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Force Constant Calculation in Mass-Weighted Cartesian Coordinates. Linear XYX and XYZ type Molecules

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Force constants of simple linear XYX and XYZ types of molecules have been calculated in using the method of mass-weighted cartesian coordinates. Relations and results between force constants in mass-weighted cartesian coordinates and in internal coordinates were also discussed.

Since the development of the theory or molecular vibration, calculations of force constants in quadratic form were approached mostly in internal coordinates[1]. The calculations are very simple in case of small molecules. For larger molecules, the complexity of the problem is increased greatly. In the latter case the well-established G-matrix method[1] was employed by most authors. But, to calculate force constants in cartesian coordinates is not so simple as in internal coordinates even in small molecules. We shall approach this problem in this work and seek the relations between the force constants calculated by the two different ways.

In this work zero order frequancies were used if available and isotopic substitutions were employed if necessary. Linear triatomic molecules are treated as examples in this paper.

Formulation of the problems

Choosing a coordinate system fixed in external space, we let the nine rectangular cartesian coordinates of the three nuclei in the, molecule be:

$x_1, x_2, x_3 \quad y_1, y_2, y_3 \quad z_1, z_2\ z_3$, where x's are along the molecule axis, then, the kinetic energy is given by:

$$2T=\sum_{i=1}^{3} m_i\left[\left(\frac{\partial x_i}{\partial t}\right)^2+\left(\frac{\partial y_i}{\partial t}\right)^2+\left(\frac{\partial z_i}{\partial t}\right)^2\right] \tag{1}$$

Define mass-weighted coordinates:

$q_1=\sqrt{m_1}\ x_1 \quad q_2=\sqrt{m_2}\ x_2 \quad q_3=\sqrt{m_3}\ x_3 \quad q_4=\sqrt{m_1}\ y_1$ etc.,

then

$$2T=\sum_{i=1}^{9} \dot{q}_i^2 \tag{2}$$

The potential energy V may be expressed as a power series in displacement x_i, y_i, z_i's

$$2V=2V_0+2\sum_{i=1}^{3}\left[\left(\frac{\partial V}{\partial x_i}\right)_0 x_i+\left(\frac{\partial V}{\partial y_i}\right)_0 y_i+\left(\frac{\partial V}{\partial z_i}\right)_0 z_i\right]$$
$$+\sum_{i,j=1}^{3}\left[\left(\frac{\partial^2 V}{\partial x_i\partial x_j}\right)_0 x_i x_j+\left(\frac{\partial^2 V}{\partial y_i\partial y_j}\right) y_i y_j+\left(\frac{\partial^2 V}{\partial z_i\partial z_j}\right) z_i z_j\right]+\cdots$$

Since $V_0=0$ [potential energy at equilibrium position]

and $\left(\frac{\partial V}{\partial x_i}\right)_0=\left(\frac{\partial V}{\partial y_i}\right)_0=\left(\frac{\partial V}{\partial z_i}\right)_0=0$ at minimum,

$$2V=\sum_{ij}[F_{ij}x_i x_j+F_{ij}' y_i y_j+F_{ij}'' z_i z_j] \tag{3}$$

where, $F_{ij}=\left(\frac{\partial^2 V}{\partial x_i\partial x_j}\right)_0 \quad F_{ij}'=\left(\frac{\partial^2 V}{\partial y_i\partial y_j}\right)_0 \quad F_{ij}''=\left(\frac{\partial^2 V}{\partial z_i\partial z_j}\right)_0$

In mass-weighted cartesian coordinates

$$2V=\sum_{ij}\frac{F_{ij}}{\sqrt{m_i m_j}}\, q_i q_j \tag{4}$$

Using Largrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)-\frac{\partial L}{\partial q_i}=0 \tag{5}$$

from eqs. 2, 4 and 5,
we get,

$$\ddot{q}_i + \sum_j \frac{F_{ij}}{\sqrt{m_i m_j}} q_j = 0 \qquad (6)$$

$$j = 1,\ 2, \cdots\cdots 9$$

One possible solution of eq. 6 is

$$q_i = A_i \ \cos\ [\sqrt{\lambda} t + e]$$

Substitute into eq. 6 a set of algebraic equation results;

$$-\lambda q_i + \sum_j \frac{F_{ij}}{\sqrt{m_i m_j}} \cdot q_j = 0 \qquad (7)$$

or in matrix form,

$$\begin{bmatrix} \frac{F_{11}}{\sqrt{m_1 m_1}} - \lambda & \frac{F_{12}}{\sqrt{m_1 m_2}} & \frac{F_{13}}{\sqrt{m_1 m_3}} & \cdots\cdots \\ \frac{F_{21}}{\sqrt{m_1 m_2}} & \frac{F_{22}}{m_2} - \lambda & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \frac{F_{89}}{\sqrt{m_2 m_3}} \\ \cdots\cdots & \cdots\cdots & \frac{F_{98}}{\sqrt{m_2 m_3}} & \frac{F_{99}}{m_3} - \lambda \end{bmatrix} \begin{bmatrix} q_1 \\ \vdots \\ q_2 \\ \vdots \\ q_9 \end{bmatrix} = 0 \qquad (8)$$

The secular equation of eq. 7 is

$$det \left| \frac{F_{ij}}{\sqrt{m_i m_j}} - \lambda\ \delta_{ij} \right| = 0 \qquad (9)$$

$$\delta_{ij} = \text{Kronecker delta}$$

$$i,\ j = 1,\ 2, \cdots\cdots 9.$$

In equation 9, some λ's are equal to zero. These λ's correspond to translational and rotational motions. Therefore, in order to calculate F_{ij}'s from vibrational frequancies, some relations between F_{ij}'s must be found from the separation of translational and rotational motions.

Linear x-y-x molecules

In these molecules, there are three types of normal mode, two are linear stretching vibrations, and one is bending vibration. One can consider x, y, z directions as independent, i. e. treat stretching and bending separately.

〔1〕 Linear stretching mode.

$q_i=\sqrt{m_i}\, x_i \qquad [F-E\lambda][Q]=0 \qquad \lambda=4\pi^2\nu^2$

ν—vibrational frequency

F—force constant matrix

E—unit matrix

or

$$\begin{bmatrix} \frac{F_{11}}{m_x}-\lambda & \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{13}}{m_x} \\ \frac{F_{21}}{\sqrt{m_x m_y}} & \frac{F_{22}}{m_y}-\lambda & \frac{F_{23}}{\sqrt{m_x m_y}} \\ \frac{F_{31}}{m_x} & \frac{F_{32}}{\sqrt{m_x m_y}} & \frac{F_{33}}{m_x}-\lambda \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix} = 0 \qquad (10)$$

By definition $F_{ij}=F_{ji}$ i and $j=1, 2, 3$

and by symmetry $F_{11}=F_{33}$

Eq. 10 becomes

$$\begin{bmatrix} \frac{F_{11}}{m_x}-\lambda & \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{13}}{m_x} \\ \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{22}}{m_y}-\lambda & \frac{F_{12}}{\sqrt{m_x m_y}} \\ \frac{F_{13}}{m_x} & \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{11}}{m_x}-\lambda \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix} = 0 \qquad (11$$

a〕 For translational motion along x-axis

Let $x_1=x_2=x_3=1$; $q_1=q_3=\sqrt{m_x}$; $q_2=\sqrt{m_y}$; $\lambda=0$,

we get $F_{11}+F_{12}+F_{13}=0$ (12

b〕 For symmetric stretching vibration

Let $q_1=1$; $q_3=-1$; $q_2=0$; $\lambda=\lambda_1$,

we get $F_{11}=F_{13}+m_x\lambda_1$ (13

c〕 For anti-symmetric stretching vibration

Knowing $\Sigma\sqrt{m_i}\, q_i=0$. Let $q_1=q_3=1$; $q_2=-2\sqrt{\frac{m_x}{m_y}}$

Substitute into eq. 11, we get

$$\frac{F_{11}}{m_x}-\lambda_2-\frac{2F_{12}}{m_y}+\frac{F_{13}}{m_x}=0 \tag{14}$$

From eq's 12, 13, 14, we get F_{ij}'s in terms of m_i's and λ as followings;

$$F_{12}=\frac{-m_x m_y \lambda_2}{m_y+2m_x} \qquad F_{11}=\frac{1}{2}\left[\frac{m_x m_y \lambda_2}{[m_y+2m_x]}\right]+m_x\lambda_1$$

$$F_{13}=\frac{1}{2}\left[\frac{m_x m_y \lambda_2}{m_y+2m_x}-m_x\lambda_1\right],\quad F_{22}=-2F_{12}-\frac{2m_x m_y \lambda_2}{m_y+2m_x} \tag{15}$$

Table 1. Force constants calculated corresponding to stretching vibrations.* F_{ij} in 10^5 *dyne/cm*. $F_{12}=F_{21}=F_{23}=F_{32}$ $F_{13}=F_{31}$, $F_{11}=F_{33}$

Molecules		F_{11}	F_{13}	F_{22}	F_{12}
$C^{12}O_2$	[g]	15.591	−1.407	28.368	−14.184
	[s]	—	—	28.248	−14.123
$C^{13}O_2$	[g]	—	—	28.414	−14.207
	[s]	—	—	28.314	−14.157
$C^{14}O_2$	[g]	—	—	28.428	−14.214
CS_2	[g]	7.589	−0.587	14.004	−7.002
	[l]	7.474	−0.680	13.587	−6.793
CSe_2	[g]	5.940	−0.358	11.162	−5.581
	[l]	5.788	−0.509	10.555	−5.278
$HgCl_2$	[g]	3.097	−0.038	5.263	−2.631
$HgBr_2$	[g]	2.316	−0.067	4.498	−2.249
HgI_2	[g]	—	—	—	—
$K[N_3]$	[s]	13.181	−1.724	22.914	−11.457
$NH_4[N_3]$	[s]	13.130	−1.796	22.668	−11.334
$K[HF_2]$	[s]	—	—	1.255	0.628
	[aq]	—	—	1.365	1.684
$K[DF_2]$	[s]	—	—	1.230	0.616
	[aq]	—	—	1.368	0.685
$[(CH_3)_4N]\,[HCl_2]$	[s]	—	—	1.434	0.718
$[NO_2]^+$(conc HNO_3)		17.227	−1.246	31.963	−15.982
$Na_2[CN_2]$	[s]	11.845	−0.717	22.257	−11.128
$[VO_2]^{2+}$	[aq]	7.078	0.107	14.372	−7.186

[2] Bending mode.

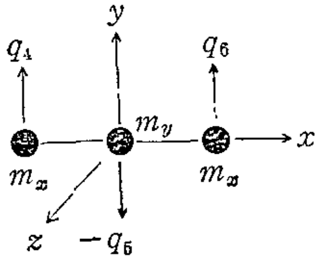
Since bending motions in xy plane and xz plane are degenerate, one can consider only the y-direction motion. The treatment is exactly the same as before, thus:

Table 2. Force constants calculated corresponding to bending vibrations.*

$F_{12}'=F_{21}'=F_{23}'=F_{32}' \quad F_{11}'=F_{13}'=F_{31}'$

Molecules		F_{11}'	F_{12}'	F_{22}'
$C^{12}O_2$	[g]	0.572	−1.143	2.288
	[s]	0.560	−1.119	2.240
	[aq]	0.548	−1.096	2.192
$C^{13}O_2$	[g]	0.574	−1.145	2.290
	[s]	0.552	−1.105	2.210
$C^{14}O_2$	[g]	0.573	−1.145	2.290
CS_2	[g]	0.235	−0.469	0.938
	[l]	0.235	−0.469	0.938
CSe_2	[g]	0.156	−0.312	0.624
	[l]	0.148	−0.296	0.592
$HgCl_2$	[g]	0.038	−0.076	0.152
$HgBr_2$	[g]	0.022	−0.044	0.088
HgI_2	[g]	0.018	−0.036	0.072
$K[N_3]$	[s]	0.572	−1.144	2.288
$NH_4[N_3]$	[s]	0.584	−1.168	2.336
$K[HF_2]$	[s]	0.220	−0.439	0.878
	[aq]	0.211	−0.420	0.840
$K[DF_2]$	[s]	0.221	−0.441	0.882
	[aq]	0.215	−0.429	0.858
$[(CH_3)_4N]\ [HCl_2]$	[s]	0.204	−0.408	0.816
$[NO_2]^+$(conc. HNO_3)		0.638	−1.276	2.552
$Na_2[CN_2]$	[s]	0.442	−0.884	1.768
$[VO_2]^{2+}$	[aq]	0.183	−0.366	0.732

* Vibrational frequencies were taken from reference [2]



$$\begin{bmatrix} \frac{F_{11}'}{m_x}-\lambda & \frac{F_{12}'}{\sqrt{m_x m_y}} & \frac{F_{13}'}{m_x} \\ \frac{F_{12}'}{\sqrt{m_x m_y}} & \frac{F_{22}'}{m_y}-\lambda & \frac{F_{12}'}{\sqrt{m_x m_y}} \\ \frac{F_{13}'}{m_x} & \frac{F_{12}'}{\sqrt{m_x m_y}} & \frac{F_{11}'}{m_x}-\lambda \end{bmatrix} \begin{bmatrix} q_4 \\ q_5 \\ q_6 \end{bmatrix} = 0$$

Where $q_4=\sqrt{m_x}\,y_1 \quad q_5=\sqrt{m_y}\,y_2 \quad q_6=\sqrt{m_x}\,y_3$

a] Translational, $\lambda=0$,

again one has $F_{11}'+F_{12}'+F_{13}'=0$

b] Rotational, $\lambda=0$, $q_1=1$, $q_3=-1$, $q_2=0$

than, $F_{11}'=F_{13}'$

c] Bending vibration $\lambda=\lambda_3$, $q_1=q_3=1$, $q_2=-2\sqrt{\frac{m_x}{m_y}}$

than,

$$\frac{F_{11}'}{m_x}-\lambda_3-\frac{2F_{12}'}{m_y}+\frac{F_{12}'}{m_x}=0$$

Therefore, bending force constants are eluciated as:

$$F_{11}'=F_{13}'=\frac{m_x m_y \lambda_3}{2[m_y+2m_x]}, \quad F_{12}'=-2F_{11}'=\frac{m_x m_y \lambda_3}{[m_y+2m_x]},$$

$$F_{22}'=-2F_{12}'=4F_{11}'=\frac{2m_x m_y \lambda_3}{[m_y+2m_x]} \tag{16}$$

Where, $\lambda=4\pi^2c^2\tilde{\nu}^2=354.810\tilde{\nu}^2$. $\tilde{\nu}$: wave number in cm^{-1}.

m_x, m_y, in gram.

Force constants calculated from eqs. 15, 16 are tabulated in Table 1 and 2.

Linear triatomic molecules, x-y-z

[1] Stretching mode:

As before, one has the determinant equals to zero.

$$\det \begin{vmatrix} \frac{F_{11}}{m_x}-\lambda & \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{13}}{\sqrt{m_x m_z}} \\ \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{22}}{m_y}-\lambda & \frac{F_{12}}{\sqrt{m_z m_y}} \\ \frac{F_{13}}{\sqrt{m_z m_z}} & \frac{F_{23}}{\sqrt{m_z m_y}} & \frac{F_{23}}{m_z}-\lambda \end{vmatrix}=0 \tag{17}$$

for translational motion, $\lambda=0$, one has the relations:

$$F_{11}+F_{12}+F_{13}=0 \qquad F_{12}+F_{22}+F_{23}=0 \qquad F_{13}+F_{23}+F_{33}=0 \tag{18}$$

Apply eq. 18 to eq. 17, resulting:

$$\frac{1}{\sqrt{m_z}}\, det \begin{vmatrix} \frac{F_{11}}{m_x}-\lambda & \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{13}}{\sqrt{m_x m_z}} \\ \frac{F_{12}}{\sqrt{m_x m_y}} & \frac{F_{22}}{m_y}-\lambda & \frac{F_{23}}{\sqrt{m_y m_z}} \\ \sqrt{m_x} & \sqrt{m_y} & \sqrt{m_z} \end{vmatrix} =0 \tag{19}$$

Expand eq. 19 into the form of $a\lambda^2+b\lambda+c=0$,

the coefficient of λ term, $\left[-\frac{b}{a}\right]$, is

$$\lambda_1+\lambda_2=\frac{F_{11}}{m_x}+\frac{F_{22}}{m_y}+\frac{F_{33}}{m_z} \tag{20}$$

We assume here isotope substitution of the molecules would simplify the above equation to calculate the force constants.

If M_y is substituted by M_y', where M_i' is an isotope of M_i. the frequencies are λ_1', λ_2', λ_3'

$$\frac{F_{11}}{m_x}+\frac{F_{22}}{m_y'}+\frac{F_{33}}{m_z}=\lambda_1'+\lambda_2' \tag{21}$$

If M_x is substitued by M_x', the frequencies are λ_1'', λ_2'', λ_3''

$$\frac{F_{11}}{m_x'}+\frac{F_{22}}{m_y}+\frac{F_{33}}{m_z}=\lambda_1''+\lambda_2'' \tag{22}$$

from eq's. 20, 21 and 22, we have a set of F_{ij} as followings:

$$\left.\begin{aligned} F_{22}&=\frac{[\lambda_1+\lambda_2-(\lambda_1'+\lambda_2')]m_y m_y'}{m_y'-m_y} \\ F_{11}&=\frac{[\lambda_1+\lambda_2-(\lambda_1''+\lambda_2')]m_x m_x'}{m_x'-m_x} \\ F_{33}&=-F_{22}\left[\frac{m_z}{m_y}\right]-F_{11}\left[\frac{m_z}{m_x}\right]+m_z[\lambda_1+\lambda_2] \\ F_{13}&=\frac{F_{22}-F_{11}-F_{33}}{2} \\ F_{23}&=\frac{F_{11}-F_{22}-F_{33}}{2} \\ F_{12}&=\frac{F_{33}-F_{11}-F_{22}}{2} \end{aligned}\right\} \tag{23}$$

〔2〕 Bending mode:

We have the determinant equation as:

$$\begin{vmatrix} \frac{F_{11}'}{m_x}-\lambda & \frac{F_{12}'}{\sqrt{m_x m_y}} & \frac{F_{13}'}{\sqrt{m_x m_z}} \\ \frac{F_{12}'}{\sqrt{m_x m_y}} & \frac{F_{22}'}{m_y}-\lambda & \frac{F_{23}'}{\sqrt{m_y m_z}} \\ \frac{F_{13}'}{\sqrt{m_x m_z}} & \frac{F_{23}'}{\sqrt{m_y m_z}} & \frac{F_{33}'}{m_z}-\lambda \end{vmatrix}=0 \qquad (24)$$

for translational motion, $\lambda=0$, we have:

$$F_{11}'+F_{12}'+F_{13}'=0 \qquad F_{12}'+F_{22}'+F_{23}'=0 \qquad F_{13}'+F_{23}'+F_{33}'=0 \qquad (25)$$

Since $\sum_{K} \lambda_k=\frac{F_{11}'}{m_x}+\frac{F_{22}'}{m_y}+\frac{F_{33}'}{m_z}$, and for rotational motion also, $\lambda=0$, then

$$\lambda_3=\frac{F_{11}'}{m_x}+\frac{F_{22}'}{m_y}+\frac{F_{33}'}{m_z} \qquad (26)$$

If M_x is substituted by M_x'

$$\lambda_3'=\frac{F_{11}'}{m_x'}+\frac{F_{22}'}{m_y'}+\frac{F_{33}'}{m_z} \qquad (27)$$

from eq's. 26 and 27, then

$$\left.\begin{aligned} F_{11}'&=\frac{m_x m_x'[\lambda_3-\lambda_3']}{m_x'-m_x} \\ F_{22}'&=\frac{m_y m_y'[\lambda_3-\lambda_3'']}{m_y'-m_y} \\ F_{33}'&=m_z\left[\lambda_3-\frac{F_{11}'}{m_x}-\frac{F_{22}'}{m_y}\right] \end{aligned}\right\} \qquad (28)$$

and by eq. 25 then:

$$\left.\begin{aligned} F_{13}'&=\frac{F_{22}'-F_{11}'-F_{33}'}{2} \\ F_{23}'&=\frac{F_{11}'-F_{22}'-F_{33}'}{2} \\ F_{12}'&=\frac{F_{33}'-F_{11}'-F_{22}'}{2} \end{aligned}\right\} \qquad (29)$$

The zero order frequencies of thiocyanate ion and nitrous oxide are taken from Ref. [3] and [4]. Force constants listed in Table 3 and 4 are the averages over several isotopic species.

Off diagonal terms in force constant matrix are very sensitive to the variations of isotopic frequency. A small change in frequency

Table 3. Linear stretching vibrational force constants [in 10^5 *dyne/cm*.]

Molecules		F_{11}	F_{22}	F_{33}	F_{12}	F_{18}	F_{23}
$N^{14}N^{14}O^{16}$	[g]	18.432	27.946	11.924	−17.224	−1.999	10.721
$N^{14}N^{15}O^{16}$	[g]						
$N^{15}N^{13}O^{16}$	[g]						
$K[S^{32}C^{12}N^{14}]$	[s]	6.095	19.409	15.431	−5.036	−1.059	−14.373
$K[S^{32}C^{13}N^{14}]$	[s]						
$K[S^{34}C^{13}N^{14}]$	[s]						

Table 4. Bending vibrational force constants [in 10^5 *dyne/cm*].

Molecules		F_{11}'	F_{22}'	F_{33}'	F_{12}'	F_{13}'	F_{23}'
$N^{14}N^{14}O^{16}$	[g]	1.991	0.536	0.407	−1.060	−0.930	+0.524
$N^{14}N^{15}O^{16}$	[g]						
$N^{15}N^{14}O^{16}$	[g]						
$K[S^{32}C^{12}N^{14}]$	[s]	*4.707	—	—	−2.389	−2.318	+2.397
$K[S^{32}C^{13}N^{14}]$	[s]						
$K[S^{34}C^{12}N^{14}]$	[s]						

* In solid K[SCN] the degenerate bending frequency splits into two closely packed frequencies. The average value is taken for the bending frequency.

may give a large differences in F_{ij}'s. Therefore, it is very important to have a set of precise isotopic frequencies to elucide the force constants.

Relations between force constants in mass-weighted cartesian coordinates and in internal coordinates

[1] Linear X-Y-X molecules.

Choose internal coordinates Q_1, Q_2, as,

$$Q_1 = x_2 - x_1 \qquad \phi_a = \frac{1}{d}[y_1 + y_3 - 2y_2]$$

$$Q_2 = x_3 - x_2 \qquad \phi_b = \frac{1}{d}[z_1 + z_3 - 2z_2] \tag{30}$$

While d is the equilibrium bond distance of X-Y bond. If the vibrations are small oscillations Q_1, Q_2 represent the bond stretching of X-Y, Y-Z bonds, ϕ_a, ϕ_b represent the bent angle in Y, Z, directions respectively. In terms of Q_1, Q_2, ϕ_a and ϕ_b, the potential energy is:

$$2V = a_{11}Q_1^2 + 2a_{12}Q_1Q_2 + a_{22}Q_2^2 + a_{33}\phi_a^2 + a_{44}\phi_b^2 \tag{31}$$

Where no cross terms, $Q_1\phi_a$, $Q_1\phi_b$, $Q_2\phi_a$, $Q_2\phi_b$, $\phi_a\phi_b$ occur because of symmetry, and also,

$$a_{11} = a_{22} \qquad a_{33} = a_{44}$$

Substituting eq. 30 into eq. 31, the potential energy is

$$\begin{aligned}2V = {}& a_{11}x_1^2 + 2[a_{11} - a_{12}]x_2^2 + a_{11}x_3^2 + 2[a_{12} - a_{11}]x_1x_2 - \\ & 2a_{12}x_1x_3 + 2[a_{12} - a_{11}]x_2x_3 + \frac{a_{33}}{d^2}y_1^2 - \frac{4a_{33}}{d^2}y_2^2 + \frac{a_{33}}{d^2}y_3^2 - \\ & \frac{4a_{33}}{d^2}y_1y_2 + \frac{2a_{33}}{d^2}y_1y_3 - \frac{4a_{33}}{d^2}y_2y_3 + \frac{a_{33}}{d^2}z_1^2 - \frac{4a_{33}}{d^2}z_2^2 + \frac{a_{33}}{d^2}z_3^2 \\ & - \frac{4a_{33}}{d^2}z_1z_2 + \frac{2a_{33}}{d^2}z_1z_3 - \frac{4a_{33}}{d^2}z_2z_3\end{aligned} \tag{32}$$

Compared the above potential energy with that in cartesian coordinates, we get:

$$a_{11} = F_{11} = \frac{1}{2}\left[\frac{m_x m_y \lambda_2}{m_y + 2m_x} + m_x\lambda_1\right] \qquad 2[a_{11} - a_{12}] = F_{22}$$

$$\therefore \quad a_{12} = F_{11} - \frac{F_{22}}{2} \tag{33}$$

from eq. 15,

$$a_{12} = \frac{1}{2}\left[m_x\lambda_1 - \frac{m_x m_y \lambda_2}{m_y + 2m_x}\right] \tag{34}$$

$$\frac{a_{33}}{d^2} = F_{11}' \qquad a_{33} = d^2F_{11}' = d^2\left[\frac{m_x m_y \lambda_3}{2(m_y + 2m_x)}\right] \tag{35}$$

These relations found are straight forward and exact.

[2] Linear X-Y-Z molecules.

Choose internal coordinates as:

$$\begin{aligned} Q_1 &= x_2 - x_1 & \phi_a &= \frac{1}{d_1}[y_1 - y_2] + \frac{1}{d_2}[y_3 - y_2] \\ Q_2 &= x_3 - x_2 & \phi_b &= \frac{1}{d_1}[z_1 - z_2] + \frac{1}{d_2}[z_3 - z_2] \end{aligned} \tag{36}$$

d_1: equilibrium length of X-Y bond

d_2: equilibrium length of Y-Z bond

The potential field in internal coordinate is:

$$2V=a_{11}Q_1^2+2a_{12}Q_1Q_2+a_{22}Q_2^2+a_{33}\phi_a^2+a_{44}\phi_b^2 \tag{37}$$

by symmetry, we should have, $a_{33}=a_{44}$

Substitute eq. 36 into eq. 37 then

$$\begin{aligned}2V=&a_{11}x_1^2+[a_{11}+a_{22}-2a_{12}]x_2^2+a_{22}x_3^2+2[a_{12}-a_{11}]x_1x_2\\&+2[a_{12}-a_{22}]x_2x_3-2a_{12}x_1x_3+\frac{a_{33}}{d_1^2}y_1^2+a_{33}\Big[\frac{1}{d_1^2}+\frac{1}{d_2^2}\Big]y_2^2\\&+\frac{2a_{33}}{d_1d_2}y_2^2+\frac{a_{33}}{d_2^2}y_3^2+2\Big[\frac{a_{33}}{d_1d_2}-\frac{a_{33}}{d_1^2}\Big]y_1y_2-2a_{33}\Big[\frac{1}{d_1d_2}+\frac{1}{d_2^2}\Big]y_2y_3\\&+\frac{2a_{33}}{d_1d_2}y_1y_3+\frac{a_{33}}{d_1^2}z_1^2+a_{33}\Big[\frac{1}{d_1^2}+\frac{1}{d_2^2}+\frac{2}{d_1d_2}\Big]z_2^2+\frac{a_{33}}{d_2^2}z_3^2\\&+2a_{33}\Big[\frac{1}{d_1d_2}-\frac{1}{d_1^2}\Big]z_1z_2-2a_{33}\Big[\frac{1}{d_1d_2}+\frac{1}{d_2^2}\Big]z_2z_3+\frac{2a_{33}}{d_1d_2}z_1z_3\end{aligned} \tag{38}$$

Compare it with potential energy in cartesian coordinates

$$\begin{aligned}2V=&F_{11}x_1^2+F_{22}x_2^2+F_{33}x_3^2+2F_{12}x_1x_2+2F_{23}x_2x_3+2F_{13}x_1x_3\\&+F_{11}'y_1^2+F_{22}'y_2^2+F_{33}'y_3^2+2F_{12}'y_1y_2+2F_{23}'y_2y_3+2F_{13}'y_1y_3\\&+F_{11}''z_1^2+F_{22}''z_2^2+F_{33}''z_3^2+2F_{12}''z_1z_2+2F_{23}''z_2z_3+2F_{13}''z_1z_3\end{aligned} \tag{39}$$

it results that:

$$a_{11}=F_{11} \qquad F_{22}=a_{11}-2a_{12}+a_{22} \qquad F_{33}=a_{22}$$

then

$$a_{11}=F_{11} \quad a_{22}=F_{33} \quad a_{12}=\frac{F_{11}+F_{33}-F_{22}}{2} \quad a_{33}=F_{11}'d_1^2 \tag{40}$$

From eq. 40, we can also calculate the internal force constants. Force constants calculated by this way are compared with those calculated by other authors in Tables 5 and 6.

Table 5. Internal coordinate force constants of NNO molecule.

	a_{11}	a_{22}	a_{12}
Ref 4.	18.48	11.83	1.13
Ref 5.	17.33	12.53	0.733
Ref 6.	18.98	11.50	1.43
Ref 7.	18.72	11.61	1.313
This work	18.423	11.920	1.200

Table 6. Internal coordinate force constants of NCS^- ion.

	a_{11}	a_{22}	a_{12}
Ref 3.	5.18	15.95	0.9
This work	6.095	15.431	1.059

In Table 5, the frequencies used in this work are the same as those of Ref [4]. They are in fairly good agreement. The discrepancies between these force constants listed in the table are primarily due to the fact that vibrational frequencies of isotopic species are difficult to assign.

Discussion

In the calculations of force constants, the number of independent force constants is generally greater than the number of vibrational frequancies. In order to calculate the force constants, special force fields are introduced by most authors. In our method, no special force field is assumed, but we assume, instead, cartesian force constants are not varied when isotopic substitutions are considered.

In the case of linear XYX molecules, force constants calculated are in fairly good agreement with those calculated from internal coordinates directly. For linear XYZ molecules, force contants obtained are also compared with those of calculated from special force field in Table 6.

In the case of more complicated molecules, with certain symmetry, the calculation of the complete force field in cartesian coordinates may be approached by two different ways. In the first one, one may use external symmetry coordinates to reduce the secular determinants to lower order, and introduce the conditions of conservation of linear and angular momenta, then use isotopic substitutions carefully, the problem may be soluble. This approach is under progress.

In the second, we treat isotopic substitutions as perturbed systems, using Green's function method we generate the complete set of cartesian force constants for bent XYX type molecules.

This will be treated in the next work of this series.

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