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 Δr, $f_{r\alpha}$ the interaction force constant between Δr and $\Delta\alpha$ having a common bond, $f_{r\alpha}{}'$ the interaction force constant between Δr and $\Delta\alpha$ having no common bond, f_α the bending force constant, $f_{\alpha\alpha}$ the interaction force constant between two $\Delta\alpha$ having a common bond, $f_{\alpha\alpha}{}'$ the interaction force constant between two $\Delta\alpha$ having no common bond, and f_θ the force constant for the out-of-plane mode. The changes of Δr_i, $\Delta\alpha_i$ 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

$$G = \mu_y, \quad F = f_r + 2f_{rr}, \tag{1}$$

for the mode in species A_2'' are

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

and for the ones in species E' are

$$\begin{aligned} G_{11} &= \mu_y + \frac{3}{2}\mu_x, \\ G_{12} &= \frac{3\sqrt{3}}{2r}\mu_x, \\ G_{22} &= \frac{3}{2r^2}(2\mu_y + 3\mu_x), \end{aligned} \tag{3}$$

$$\begin{aligned} F_{11} &= f_r - f_{rr}, \\ F_{12} &= r(f_{r\alpha}{}' - f_{r\alpha}), \\ F_{22} &= r^2(f_\alpha - f_{\alpha\alpha}). \end{aligned} \tag{4}$$

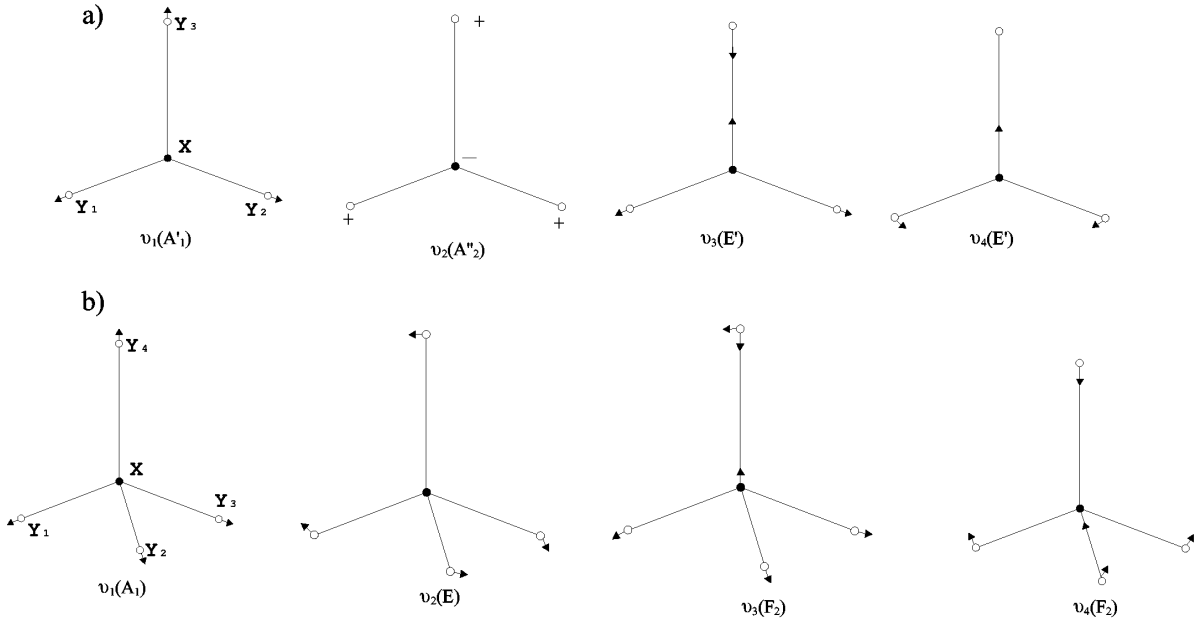

Fig. 1. Normal modes of vibration of a) planar XY_3 molecules, and b) tetrahedral XY_4 molecules.

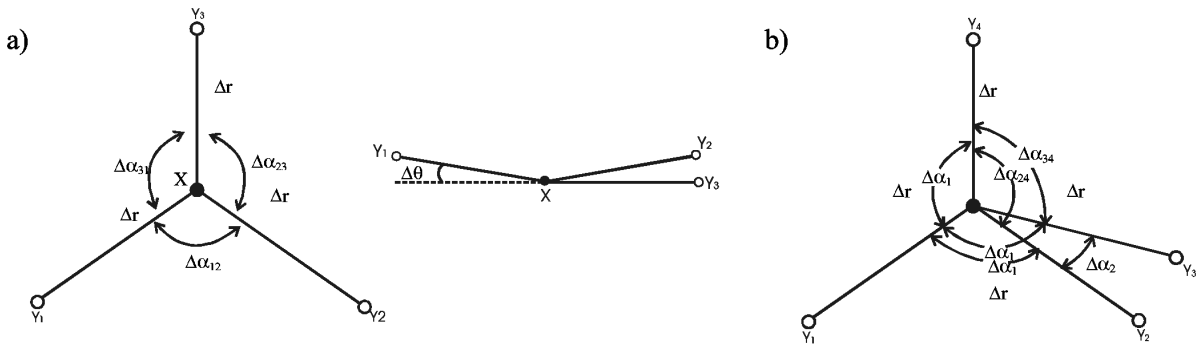

Fig. 2. The changes Δr_i, $\Delta\alpha_i$ and $\Delta\theta$ of a) a planar XY_3 molecule, and b) a tetrahedral XY_4 molecule.

2.2. Tetrahedral XY_4 Molecule

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

$$G = \mu_y, \quad F = f_r + 3f_{rr}, \tag{5}$$

for the mode in species E are

$$G = \frac{3}{r^2}\mu_y, \quad F = r^2(f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}), \tag{6}$$

and for the ones in species F_2 are

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

$$G_{12} = -\frac{8}{3r}\mu_x, \tag{7}$$

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

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

$$F_{12} = \sqrt{2}r(f_{r\alpha} - f_{r\alpha'}), \tag{8}$$

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

[3–4]. μ_x and μ_y are the reciprocals of masses of X and Y atoms. The secular equation of the GF matrix is given by

$$|\mathrm{GF} - \mathrm{E}\lambda| = 0 \tag{9}$$

Table 1. Bond lengths r [9] and force constants f of planar XY_3 molecules. Force constants are in units of mdyn/Å.

Molecule	r(Å)	f_r	f_{rr}	$f_{r\alpha}$	f_α	$f_{r\alpha}'$	$f_{\alpha\alpha}$	f_θ
$^{10}BF_3$	1.313	6.99956	0.91278	0.01630	0.38288	−0.03260	−0.19144	0.40884
$^{11}BF_3$	1.313	6.68966	1.06773	0.01743	0.38353	−0.03486	−0.19176	0.37867
$^{10}BCl_3$	1.742	3.59016	0.52147	0.01530	0.17040	−0.03061	−0.08520	0.19732
$^{11}BCl_3$	1.742	3.41753	0.60779	0.01642	0.17005	−0.03284	−0.08502	0.18122
$^{10}BBr_3$	1.893	2.84083	0.39859	0.01462	0.14186	−0.02924	−0.07093	0.14085
$^{11}BBr_3$	1.893	2.68744	0.47528	0.01580	0.14328	−0.03161	−0.07164	0.12695
$^{10}BI_3$	2.118	2.18985	0.25444	0.01402	0.09441	−0.02804	−0.04720	0.11367
$^{11}BI_3$	2.118	2.06937	0.31468	0.01512	0.09451	−0.03023	−0.04725	0.10357
SO_3	1.472	4.82449	2.96294	0.04290	2.28169	−0.08581	−1.14085	0.41271

Table 2. Bond lengths r [9] and force constants f of planar XY_4 molecules. Force constants are in units of mdyn/Å.

Molecule	r(Å)	f_r	f_{rr}	$f_{r\alpha}$	$f_{r\alpha}'$	f_α	$f_{\alpha\alpha}$	$f_{\alpha\alpha}'$
CI_4	2.150	12.23877	−3.29005	2.65063	−2.65063	1.88704	−0.03364	−1.75248
$^{12}CF_4$	1.323	12.12104	−0.95785	1.86773	−1.86773	1.51636	−0.11765	−1.04575
CBr_4	1.935	11.66016	−2.76812	2.41365	−2.41365	1.71373	−0.03892	−1.55804
$^{13}CF_4$	1.323	11.49810	−0.75699	1.75086	−1.75086	1.44667	−0.11765	−0.97606
SiF_4	1.553	8.55447	−0.46393	1.02408	−1.02408	0.70547	−0.04465	−0.52684
OsO_4	1.712	8.16205	0.20492	0.25559	−0.25559	0.35728	−0.05806	−0.12503
CCl_4	1.767	7.63367	−1.07788	1.36557	−1.36557	1.02353	−0.05464	−0.80499
RuO_4	1.706	7.06629	0.10520	0.36345	−0.36345	0.37150	−0.05429	−0.15434
$SiBr_4$	2.150	6.53723	−1.20621	1.20914	−1.20914	0.82331	−0.02118	−0.73858
GeF_4	1.680	5.98002	0.03848	0.43063	−0.43063	0.28850	−0.02613	−0.18398
$SiCl_4$	2.019	5.29852	−0.51464	0.79130	−0.79130	0.54148	−0.02610	−0.43706
CH_4	1.090	4.98200	0.02347	0.16184	−0.16184	0.38327	−0.07763	−0.07277
$TiBr_4$	2.339	4.30008	−0.60330	0.70732	−0.70732	0.45466	−0.01432	−0.39738
ZrF_4	1.902	4.18533	−0.05211	0.26658	−0.26658	0.16000	−0.01399	−0.10404
$TiCl_4$	2.170	3.70677	−0.18215	0.45530	−0.45530	0.27586	−0.01508	−0.21554
VCl_4	2.138	3.43330	−0.12324	0.40780	−0.40780	0.25502	−0.01901	−0.17898
$GeBr_4$	2.272	3.41086	−0.27777	0.48561	−0.48561	0.32439	−0.01591	−0.26075
$GeCl_4$	2.113	3.32439	−0.01644	0.33313	−0.33313	0.24163	−0.02083	−0.15829
GeI_4	2.490	3.24058	−0.45021	0.53662	−0.53662	0.36312	−0.01495	−0.30331
$ZrCl_4$	2.320	2.92373	0.01487	0.26136	−0.26136	0.14896	−0.01114	−0.10439
$HfCl_4$	2.330	2.79272	0.08496	0.16455	−0.16455	0.10696	−0.01207	−0.05867
$SnCl_4$	2.280	2.78170	0.00531	0.21704	−0.21704	0.14515	−0.01255	−0.09495
SiH_4	1.480	2.75837	0.02722	0.04244	−0.04244	0.17853	−0.03136	−0.05309
$SnBr_4$	2.440	2.64975	−0.12380	0.31449	−0.31449	0.19666	−0.01071	−0.15381
GeH_4	1.525	2.61367	0.00663	0.01751	−0.01751	0.15367	−0.02859	−0.03930
SnI_4	2.640	2.32410	−0.22147	0.33280	−0.33280	0.21165	−0.00917	−0.17495
$PbCI_4$	2.430	2.19829	0.01163	0.12193	−0.12193	0.07504	−0.00939	−0.03744

where E is the diagonal-unit matrix and the λ's are eigenvalues of the matrix. The values of λ_i depend on the vibration frequencies by

$$\lambda_i = 4\pi^2 c^2 \overline{\nu}_i^2. \tag{10}$$

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 $f_r = 3.59016$ 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_α of some molecules with the ones obtained by neglecting the interaction constants in [4] for same 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_α 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,

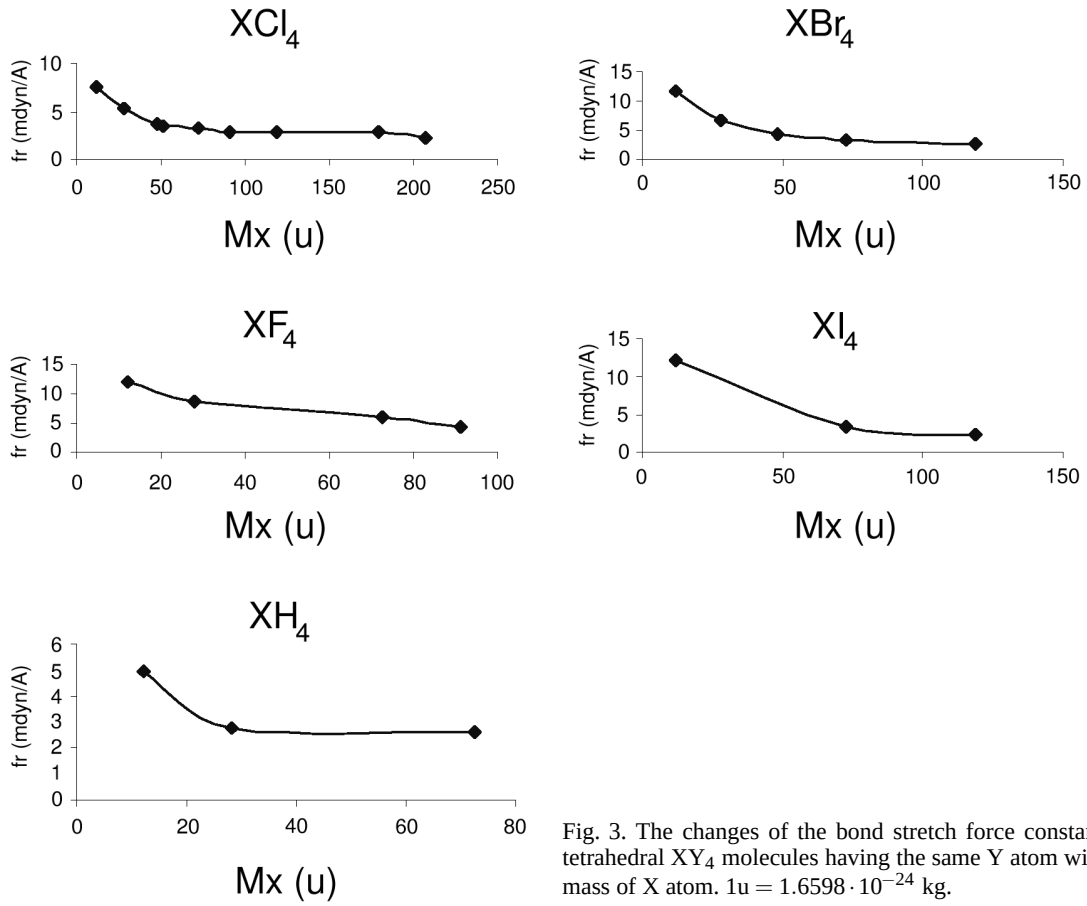

Fig. 3. The changes of the bond stretch force constants of tetrahedral XY_4 molecules having the same Y atom with the mass of X atom. $1u = 1.6598 \cdot 10^{-24}$ kg.

the force constants decrease with increasing mass of the X atom. These changes are also seen for planar XY_3 molecules from Table 1. As seen from the table, the force constants are lower for the molecules consisting of ^{11}B atom as X atom than the ones consisting of ^{10}B atom for XY_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.

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