Determination of Force Constants of Octahedral XY_6 Molecules by the GF Matrix Method

Fatih Ucun and M. Gökhan Şengül

Department of Physics, Faculty of Arts and Sciences, Suleyman Demirel University, Isparta, Turkey

Reprint requests to Dr. F. U.; Fax: +90-246-2371106; E-mail: fucun@fef.sdu.edu.tr

Z. Naturforsch. **60a,** 819 – 822 (2005); received June 6, 2005

The force constants of the internal coordinates of octahedral XY_6 molecules and complex ions were calculated by using the GF matrix method. The matrix solutions were found by means of a computer program using the Newton-Raphson method. From the calculations it has been observed that the bond stretch force constants of octahedral XF_6 molecules and XY_6 complex ions having the same centre X atom decrease with the increasing molar mass of the centre X atom for the former and the ligand Y atom for the latter, respectively. This was attributed to the slowing down of the molecule with increasing molar mass of the molecule as the whole. In addition we have concluded that the difference of squares of the vibration frequencies ν_1 and ν_2 of octahedral XY_6 complex ions decreases with the increasing mass of the Y atom since the interaction force constant of these ions decreases with the increasing mass.

Key words: GF Matrix Method; Force Constants; XY_6 Molecules; XY_6 Ions.

1. Introduction

The most convenient method for the analysis of vibration spectra of molecules is the GF matrix method [1 – 4]. In [5 – 7] the force constants of octahedral MX_6 molecules and ions have been calculated by this method. In our previous studies we have found the force constants of non-linear XY_2, planar XY_3 and tetrahedral XY_4 molecules [8, 9].

In the present work, the force constants of octahedral XY_6 molecules and ions have been calculated by the GF matrix method. The matrix solutions were founds by means of a computer program based on the Newton-Raphson method, and the changes of the force constants with the masses of centre atom X and ligand atoms Y were discussed.

2. Theory

Octahedral XY_6 molecules have six normal modes of vibration, as shown in Figure 1. They have the symmetry O_h and can be described in terms of seven force constants of the internal coordinates. f_r denotes the bond stretch force constant, f_{rr} the interaction force constant between two Δr perpendicular to each other, f'_{rr} the interaction force constant between two Δr on the same straight line, f_α the bending force constant, $f_{r\alpha}$ the interaction force constant between Δr and $\Delta\alpha$, $f_{\alpha\alpha}$ the interaction force constant between two $\Delta\alpha$ perpendicular to each other, and $f'_{\alpha\alpha}$ the interaction force constant between two $\Delta\alpha$ in the same plane. The changes of Δr_i and $\Delta\alpha_i$ can be seen in Figure 2.

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

$$G = \mu_Y, \quad F = f_r + 4f_{rr} + f_{rr}', \tag{1}$$

for the mode in species E_g are

$$G = \mu_Y, \quad F = f_r - 2f_{rr} + f_{rr}', \tag{2}$$

for the modes in species F_{1u} are

$$G_{11} = \mu_Y + 2\mu_X, \quad G_{12} = -\frac{4}{r}\mu_X, \quad G_{22} = \frac{2}{r^2}(\mu_Y + 4\mu_X), \tag{3}$$

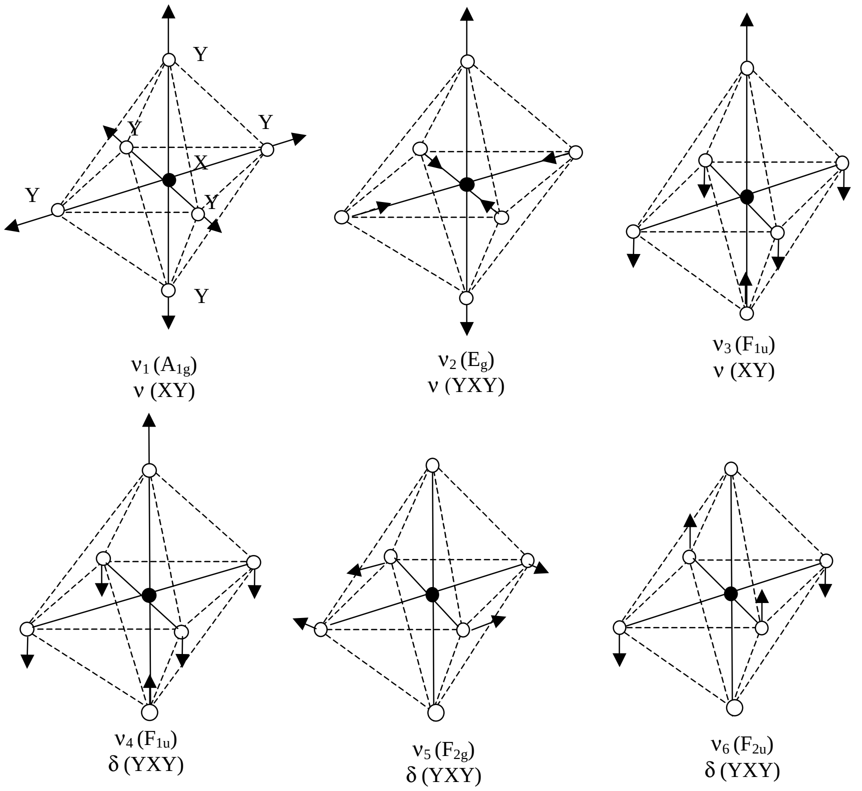
$$F_{11} = f_r - f_{rr}', \quad F_{12} = 2r f_{r\alpha}, \quad F_{22} = r^2(f_\alpha + 2f_{\alpha\alpha}), \tag{4}$$

for the mode in species F_{2g} are

$$G = \frac{4}{r^2}\mu_Y, \quad F = r^2(f_\alpha - 2f_{\alpha\alpha}'), \tag{5}$$

and for the ones in species F_{2u} are

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



ν_1 (A_{1g})
ν (XY)

ν_2 (E_g)
ν (YXY)

ν_3 (F_{1u})
ν (XY)

ν_4 (F_{1u})
δ (YXY)

ν_5 (F_{2g})
δ (YXY)

ν_6 (F_{2u})
δ (YXY)

Fig. 1. Normal modes of vibration of octahedral XY$_6$ molecules.

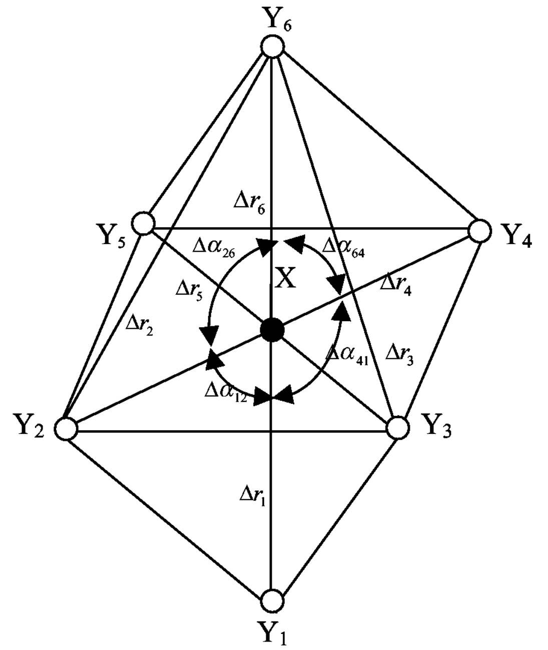


Fig. 2. The changes of Δr_i and $\Delta\alpha_i$ of an octahedral XY$_6$ molecule.

[3]. μ_X and μ_Y are the reciprocals of the masses of the X and Y atoms. The secular equation of the GF matrix is given by

$$|GF - E\lambda| = 0, \tag{7}$$

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

$$\lambda_i = 4\pi^2 c^2 \nu^2. \tag{8}$$

If one uses (1) and (2) in (7) and solves for the eigenvalues as λ_1 and λ_2, respectively, one finds

$$\begin{aligned} \lambda_1 &= \mu_\mathrm{Y}(f_r + 4 f_{rr} + f_{rr}'), \\ \lambda_2 &= \mu_\mathrm{Y}(f_r - 2 f_{rr} + f_{rr}'), \end{aligned} \tag{9}$$

and from these two equations

$$f_{rr} = \frac{\lambda_1 - \lambda_2}{6\mu_\mathrm{Y}}. \tag{10}$$

By using of (8), this becomes

$$f_{rr} = 4\pi c^2 \frac{(\nu_1^2 - \nu_2^2)}{6\mu_\mathrm{Y}}. \tag{11}$$

Table 1. Bond lengths r [7] and force constants f of octahedral XY_6 complex ions. The force constants are in units of mdyn/Å.

Complex ion	r (Å)	f_r	f_{rr}	f_{rr}'	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	$f_{\alpha\alpha}'$
$[TaF_6]^{2-}$	1.21	3.580905	0.259843	0.600515	0.324638	0.145600	0.071657	0.068246
$[TaCl_6]^{2-}$	1.70	1.883299	0.180278	0.270197	0.516506	0.111874	0.055677	0.054896
$[TaBr_6]^{2-}$	1.85	1.738934	0.163187	0.012628	0.942224	0.134624	0.067266	0.067117
$[TaI_6]^{2-}$	2.09	1.284918	0.143048	−0.061064	1.083646	0.123586	0.061775	0.061721
$[NbF_6]^{2-}$	1.21	3.589157	0.276932	0.387221	0.529476	0.173014	0.085316	0.081748
$[NbCl_6]^{2-}$	1.70	1.870620	0.157402	0.176454	0.740782	0.133438	0.066430	0.065557
$[NbBr_6]^{2-}$	1.85	1.775095	0.133939	−0.114604	1.249449	0.173178	0.086534	0.086369
$[NbI_6]^{2-}$	2.09	1.142297	0.105670	0.006800	1.045581	0.121831	0.060895	0.060832
$[SbF_6]^{3-}$	1.23	3.837590	0.234891	−0.092220	0.572458	0.269837	0.133590	0.129594
$[SbCl_6]^{3-}$	1.72	1.744205	0.097908	−0.037142	0.711730	0.145079	0.072335	0.071720
$[SbI_6]^{-}$	2.06	0.709504	0.038027	0.144326	0.484079	0.061522	0.032131	0.032100

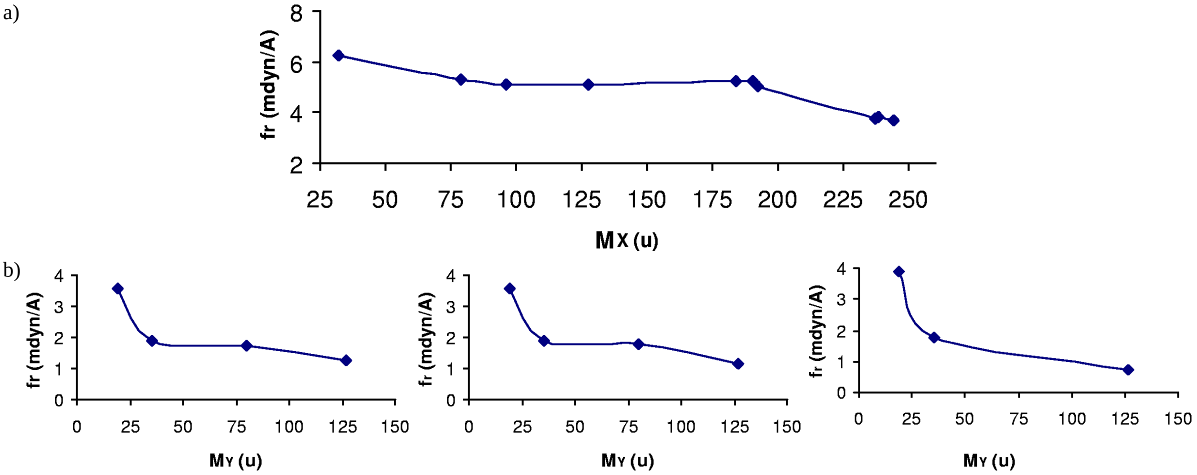


Fig. 3. The changes of the bond stretch force constants of a) octahedral XF_6 molecules and b) octahedral XY_6 complex ions having the same centre X atom with the molar masses of the X atom for (a) and the Y atom for (b). 1 u = $1.6598 \cdot 10^{-24}$ kg.

Table 2. The force constants of some octahedral XF_6 molecules. The force constants are in units of mdyn/Å.

Molecule	$(f_r + f_{rr}')$		f_{rr}
SF_6	5.268(5.335)		0.342 (0.347)
SeF_6	5.130(5.151)		0.120 (0.123)
IrF_6	4.947(4.893)		0.138 (0.132)
PuF_6	3.512(3.502)		0.225 (0.223)
	f_r	f_{rr}'	f_{rr}
MoF_6	5.083(5.080)	0.050(0.040)	0.253(0.246)
WF_6	5.266(5.120)	0.330(0.455)	0.263(0.268)

The values in the parenthesis are taken from [7].

As seen from (11), f_{rr} depends only on $(\nu_1^2 - \nu_2^2)$ and μ_Y.

3. Calculations

After construction of the GF matrix in (7), the solution of the matrix was carried out by using a computer program based on the Newton-Raphson method [10], taking the vibration frequencies and bond lengths into account. We have done this for some octahedral XY_6 complex ions and calculated the force constants, being very close to the values found by Hahn and Hebisch [5] for the same molecules. These results are given in Table 1. The authors have used the conditions $\bar{\nu}_6 = \bar{\nu}_5/\sqrt{2}$ (regarding the estimation $f_{\alpha\alpha} = f_{\alpha\alpha}'$) and f_r is minimum to obtain a uniform set of force constants. From our values in Table 1 it can be seen that $f_{\alpha\alpha} \cong f_{\alpha\alpha}'$. Pistorius has calculated the force constants of some octahedral XY_6 molecules and ions [7] from the frequencies observed by the Wilson's GF matrix method. But in the calculations he has neglected the force constant of f_{rr}' and found the other force constants in the following forms: $(f_r + f_r')$, f_{rr}, $(f_{r\alpha} - f_{r\alpha}'')$, $(f_\alpha - f_{\alpha\alpha}''')$, $(f_{\alpha\alpha} - f_{\alpha\alpha}'')$, $(f_{\alpha\alpha}' - f_{\alpha\alpha}''')$. In the case of MoF_6 he has found an imaginary value for $f_{r\alpha} - f_{r\alpha}''$ and commented the most probable reason as the negligence of f_{rr}', and in the case of WF_6 he has neglected $(f_{r\alpha} - f_{r\alpha}'')$ to find the other force constants in the forms given above. Table 2 shows our values and some of Pistorius calculated in the same forms for some octahedral XY_6 molecules. As seen, our values are very close to Pistorius' ones. After reaching

Molecule	r (Å)	f_r	f_{rr}	f_{rr}'	$f_{r\alpha}$	f_α	$f_{\alpha\alpha}$	$f_{\alpha\alpha}'$
PuF_6	1.638	3.652777	0.225428	−0.140675	0.889846	0.116335	0.057240	0.055407
UF_6	1.996	3.841312	0.295953	−0.046072	0.944222	0.101309	0.050049	0.048149
NpF_6	1.981	3.766261	0.263228	−0.119746	0.931355	0.112890	0.055601	0.053839
IrF_6	1.830	5.007254	0.138189	−0.060413	1.193118	0.204152	0.100760	0.097948
OsF_6	1.831	5.205382	0.169862	0.128332	1.209540	0.200484	0.098939	0.095518
WF_6	1.832	5.266395	0.263959	0.330554	1.202702	0.184364	0.091625	0.860284
TeF_6	1.815	5.107319	0.183959	−0.169608	1.613228	0.217977	0.106547	0.102018
MoF_6	1.820	5.083016	0.252991	0.050150	1.834177	0.229479	0.114278	0.108703
SeF_6	1.690	5.299019	0.120018	−0.169109	1.908438	0.437707	0.216725	0.208782
SF_6	1.561	6.284319	0.341905	−1.016401	3.123172	0.766803	0.379962	0.366504

Table 3. Bond lengths r [11] and force constants f of octahedral XF_6 molecules. The force constants are in units of mdyn/Å.

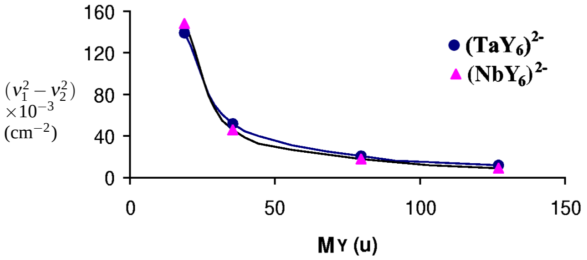


Fig. 4. The change of $(\nu_1^2 - \nu_2^2)$ with the molar mass of the Y atom for the complex ions $[NbY_6]^{2-}$ and $[TaY_6]^{2-}$. 1 u = $1.6598 \cdot 10^{-24}$ kg.

this agreement, we have found the force constants of octahedral XF_6 molecules. The results of these calculations are given in Table 3. The values are quite suitable in the error limits and also depend on the values taken from [3, 5, 11].

4. Discussion

Figure 3 shows the changes of the force constants f_r of octahedral XF_6 molecules and XY_6 complex ions having the same centre X atom with the masses of the X atom and the Y atom, respectively. As seen from Fig. 3, f_r decreases with increasing mass of the molecule as the whole. This was attributed to the slowing down of the molecule with increasing mass. Since the more condensed phase has the lower frequency and force constant [8, 9, 12], we think that the molecule moves more slowly with increasing mass, like taking it to a more condensed phase.

The force constants f_{rr} of the octahedral XY_6 complex ions, having the same centre X atom, decrease while the molar masses of the Y atoms increase (see Table 1, since $M_F < M_{Cl} < M_{Br} < M_I$). This change results in a decrease of $(\nu_1^2 - \nu_2^2)$, cf. (11). This decrease of $(\nu_1^2 - \nu_2^2)$ is drawn for the complex ions $[NbY_6]^{2-}$ and $[TaY_6]^{2-}$ (Y = F, Cl, Br and I) in Fig. 4 and can also be confirmed for other octahedral XY_6 complex ions, reminding their vibrations frequencies given in [3, 7]. Therefore, we conclude that the discrepancy of the vibration frequencies ν_1 and ν_2 of octahedral XY_6 complex ions decreases with increasing molar mass of the Y atom.

[1] E. B. Wilson Jr., J. Chem. Phys. **7**, 1047 (1939).
[2] E. B. Wilson Jr., J. Chem. Phys. **9**, 76 (1940).
[3] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley and Sons Inc., New York 1970, p. 58.
[4] E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955, p. 175.
[5] E. Hahn and R. Hebisch, Spectrochim. Acta. **47A**, 1097 (1991).
[6] E. M. Nour, M. Zaky, and S. Sallam, Polyhedron **5/4**, 929 (1986).
[7] C. W. F. T. Pistorius, J. Chem. Phys. **29**, 1328 (1958).
[8] F. Ucun and V. Güçlü, Z. Naturforsch. **59a**, 621 (2004).
[9] V. Güçlü and F. Ucun, Z. Naturforsch. **60a**, 183 (2005).
[10] L. Bostock and S. Chandler, Core Maths, 2. Ed., Nelson Thornes, Cheltenham, U. K. 1994, p. 763.
[11] D. R. Lide, Handbook of Chemistry and Physics, 83. Ed., CRC Press, New York 2002.
[12] C. N. Banwell and E. M. McCash, Fundamentals of Molecular Spectroscopy, McGraw-Hill Pub. Com., U. K. 1994, p. 87.