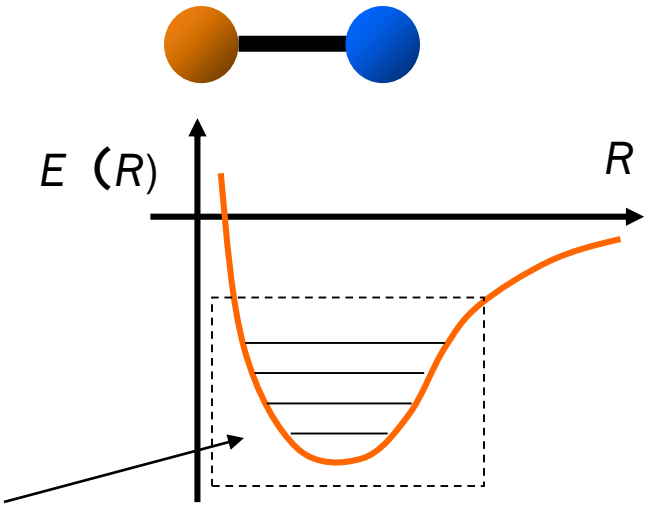
東京大学　生産技術研究所
北條　博彦

化学生命工学専攻

有機機能材料学特論II

基準振動解析



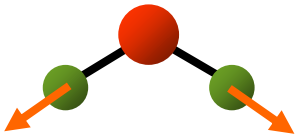
部分的に二次関数で近似できる

$$E_{vib} = \left(n + \frac{1}{2}\right) h\nu,\ \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$$

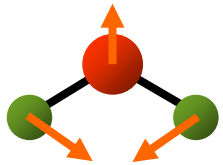
$$\Delta E_{vib} = h\nu$$

→赤外領域の振動スペクトル

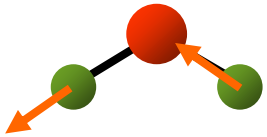
N（>2）個の原子からなる分子
→3N－6個の基準振動
（3N－3（並進）－3（回転））



対称伸縮
(3657 cm^{-1})

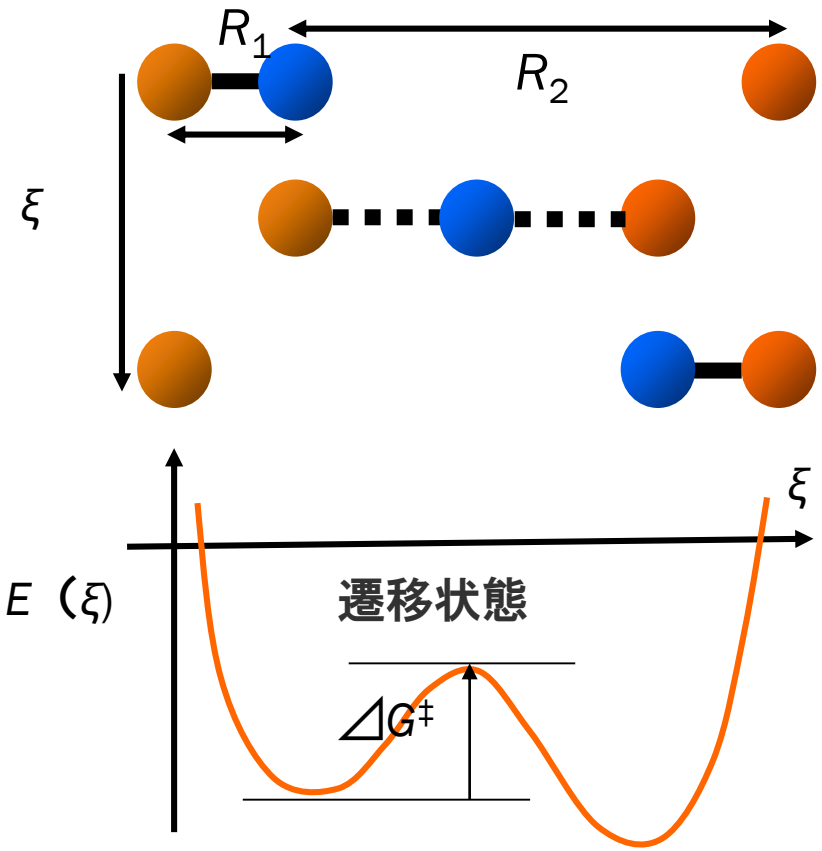


変角
(1595 cm^{-1})

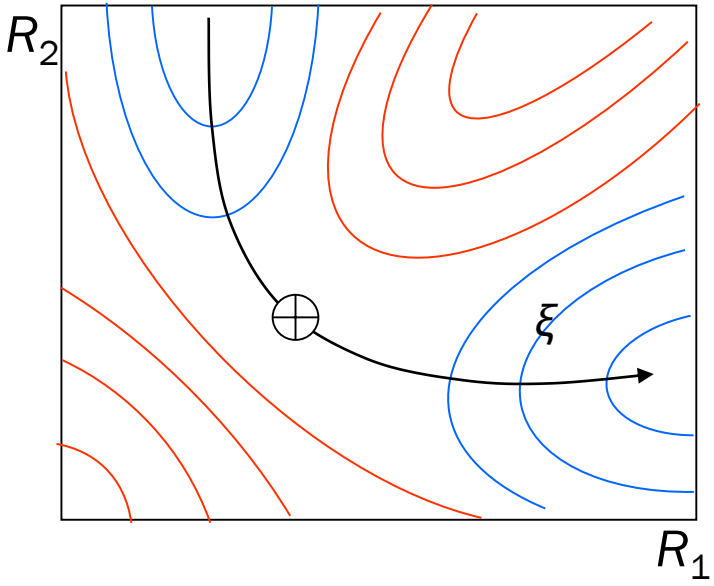


非対称伸縮
(3756 cm^{-1})

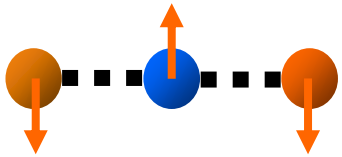
反応経路の探索



ξの方向のみ$k < 0$
→虚の固有振動数



対称伸縮（実数）



変角（実数）

非対称伸縮（虚数）

連成振動系の運動方程式

$$F_{ix} = m_i \frac{d^2}{dt^2} x_i$$

$$= \sum_j \frac{d^2\phi}{dx_i dx_j}(x_j - x_i) \equiv \sum_j k_{ij}(x_j - x_i)$$

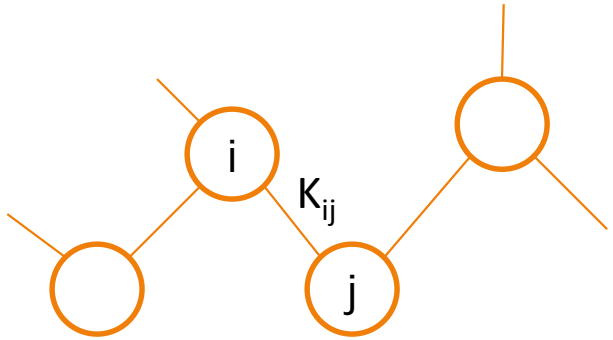
$$\left.\begin{aligned} K_{ij} &= -k_{ij} \\ K_{ii} &= \sum_j k_{ij} \end{aligned}\right\} \Rightarrow F_{ix} = -\sum_j K_{ij} x_j$$

$$x_i = x_{0i} \exp(-i\omega t)$$

$$\Rightarrow F_{ix} = -m_i \omega^2 x_i$$

$$\sum_j K_{ij} x_j = m_i \omega^2 x_i \Rightarrow Kx = Mx\omega^2$$

$$V = \frac{1}{2} x^t K x = \frac{1}{2} x^t M x \omega^2$$



ϕ： 二体間ポテンシャル
変位に比例する力のみ考慮→調和近似

K：剛性行列

xとして振動解を仮定

すべての粒子についての連立方程式
→行列の方程式

V: 振動エネルギー

HESSE行列法

$$M^{-1}Kx = x\omega^2$$

$$M = \begin{pmatrix} m_1 & & & & & & \\ & m_1 & & & & 0 & \\ & & m_1 & & & & \\ & & & \ddots & & & \\ & & & & m_N & & \\ & 0 & & & & m_N & \\ & & & & & & m_N \end{pmatrix}, \quad K = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & & & & \\ \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \cdots & & \cdots & \\ \frac{\partial^2 U}{\partial z_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \frac{\partial^2 U}{\partial z_1^2} & & & & \\ & \vdots & & \ddots & & & \\ & & & & \frac{\partial^2 U}{\partial x_N^2} & \frac{\partial^2 U}{\partial x_N \partial y_N} & \frac{\partial^2 U}{\partial x_N \partial z_N} \\ & \vdots & & & \frac{\partial^2 U}{\partial y_N \partial x_N} & \frac{\partial^2 U}{\partial y_N^2} & \frac{\partial^2 U}{\partial y_N \partial z_N} \\ & & & & \frac{\partial^2 U}{\partial z_N \partial x_N} & \frac{\partial^2 U}{\partial z_N \partial y_N} & \frac{\partial^2 U}{\partial z_N^2} \end{pmatrix}$$

$$M^{-1} = \begin{pmatrix} \mu_1 & & & & & & \\ & \mu_1 & & & & 0 & \\ & & \mu_1 & & & & \\ & & & \ddots & & & \\ & & & & \mu_N & & \\ & 0 & & & & \mu_N & \\ & & & & & & \mu_N \end{pmatrix}, \quad x = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix}$$

xは$M^{-1}K$の固有ベクトル

→ $M^{-1}K$を対角化するxの組を探す問題に帰着

GF行列法

分子の幾何パラメータ（結合長，結合角など）が変数となるように
Hessian方程式を変換して解く

$$\begin{cases} M^{-1}Kx = x\omega^2 \\ x' = U^t x \end{cases}$$

$$\Rightarrow U^t M^{-1} U U^t K U x' = U^t U x' \omega^2$$

$$\begin{cases} U^t M^{-1} U \equiv G \\ U^t K U \equiv F \end{cases}$$

$$\Rightarrow GFx' = x'\omega^2$$

UはCartesian座標を分子内座標に変換する行列

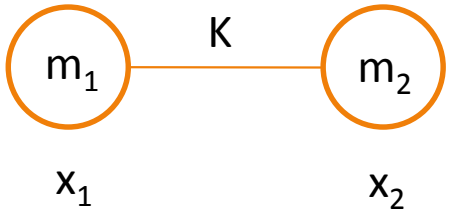
Fは伸縮・変角など直観的に理解しやすいパラメータ群

x'はGFの固有ベクトル

→ GFを対角化するx'の組を探す問題に帰着

二原子分子の固有振動

$$\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}=\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}\omega^2$$



Hesse行列法

$$\begin{pmatrix} \mu_1 K-\omega^2 & -\mu_1 K \\ -\mu_2 K & \mu_2 K-\omega^2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}=0$$

$when\ \omega^2=0$

$$x_1=\frac{1}{\sqrt{2}},\ x_2=\frac{1}{\sqrt{2}}$$

$when\ \omega^2=(\mu_1+\mu_2)K$

$$x_1=\frac{\mu_1}{\sqrt{\mu_1^2+\mu_2^2}},\ x_2=-\frac{\mu_2}{\sqrt{\mu_1^2+\mu_2^2}}$$

GF行列法

$$x'=U^t x=\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix} x_1+x_2 \\ x_1-x_2 \end{pmatrix}$$

$$G=\frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}=\frac{1}{2}\begin{pmatrix} \mu_1+\mu_2 & \mu_1-\mu_2 \\ \mu_1-\mu_2 & \mu_1+\mu_2 \end{pmatrix}$$

$$F=\frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}=\begin{pmatrix} 0 & 0 \\ 0 & 2K \end{pmatrix}$$

$$GF=\begin{pmatrix} 0 & (\mu_1-\mu_2)K \\ 0 & (\mu_1+\mu_2)K \end{pmatrix}$$

$$\begin{pmatrix} -\omega^2 & (\mu_1-\mu_2)K \\ 0 & (\mu_1+\mu_2)K-\omega^2 \end{pmatrix}\begin{pmatrix} x_1' \\ x_2' \end{pmatrix}=0$$

質量換算HESSE行列法

$$M^{-1}Kx = x\omega^2$$

M^{-1}Kは対称行列ではない
→xは互いに直交しない
→ωが実になる保障がない

$$M^{-1/2}KM^{-1/2}M^{1/2}x = M^{1/2}x\omega^2$$

両辺に$M^{1/2}$をかける

$$M^{1/2} = \begin{pmatrix} \sqrt{m_1} & & & & & 0 \\ & \sqrt{m_1} & & & & \\ & & \sqrt{m_1} & & & \\ & & & \ddots & & \\ & & & & \sqrt{m_N} & \\ 0 & & & & & \sqrt{m_N} \\ & & & & & & \sqrt{m_N} \end{pmatrix}$$

Mは対角行列
→$M^{1/2}$は容易に求められる

$$\left.\begin{aligned} M^{-1/2}KM^{-1/2} &\equiv D \\ M^{1/2}x &\equiv w \end{aligned}\right\} \Rightarrow Dw = w\omega^2 \qquad D_{ij} = \sqrt{\mu_i}\sqrt{\mu_j}K_{ij}$$

Dは対角行列
→動力学行列
(dynamical matrix)

二原子分子の固有振動

$$\begin{pmatrix} \mu_1 K & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} w_1 \\ w_2 \end{pmatrix}\omega^2$$

$$\begin{pmatrix} \mu_1 K-\omega^2 & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K-\omega^2 \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = 0$$

$when \quad \omega^2 = 0$

$$w_1 = \sqrt{\frac{\mu_2}{\mu_1+\mu_2}},\quad w_2 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}}$$

$when \quad \omega^2 = (\mu_1+\mu_2)K$

$$w_1 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}},\quad w_2 = -\sqrt{\frac{\mu_2}{\mu_1+\mu_2}}$$

GF行列法との関係

$$GFx' = x'\omega^2$$

$$G^{1/2}FG^{1/2}G^{-1/2}x'$$

$$\begin{cases} G^{1/2}FG^{1/2} \equiv D' \\ G^{-1/2}x' \equiv w' \end{cases}$$

$$\Rightarrow D'w' = w'\omega^2$$

$$\begin{cases} w' = G^{-1/2}x' \\ \quad = U^t M^{1/2}UU^t M^{-1/2}w = U^t w \\ D' = G^{1/2}FG^{1/2} \\ \quad = U^t M^{-1/2}UU^t KUU^t M^{-1/2}U \\ \quad = U^t DU \end{cases}$$

GF行列を直交化
→DとD'は変換Uで結ばれる

基準振動解析

```
%chk=default
```
チェックポイントファイルの指定

```
#N HF/6-311G** Opt Freq
```
最適化の後、基準振動解析を行う

```
water molecule
```
コメント

```
0 1
```
電荷、スピン多重度

```
O
H 1 r2
H 1 r3   2 a3
```
構造情報

```
r2 1.0
r3 1.0
a3 104.5
```

【重要】基準振動解析は最適化された座標で行わないと意味がない

基準振動ベクトル

```
Full mass-weighted force constant matrix:
Low frequencies ---   -49.1758   -48.7150   -47.8111     0.0009     0.0013     0.0013
Low frequencies ---  1750.6155  4143.9531  4239.2189
Diagonal vibrational polarizability:
       0.0000000       0.0857239       0.7214610
Diagonal vibrational hyperpolarizability:
       0.0000000       0.0000000      -6.7501010
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:
                      1          2          3
                     A1         A1         B2
      Frequencies ---  1750.6155  4143.9531  4239.2189
   Reduced masses ---     1.0822     1.0456     1.0828
   Force constants ---     1.9541    10.5791    11.4650
    IR Intensities ---    78.9900    17.7638    57.2454
 Raman Activities ---     6.3854    65.3982    32.4046
   Depol. (Plane) ---     0.5156     0.1838     0.7500
   Depol. (Unpol) ---     0.6804     0.3105     0.8571
Coord Atom Element:
  1     1     8          0.00000    0.00000    0.00000
  2     1     8          0.00000    0.00000    0.07073
  3     1     8          0.07045    0.05021    0.00000
  1     2     1          0.00000    0.00000    0.00000
  2     2     1         -0.43012    0.58309   -0.56129
  3     2     1         -0.55903   -0.39843    0.42714
  1     3     1          0.00000    0.00000    0.00000
  2     3     1          0.43012   -0.58309   -0.56129
  3     3     1         -0.55903   -0.39843   -0.42714
```

低振動数の解（負値か0に近ければよい）

振動数（大きめにでる→非調和項を入れると改善される）

モード質量とモード剛性

IRとラマンの強度

原子の座標変位

熱力学諸量(1)

```
-------------------
- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Atom  1 has atomic number  8 and mass  15.99491
Atom  2 has atomic number  1 and mass   1.00783
Atom  3 has atomic number  1 and mass   1.00783
Molecular mass:    18.01056 amu.
Principal axes and moments of inertia in atomic units:
                          1         2         3
    EIGENVALUES --     2.07515   4.03496   6.11011
          X            0.00000   0.00000   1.00000
          Y            1.00000   0.00000   0.00000
          Z            0.00000   1.00000   0.00000
This molecule is an asymmetric top.
Rotational symmetry number  2.
Rotational temperatures (Kelvin)      41.73861    21.46583    14.17549
Rotational constants (GHZ):          869.69251   447.27574   295.36958
Zero-point vibrational energy       60613.5 (Joules/Mol)
                                    14.48698 (Kcal/Mol)
Vibrational temperatures:   2518.74  5962.22  6099.28
          (Kelvin)
```

温度、圧力、同位体は指定可能

慣性モーメントの主値と慣性主軸

回転温度、回転定数、零点エネルギー、振動温度

熱力学諸量(2)

```
Zero-point correction=                           0.023086 (Hartree/Particle)
 Thermal correction to Energy=                    0.025921
 Thermal correction to Enthalpy=                  0.026865
 Thermal correction to Gibbs Free Energy=         0.005509
 Sum of electronic and zero-point Energies=           -76.023926
 Sum of electronic and thermal Energies=              -76.021091
 Sum of electronic and thermal Enthalpies=            -76.020147
 Sum of electronic and thermal Free Energies=         -76.041503

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  16.266             5.992            44.948
 Electronic              0.000             0.000             0.000
 Translational           0.889             2.981            34.608
 Rotational              0.889             2.981            10.335
 Vibrational            14.488             0.030             0.004
                           Q            Log10(Q)             Ln(Q)
 Total Bot        0.292489D-02          -2.533891         -5.834499
 Total V=0        0.121654D+09           8.085125         18.616687
 Vib (Bot)        0.240479D-10         -10.618922        -24.450972
 Vib (V=0)        0.100021D+01           0.000093          0.000214
 Electronic       0.100000D+01           0.000000          0.000000
 Translational    0.300432D+07           6.477746         14.915562
 Rotational       0.404842D+02           1.607285          3.700911
```

= 25.0 J K^{-1} mol^{-1}

(実験値（水蒸気）
28.8 J K^{-1} mol^{-1})

= 12.47 J K^{-1} mol^{-1}

= 3*R*/2

JCTC Journal of Chemical Theory and Computation

Coarse Graining of Intermolecular Vibrations by a Karhunen-Loève Transformation of Atomic Displacement Vectors

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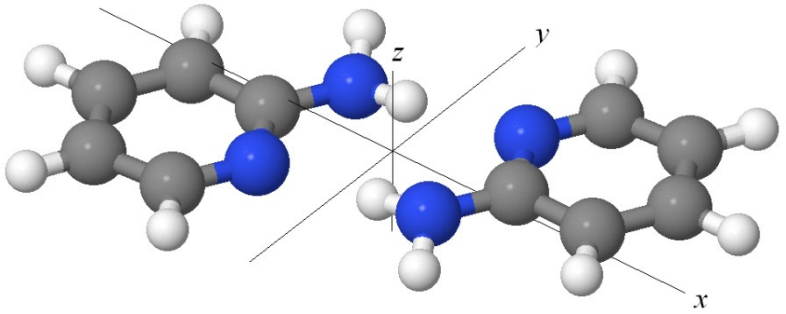

J. Chem. Theor. Comput. **5** (2009) 1814-1821.

Evaluation of coupling terms between intra- and intermolecular vibrations in coarse-grained normal-mode analysis: Does a stronger acid make a stiffer hydrogen bond?

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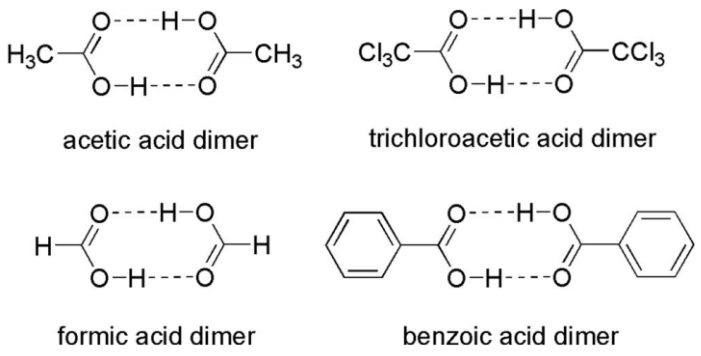


FIG. 1. Molecular structures of carboxylic acid dimers studied in this report.

分子間振動の粗視化

振動の自由度

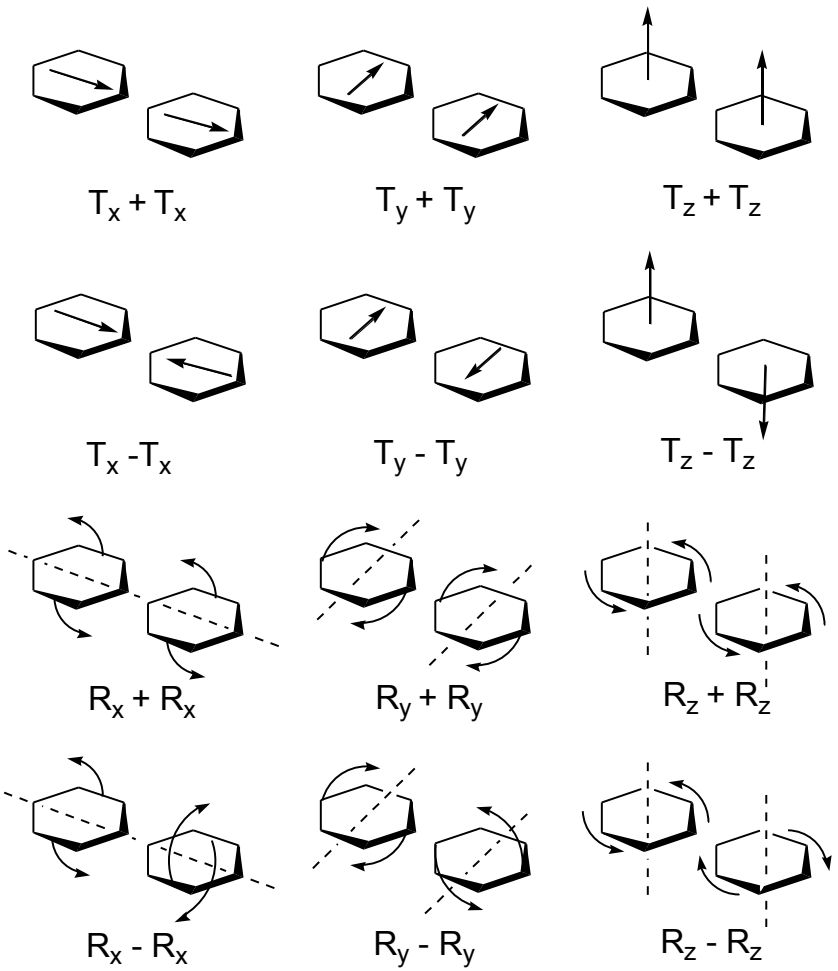
$3(N_1+N_2)-6$

$=(3N_1-6)+(3N_2-6)+6$

分子内振動　　分子間振動

分子間振動では分子内構造はほぼ不変

→変位ベクトルの次元を縮約することが可能



質量換算HESSIANの粗視化

$$\mathbf{M}^{-1}\mathbf{K}\mathbf{X}=\mathbf{X}\boldsymbol{\Omega}^2$$

$$\left(\mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2}\right)\left(\mathbf{M}^{1/2}\mathbf{X}\right)=\left(\mathbf{M}^{1/2}\mathbf{X}\right)\boldsymbol{\Omega}^2$$

$$\begin{cases}\boldsymbol{\Gamma}^{-1}=\mathbf{B}^t\mathbf{M}\mathbf{B}\\ \boldsymbol{\Phi}=\mathbf{B}^t\mathbf{K}\mathbf{B}\\ \boldsymbol{\Gamma}^{-1/2}\mathbf{U}=\left(\mathbf{B}^t\mathbf{M}^{1/2}\right)\left(\mathbf{M}^{1/2}\mathbf{X}\right)\end{cases}$$

$$\left(\boldsymbol{\Gamma}^{1/2}\boldsymbol{\Phi}\boldsymbol{\Gamma}^{1/2}\right)\left(\boldsymbol{\Gamma}^{-1/2}\mathbf{U}\right)=\left(\boldsymbol{\Gamma}^{-1/2}\mathbf{U}\right)\boldsymbol{\Omega}^2$$

$$\boldsymbol{\Gamma}\boldsymbol{\Phi}\mathbf{U}=\mathbf{U}\boldsymbol{\Omega}^2$$

$$\boldsymbol{\Gamma}\boldsymbol{\Phi}\mathbf{U}=\mathbf{U}\boldsymbol{\Omega}^2$$

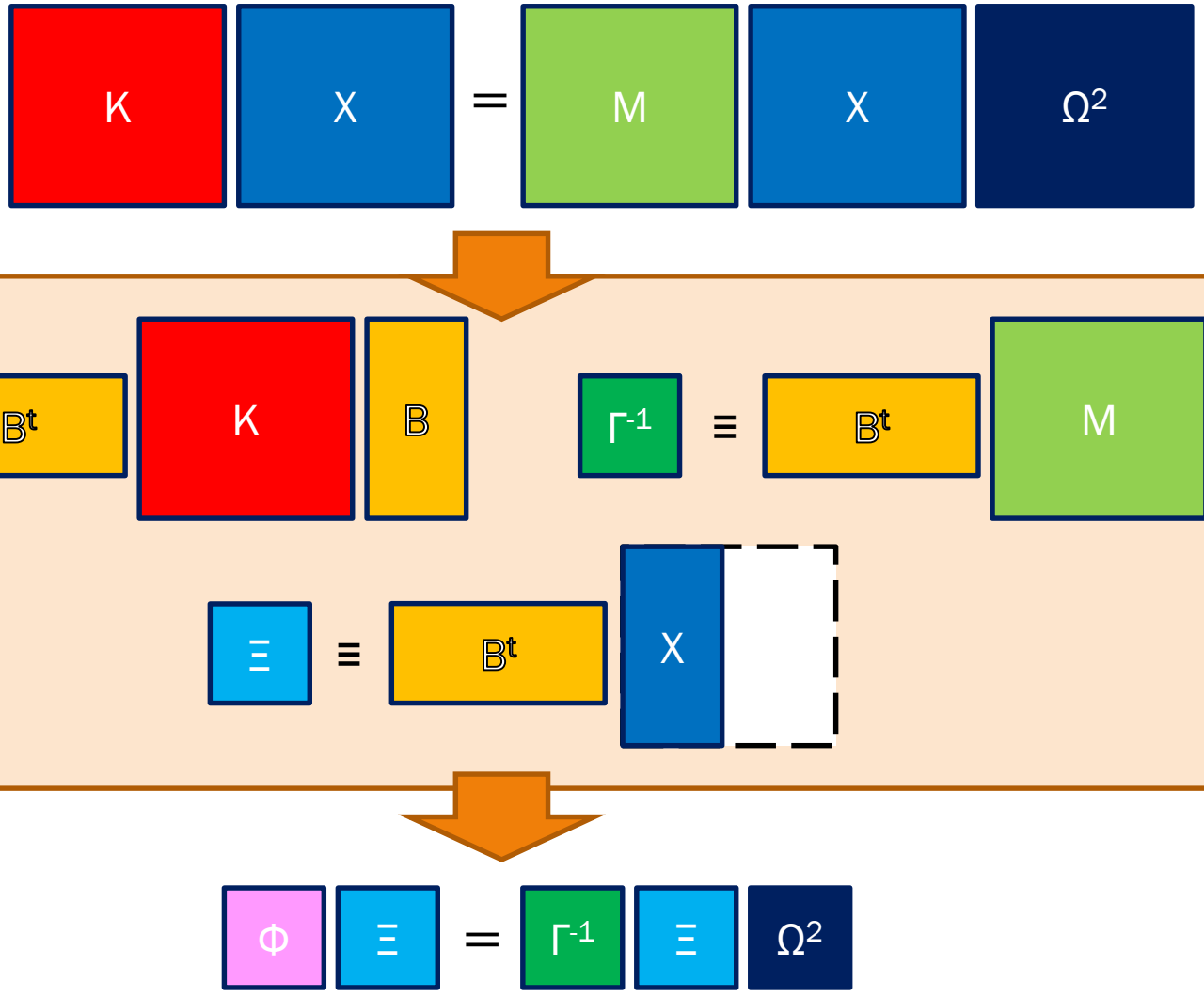
$$\boldsymbol{\Phi}=\boldsymbol{\Gamma}^{-1/2}\mathbf{U}\boldsymbol{\Omega}^2\mathbf{U}^t\boldsymbol{\Gamma}^{-1/2}$$

$$\left(\boldsymbol{\Gamma}^{-1/2}\mathbf{U}\right)^t\boldsymbol{\Gamma}^{-1/2}\mathbf{U}=\mathbf{U}^t\boldsymbol{\Gamma}^{-1}\mathbf{U}$$

$$=\left(\mathbf{B}^t\mathbf{M}\mathbf{X}\right)^t\mathbf{B}^t\mathbf{M}\mathbf{X}$$

$$=\mathbf{X}^t\mathbf{M}\mathbf{X}$$ （モード質量）

行列の縮約



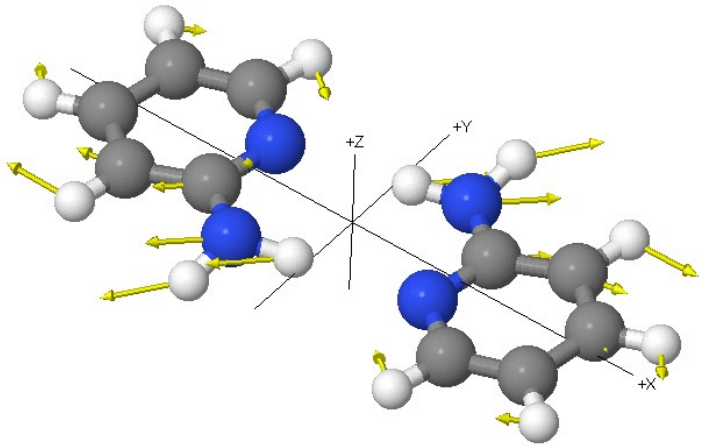
剛性定数の計算

		stiffness constant		
		$T_x - T_x$	$T_y - T_y$	$R_z + R_z$
A_g	$T_x - T_x$	37.9	0.4	30.9
	$T_y - T_y$		13.1	36.3
	$R_z + R_z$			124.8
B_g	$R_x + R_x$	4.2	3.8	13.7
	$R_y + R_y$	3.2	–0.6	-0.1
	$T_z - T_z$	–5.1	0.1	–3.4

	modal mass	
	coarse-grain	full-atom
Twist	4.03	4.11
Buckle	4.73	4.71
Opening	4.29	4.36
Staggered	6.20	6.30
Shear	6.21	6.27
Stretch	5.68	5.70

H. Houjou, *J. Chem. Theor. Comput.* (2009)

分子間振動の主成分分析

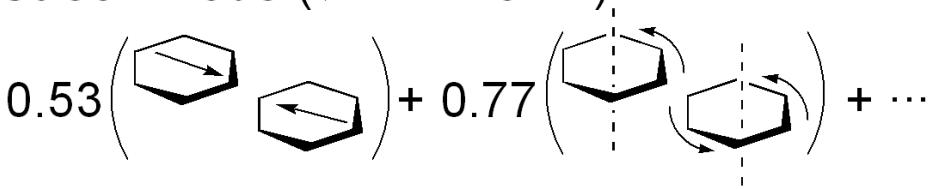


$$\mathbf{\Gamma\Phi U} = \mathbf{U\Omega}^2$$

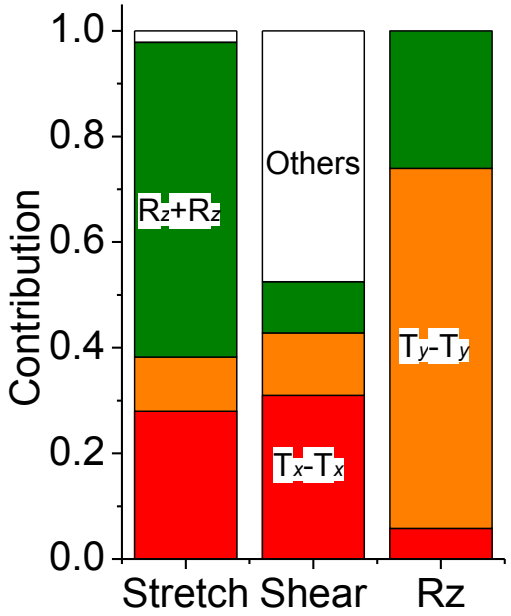
$$\mathbf{P} = \mathbf{U}^t\mathbf{U}$$

⇒各モードにおける基本変位の分率

Strech mode ($\tilde{\nu}$ = 109 cm^{-1}) =

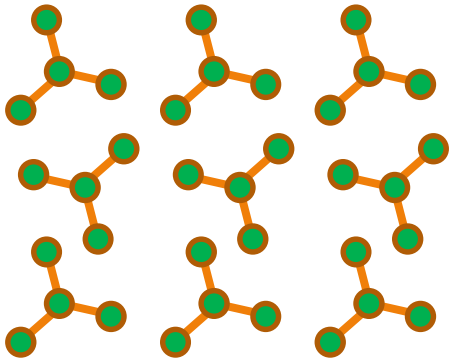


Stretch modeの約60%はｚ軸周りの同旋運動である！！

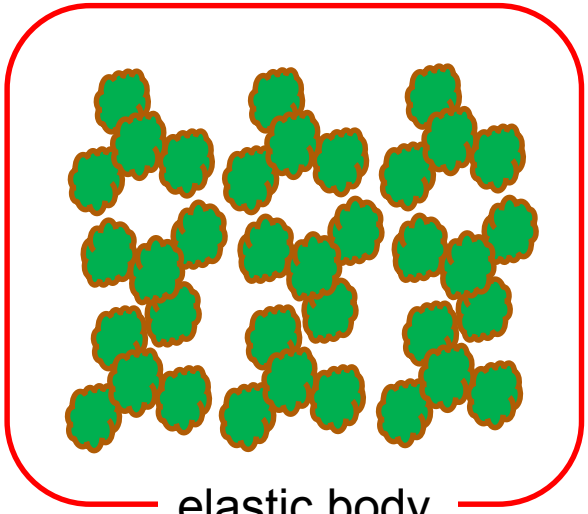


H. Houjou, *J. Chem. Theor. Comput.* (2009)

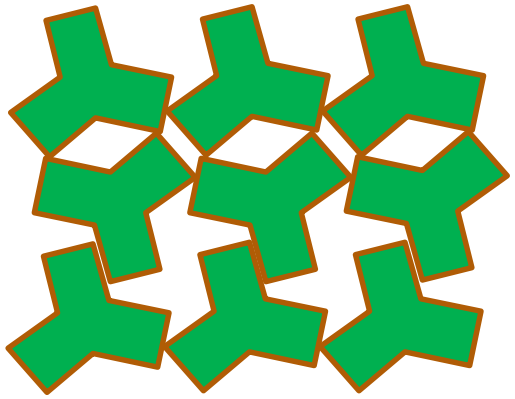
粗視化弾性体近似



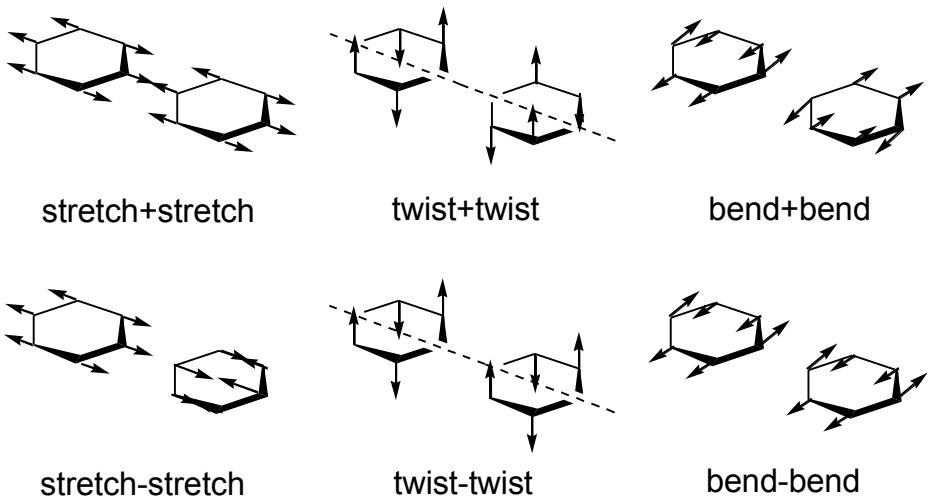
atomistic



elastic body



rigid body



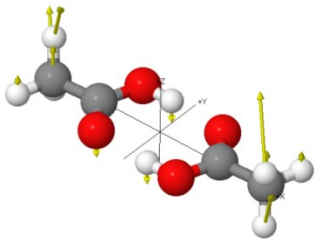
stretch+stretch　twist+twist　bend+bend

stretch-stretch　twist-twist　bend-bend

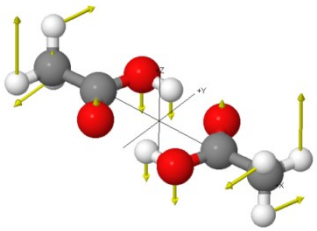
$$\mathbf{\Gamma}^{-1} = \begin{pmatrix} \mathbf{B}^t\mathbf{M}\mathbf{B} & \cdots & \mathbf{B}^t\mathbf{M}\mathbf{b}_i & \cdots \\ \vdots & \ddots & \vdots & \\ \mathbf{b}_i^t\mathbf{M}\mathbf{B} & \cdots & \mathbf{b}_i^t\mathbf{M}\mathbf{b}_i & \cdots \\ \vdots & & \vdots & \ddots \end{pmatrix}$$

H. Houjou, *J. Chem. Phys.* (2011)

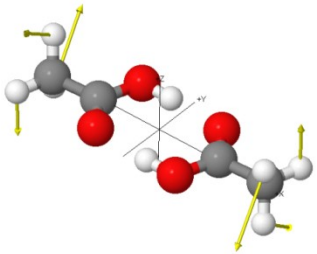
酢酸二量体の主成分解析



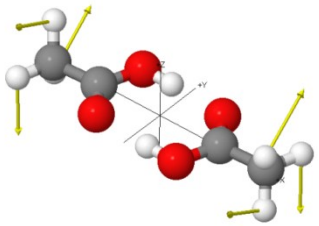
#1　50.0 cm^{-1}



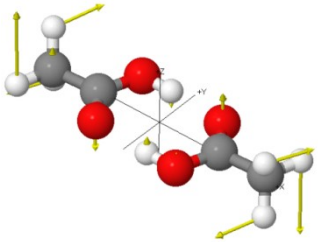
#2　75.4 cm^{-1}



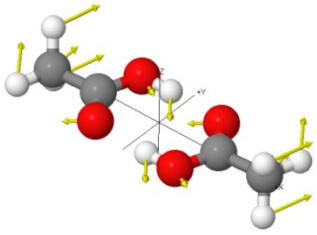
#3　81.8 cm^{-1}



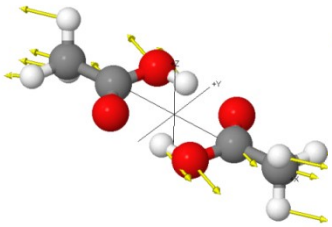
#4　89.7 cm^{-1}



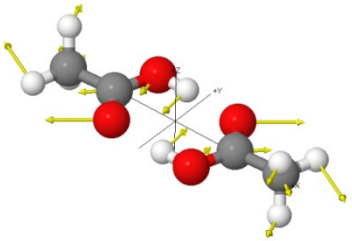
#5　116.7 cm^{-1}



#6　148.9 cm^{-1}



#7　153.0 cm^{-1}

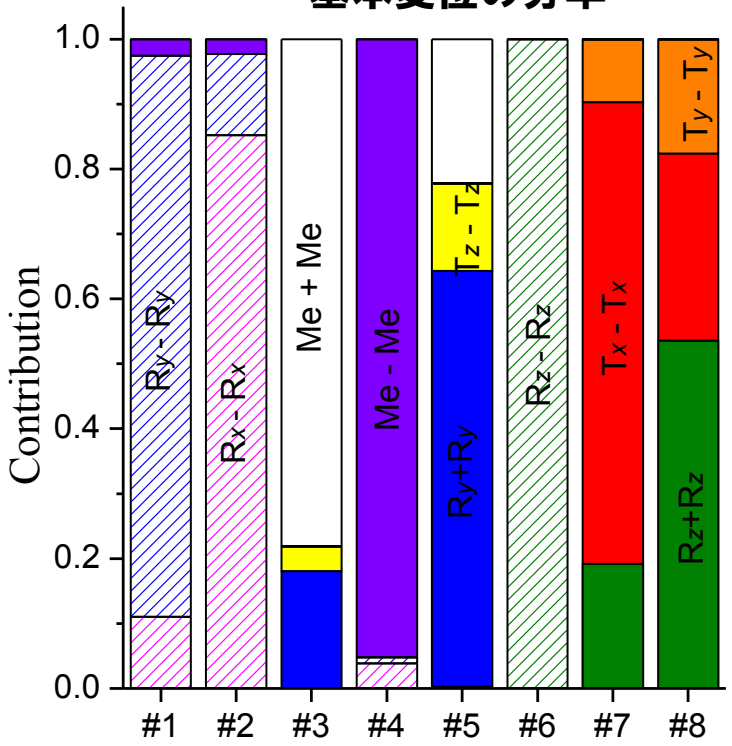


#8　156.4 cm^{-1}

$$\Gamma\Phi\mathbf{U} = \mathbf{U}\Omega^2$$

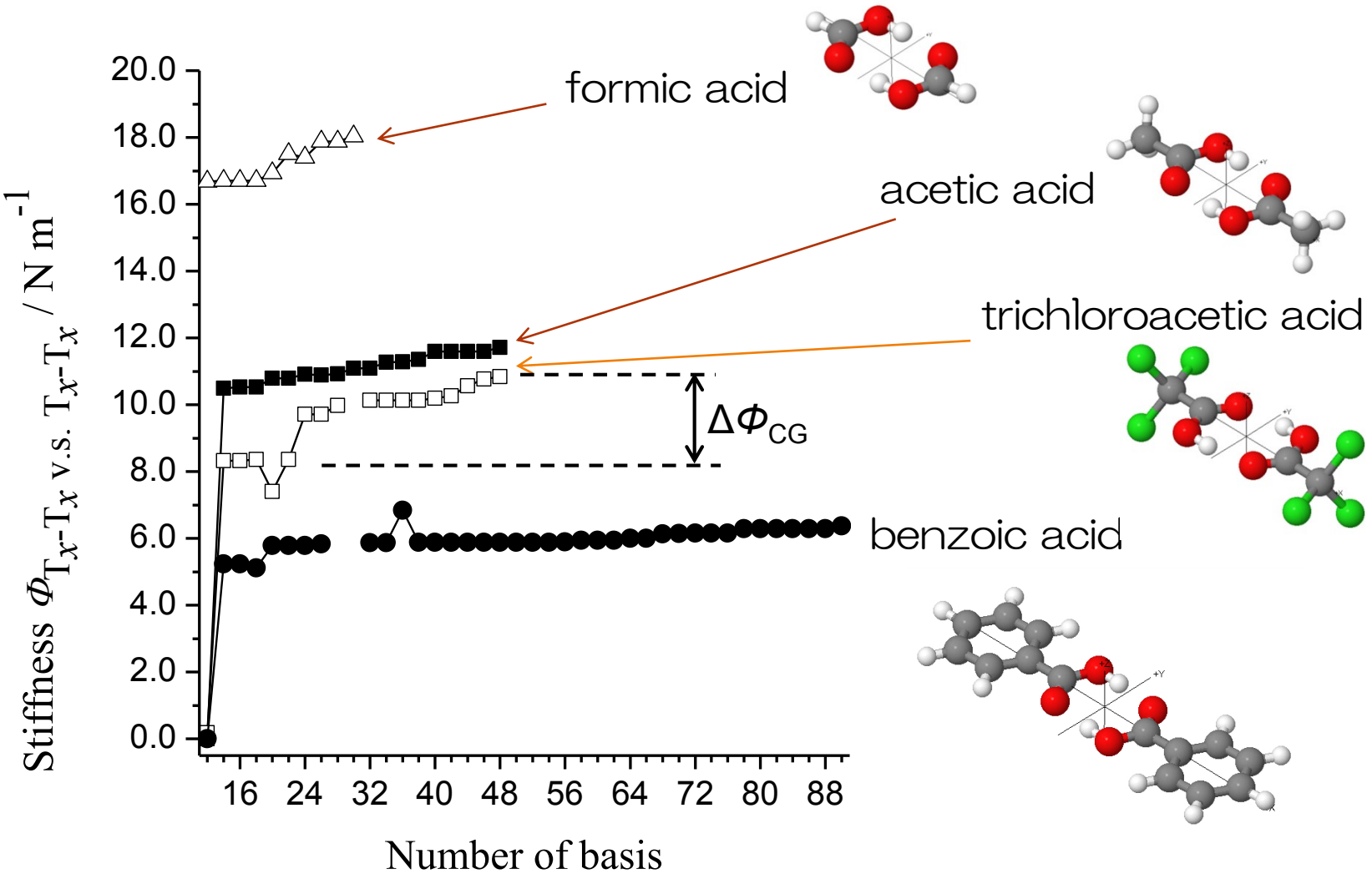
$$\mathbf{P} = \mathbf{U}^t\mathbf{U}$$

⇒各モードにおける
基本変位の分率



H. Houjou, *J. Chem. Phys.* (2011)

カルボン酸二量体の解析



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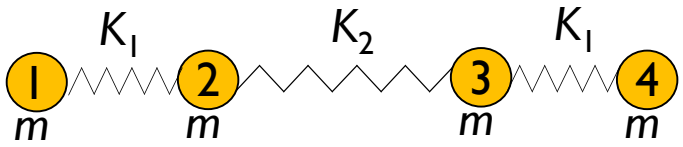
連結ばねモデル

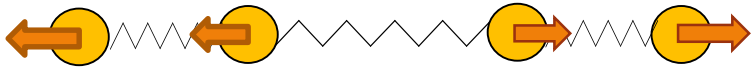


$$\omega^2 = 0,\ \frac{2K_1}{m},\ \frac{1}{m}\left(K_1 + K_2 \pm \sqrt{K_1^2 + K_2^2}\right)$$

coarse-grain

$$K_{\text{total}} = K_1 + K_2 - \sqrt{K_1^2 + K_2^2}$$

full-atom



$$K_{\text{inter}} = K_2$$

$$\Delta\phi_{\text{CG}} = \phi_{\text{inter}} - \phi_{\text{total}}$$

$$\phi_{\text{intra}} = \frac{\phi_{\text{inter}}^2 - \Delta\phi_{\text{CG}}^2}{2\Delta\phi_{\text{CG}}}$$

Stiffness constants (in N m^{-1})

	Φ_{inter}	Φ_{intra}	Φ_{total}
formic acid	45.1	299	41.7
acetic acid	46.8	223	42.0
trichloroacetic acid	43.4	88	33.3
benzoic acid	47.8	129	39.2

H. Houjou, *J. Chem. Phys.* (2011)