BILJEŠKE NOTES

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G Matrix for Tetrahedral X_4Y_4 Molecules

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Since the development of the so called GF matrix method[1] force constants calculations for many molecules of different structure have been performed. It is not difficult to obtain the elements of the G matrix for a molecule directly from s vectors, or from the general tables of g matrix elements[2]. However, the final G_{ik} elements are reported for most molecular structures. To complete the material we list the G_{ik} for tetrahedral $X_4 Y_4$, one of a few simple structures so far not being discussed. This structure is realized, *e. g.* in boron tetrachloride[3].

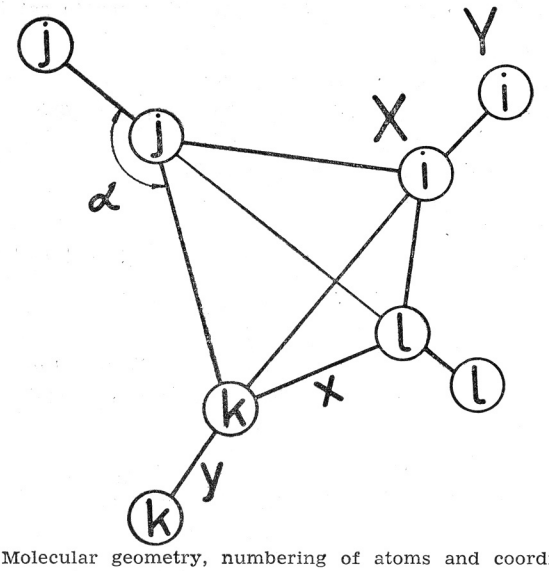

Fig. 1. Molecular geometry, numbering of atoms and coordinates.

Fig. 1. shows a molecular model with the numbering of atoms. Four bridged X atoms, to each of which an Y atom is bonded, form the inner tetrahedron X_4. The internal coordinates used are:

(ii) four $X_i Y_i$ bond length changes y,
(ij) six $X_i X_j$ bond length changes x, and
(iij) twelve $Y_i X_i X_j$ interbond angle changes α.

TABLE I

g matrix elements o tetrahedral X_4Y_4 molecules: (ii) represents X_iY_i bond length stretching, (ij) represents X_iX_j bond length stretching, and (iij) represents $X_iX_iY_j$ interbond angle deformation.

$$
\begin{aligned}
g\ (ii, ii) &= \mu_y + \mu_x \\
g\ (ii, ij) &= -(2/3)^{1/2}\,\mu_x \\
g\ (ii, iij) &= -(y/3x)^{1/2}\,\mu_y - (y/3x)^{1/2}\,\mu_x \\
g\ (ii, jji) &= [2\,(2x)^{1/2}/3\,y^{1/2}]\,\mu_x \\
g\ (ij, ij) &= 2\,\mu_x \\
g\ (ij, ik) &= \mu_x/2 \\
g\ (ij, iij) &= [-2x^{1/2}/(3y)^{1/2}]\,\mu_x \\
g\ (ij, iik) &= [x^{1/2}/2(3y)^{1/2} + (y/2x)^{1/2}]\,\mu_x \\
g\ (ij, kki) &= [-(3x)^{1/2}/2\,y^{1/2}]\,\mu_x \\
g\ (iij, iij) &= (y/x)\,\mu_y + [2x/y + y/x + 2\,(2/3)^{1/2}]\,\mu_x \\
g\ (iij, iik) &= [-x/2y - (2/3)^{1/2}]\,\mu_x \\
g\ (iij, jjk) &= (x/6y - 1/6^{1/2})\,\mu_x \\
g\ (iij, jji) &= [-x/3y - (2/3)^{1/2}]\,\mu_x \\
g\ (iij, kkj) &= (5x/6y)\,\mu_x
\end{aligned}
$$

Elements g (ii, jj), g (ii, jk), g (ii, jjk), g (ij, kl), g (ij, kkl), and g (iij, kkl), with no common atom to link the two coordinates, are zero.

TABLE II

G *matrix elements of tetrahedral X_4Y_4 molecules with the list of symmetry coordinates used (only one component for each degenerate set is given).*

$$
\begin{aligned}
A_1 : S_1 &= (y_1 + y_2 + y_3 + y_4)/2 \\
S_2 &= (x_{12} + x_{23} + x_{34} + x_{13} + x_{14} + x_{24})/6^{1/2} \\
E : S_3 &= (xy)^{1/2}\,(\alpha_{14} + \alpha_{41} + \alpha_{23} + \alpha_{32} - \alpha_{13} - \alpha_{31} - \alpha_{24} - \alpha_{42})/8^{1/2} \\
S_4 &= (x_{14} - x_{13} + x_{23} - x_{24})/2 \\
F_1 : S_5 &= (xy)^{1/2}\,(\alpha_{12} - \alpha_{21} - \alpha_{13} + \alpha_{31} + \alpha_{23} - \alpha_{32}/6^{1/2} \\
F_2 : S_6 &= (y_1 + y_2 - y_3 - y_4)/2 \\
S_7 &= (x_{12} - x_{34})/2^{1/2} \\
S_8 &= (xy)^{1/2}\,[2(\alpha_{12}+\alpha_{21}-\alpha_{34}-\alpha_{43})-\alpha_{13}-\alpha_{14}-\alpha_{23}-\alpha_{24}+\alpha_{32}+\alpha_{31}+\alpha_{42}+\alpha_{41}]24^{1/2}
\end{aligned}
$$

A_1 class

$$
\begin{aligned}
G_{11} &= \mu_y + \mu_x \\
G_{12} &= -2\,\mu_x \\
G_{13} &= 4\,\mu_x
\end{aligned}
$$

F_1 class

$$G_{55} = y^2\mu_y + (8x^2/3 + y^2 + 5\,xy/6^{1/2})\,\mu_x$$

E class

$$
\begin{aligned}
G_{33} &= \mu_x \\
G_{34} &= [(2/3)^{1/2}\,x - y]\,\mu_x \\
G_{44} &= y^2\,\mu_y/2 + (y^2/2 + 24^{1/2}\,xy)\,\mu_x
\end{aligned}
$$

F_2 class

$$
\begin{aligned}
G_{66} &= \mu_y + \mu_x \\
G_{67} &= -2\mu_x/3^{1/2} \\
G_{68} &= 0 \\
G_{77} &= 2\,\mu_x \\
G_{78} &= 0 \\
G_{88} &= y^2\,\mu_y + (11x^2/6 + y^2 + 6^{1/2}\,xy)\,\mu_x
\end{aligned}
$$

The corresponding g elements are listed in Table I. When symmetry of the molecule is taken into account considerable reduction of g matrix results. The equivalent internal coordinates are grouped into combinations which transform according to the character table[4] of the symmetry point group T_d.

The $X_4 Y_4$ molecule has 18 internal degrees of freedom which are distributed among classes of point group T_d as

$$2 A_1 + 2 E + F_1 + 3 F_2$$

A suitable set of orthonormal symmetry coordinates, with only one component for each degenerate set, and final G_{ik} elements are listed in Table II.

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IZVOD

G matrica za tetraedrijske molekule $X_4 Y_4$

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Koristeći standardnu methodu Wilsona i Eliashevicha (ref. 1.) izračunati su elementi inverzne matrice kinetičke energije (tablica I) za interne valentne koordinate, a zatim uvađanjem simetrije i za koordinate simetrije (tablica II) za tetraedrijske molekule $X_4 Y_4$.

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