3} R^2 \Theta_{12} + \frac{3}{2} R^2 \Theta_{22}.
\]

Here the symbol \( \Theta \) refers to the element belonging to species \( A_{1}' \), and actually \( \Theta = m_{\Sigma}/l_{1}' \). The constants \( \Theta_{11}, \Theta_{12} \) and \( \Theta_{22} \) belong to the species \( E' \). It is clear that only two of the above three \( t_{abij} \) constants are independent. Next we have the following nonvanishing constants expressed in terms of those given above:

\[
t_{xyyz} = \frac{1}{2} (t_{xxxx} - t_{zzzz}) = \frac{3}{2} R^2 \Theta_{11} - 3 \sqrt{3} R^2 \Theta_{12} + \frac{3}{2} R^2 \Theta_{22},
\]

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

\[
t_{zzzz} = t_{yyyy} = t_{zzzz} + t_{zzzz} = 6 R^2 \Theta.
\]

### 3.3. Regular pyramidal \( XY_3 \) model

In the regular pyramidal \( XY_3 \) model four of the \( t_{abij} \) constants may be expressed in terms of two independent constants (say \( t_{xxxx} \) and \( t_{yyyy} \)) similarly to the above planar case:

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

\[
t_{zzzz} = t_{zzzz} = K(A_1) - K(E),
\]

\[
t_{xyzz} = \frac{1}{2} (t_{xxxx} - t_{zzzz}) = K(E).
\]

Here \( K(A_1) \) and \( K(E) \) are certain combinations of \( \Theta_{ij} \) 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.

\[
t_{zzzz} = t_{yyyy} = t_{xyzz} = t_{yyyy} = t_{zzzz} = t_{zzzz} = t_{yyyy}.
\]

### 3.4. Planar molecules with \( X \) perpendicular to the molecular plane

For all 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 \( t_{xxxx}, t_{yyyy}, t_{zzzz}, t_{xyzz}, t_{zzzz} \) and \( t_{yyyy} \), only three of them being independent. These relations have already been given in connection with the bent symmetrical \( XY_2 \) model, and shall not be repeated here.