Determination of Force Constants of Planar $XY_3$ and Tetrahedral $XY_4$
Molecules by the GF Matrix Method

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The force constants of the internal coordinates of planar $XY_3$ and tetrahedral $XY_4$ molecules were calculated using the GF matrix method. The matrix solutions were carried out by means of a computer program built relative to the Newton-Raphson method, and the calculations were listed in tables. For tetrahedral $XY_4$ molecules having the same Y atom it was found that the force constants decrease with the increasing mass of the X atom, and this was attributed to the slowing of the molecule with increasing mass of the centre X atom.

Key words: GF Matrix Method; Force Constants; $XY_3$ Molecules; $XY_4$ Molecules.

1. Introduction

The normal vibration theory of molecules by the GF matrix method has been given by many authors [1 – 4], and some authors have calculated the force constants of octahedral MX$_6$ molecules [5 – 6]. In our previous study we have calculated the force constants of non-linear $XY_2$ molecules by this method [7].

In this present work, the force constants of planar $XY_3$ and tetrahedral $XY_4$ molecules were calculated by the GF matrix method. The matrix solutions were obtained by means of a computer program based on the Newton-Raphson method, and the exchanges of force constants with the mass of centre atom X for tetrahedral $XY_4$ molecules having the same Y atom were examined and commented.

2. Theory and Calculation

Planar $XY_3$ and tetrahedral $XY_4$ molecules have four normal modes of vibration as shown in Figs. 1a and 1b. They have the symmetry $D_{3h}$ and $T_d$, respectively. The symmetry species of the vibrations are also given in the figure. These molecules have been described in terms of seven force constants in the internal coordinates. $f_r$ denotes the bond stretch force constant, $f_{rr}$ the interaction force constant between two $\Delta r$, $f_{\alpha\alpha}$ the interaction force constant between $\Delta r$ and $\Delta\alpha$ having a common bond, $f_{\alpha\alpha}'$ the interaction force constant between $\Delta r$ and $\Delta\alpha$ having no common bond, $f_{\theta}$ the bending force constant, $f_{\theta\theta}$ the interaction force constant between two $\Delta\alpha$ having no common bond, and $f_{\alpha\alpha}$ the force constant for the out-of-plane mode. The changes of $\Delta r$, $\Delta\alpha$ and $\Delta\theta$ can be seen in Figs. 2a and 2b.

2.1. Planar $XY_3$ Molecule

The elements of the G and F matrix for the mode in species $A'_1$ are

$$G = \mu_y, \quad F = f_r + 2f_{rr},$$  

for the mode in species $A''_2$ are

$$G = \frac{9}{4r^2}(\mu_y + 3\mu_x), \quad F = r^2f_{\theta},$$

and for the ones in species $E'$ are

$$G_{11} = \mu_y + \frac{3}{2}\mu_x,$$

$$G_{12} = \frac{3}{2r}\mu_x,$$

$$G_{22} = \frac{3}{2r^2}(2\mu_y + 3\mu_x),$$

$$F_{11} = f_r - f_{rr},$$

$$F_{12} = r(f_{\alpha\alpha}' - f_{\alpha\alpha}),$$

$$F_{22} = r^2(f_{\alpha} - f_{\alpha\alpha}).$$

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Fig. 1. Normal modes of vibration of a) planar XY3 molecules, and b) tetrahedral XY4 molecules.

Fig. 2. The changes $\Delta r_i$, $\Delta \alpha_i$ and $\Delta \theta$ of a) a planar XY3 molecule, and b) a tetrahedral XY4 molecule.

2.2. Tetrahedral XY4 Molecule

The elements of the $G$ and $F$ matrix for the mode in species $A_1$ are

$$G = \mu_y, \quad F = f_r + 3f_{rr},$$

for the mode in species $E$ are

$$G = \frac{3}{r^2}\mu_y, \quad F = r^2(f_a - 2f_{aa} + f_{aa'}),$$

and for the ones in species $F_2$ are

$$G_{11} = \mu_y + \frac{4}{3}\mu_x,$$

$$G_{12} = -\frac{8}{3r}\mu_x,$$

$$G_{22} = \frac{1}{r^3}\left(\frac{16}{3}\mu_x + 2\mu_y\right),$$

$$F_{11} = f_r - f_{rr},$$

$$F_{12} = \sqrt{2}r(f_{aa} - f_{aa'}),$$

$$F_{22} = r^2(f_a - f_{aa'}).$$

The secular equation of the GF matrix is given by

$$|\text{GF} - E\lambda| = 0$$

[3–4]. $\mu_x$ and $\mu_y$ are the reciprocals of masses of X and Y atoms.
where $E$ is the diagonal-unit matrix and the $\lambda$’s are the eigenvalues of the matrix. The values of $\lambda_i$ depend on the vibration frequencies by

$$\lambda_i = 4\pi^2 c^2 \nu^2_i.$$  \hfill (10)

After forming of the GF matrix in (9), the solution of the matrix was carried out using a computer program based on the Newton-Raphson method [8], taking the vibration frequencies and the bonding distances into account. We calculated the force constants as $f_r = 6.99956$ and $f_{\alpha} = 3.59016$ for planar BF$_3$ and BCl$_3$ molecules, respectively, and as $f_r = 2.75837$ for the tetrahedral SiH$_4$ molecule. These values are very close to the values given in [4] for the same molecules. After this agreement, we found the force constants for planar XY$_3$ and tetrahedral XY$_4$ molecules, and the results of these calculations are given in Tables 1 and 2, respectively. The values are suitable in error limits, also depend on the values taking from [3, 9]. This suitableness can be confirmed by comparing the values of $f_r$ and $f_{\alpha}$ of some molecules with the ones obtained by neglecting the interaction constants in [4] for some molecules. As doing this, we found $f_r = 8.82512$, $f_{\alpha} = 0.39671$ for BF$_3$, and $f_r = 4.63310$, $f_{\alpha} = 0.17078$ for BCl$_3$ molecules. These values of $f_r$ are absolutely same and the values of $f_{\alpha}$ are very close to the ones in [4] for the same molecule.

3. Discussion

Figure 3 shows the changes of the force constants of tetrahedral XY$_4$ molecules having the same Y atom with the mass of the X atom. As seen from the figure,

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$r(A)$</th>
<th>$f_r$</th>
<th>$f_{\alpha}$</th>
<th>$f_{\alpha}'$</th>
<th>$f_{\alpha}''$</th>
<th>$f_{\alpha}'''$</th>
<th>$f_{\alpha}''''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrF$_3$</td>
<td>1.313</td>
<td>6.99956</td>
<td>0.122378</td>
<td>0.016308</td>
<td>0.38288</td>
<td>-0.38260</td>
<td>-0.00144</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>1.742</td>
<td>3.59016</td>
<td>0.52147</td>
<td>0.015300</td>
<td>0.17040</td>
<td>-0.03061</td>
<td>-0.08520</td>
</tr>
<tr>
<td>Cl$_3$</td>
<td>1.742</td>
<td>3.41753</td>
<td>0.60779</td>
<td>0.016420</td>
<td>0.17005</td>
<td>-0.03284</td>
<td>-0.08502</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>1.893</td>
<td>2.84083</td>
<td>0.39859</td>
<td>0.014620</td>
<td>0.14186</td>
<td>-0.02924</td>
<td>-0.07093</td>
</tr>
<tr>
<td>BBr$_3$</td>
<td>1.893</td>
<td>2.68744</td>
<td>0.47528</td>
<td>0.015800</td>
<td>0.14328</td>
<td>-0.03161</td>
<td>-0.07164</td>
</tr>
<tr>
<td>BiF$_3$</td>
<td>2.118</td>
<td>2.18985</td>
<td>0.25444</td>
<td>0.014020</td>
<td>0.09441</td>
<td>-0.02804</td>
<td>-0.04720</td>
</tr>
<tr>
<td>Bi$_3$</td>
<td>2.118</td>
<td>2.06937</td>
<td>0.31468</td>
<td>0.015120</td>
<td>0.09451</td>
<td>-0.03023</td>
<td>-0.04725</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.472</td>
<td>4.84244</td>
<td>2.96294</td>
<td>0.042900</td>
<td>2.28169</td>
<td>-0.08581</td>
<td>-1.14085</td>
</tr>
</tbody>
</table>

Table 1. Bond lengths $r$ [9] and force constants $f$ of planar XY$_3$ molecules. Force constants are in units of mdyn/A.
the force constants decrease with increasing mass of the X atom. These changes are also seen for planar XY\textsubscript{3} molecules from Table 1. As seen from the table, the force constants are lower for the molecules consisting of \textsuperscript{11}B atom as X atom than the ones consisting of \textsuperscript{10}B atom for XY\textsubscript{3} molecules having the same Y atom. These were attributed to the slowing of the molecule with the increasing mass of the X atom. Because the more condensed phase has the lower frequency and force constants [7, 10] we think the molecule mobilises more slowly with the increasing mass of centre atom X like taking it to a more condensed phase.

Fig. 3. The changes of the bond stretch force constants of tetrahedral XY\textsubscript{4} molecules having the same Y atom with the mass of X atom. 1u = 1.6598 \times 10^{-24} \text{ kg}.