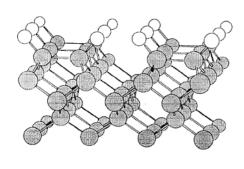
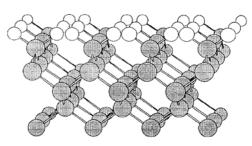
水素化ダイヤモンド表面 CHの SFG テンソル

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(b) Diamond (100)-1x1

1.序論

水素化ダイヤモンド表面の CH 伸縮振動を例にとって、単結晶表面の化学結合からの SFG スペクトルの解析に有効な事項について記す。

最初に、水素化 C(100) 表面についてまとめておこう。一般に言われているのは、as cut 表面の C 原子から出ている 2 本のダングリングボンド (dangling bond) のうちの 1 本が隣の C 原子のダングリングボンドと単結合を形成して(再構成表面の形成) 残る 1 本が水素化する(上の図の (a)、以後、monohydride モ

デルと呼ぶ)というものである。しかし、as cut 表面のままで、2本のダングリングボンドの両方が水素化することも(上の図の (b) 、以後、dihydride モデルと呼ぶ)考えとしては可能である。図から明らかなように、CH 結合に注目すると、前者では HCCH がユニットになり、後者では CH2 がユニットになる。そして、これらのユニットが表面上での広がりを持つために、表面単位胞の対称性は裸の表面の対称性と異なる。本稿では、HCCH および CH2 ユニットに付随する SFG テンソルについて考察する。

ダイヤモンド結晶の格子定数は 3.567 Å であるから、C—C 結合距離は 1.545 Å である。そして、表面に出ている C 原子間の距離は、as cut 表面で 2.51 Å である。再構成表面については、表面単位胞のサイズが 2.51×5.1 Å であるとの報告がある (R. E. Stallcup et al., *Appl. Phys. Lett.* <u>66</u>, 2331(1995))。再構成によって形成される C—C 結合の原子間隔を 2.0 Å と仮定すると、非結合炭素原子の間隔は 3.1 Å になる。

C—H 結合距離は $1.1 \sim 1.2\,\text{Å}$ である。表面 CH_2 基が図 (b) の配向を取っているときには、隣りあう CH_2 基の H 原子の間隔が $0.7\,\text{Å}$ 程度になる。また、表面 HCCH ユニットが図 (a) のような配向を取るときには、隣りあうユニットの H 原子間隔が $2\,\text{Å}$ 程度になる (CH 結合が表面法線に対してなす角を 30° と仮定したときの値、これを 55° のままとするときにはもっと短い)。

ところで、水素原子の間には反発力働く。この反発力がが働きはじめる距離の目安が H 原子のファンデルワールス半径で、その値は 1.20 Å である。よって、水素原子の中心の間の距離が 2.4 Å 程度以下になると、立体障害が働くはずである。図 (b) の状況がこれに該当することは明らかであろう。また、図 (a) のケースでも、隣りあう HCCH ユニットの H 原子の間隔がかなり短いから、立体障害の存在が十分疑われる。従って、立体障害を解消するために、表面 CH 結合の配向に何らかの歪みが生じる可能性が高い。

立体障害を解消するには、角を突き合わせている H 原子が、表面から等距離を保ったまま前後にずれた状態と、どちらか一方の H 原子が表面側に潜り、他方の H 原子が上方にずれた状態が考えられる。 CH_2 基で言えば、 C_2 軸周りの回転または分子面の傾斜による方法と、分子面に垂直な軸の周りでの回転である。また、HCCH 基で言えば、表面法線の周りでの CH 結合の回転、HCC 結合角の増減、あるいは、分子面の傾斜(平面を保つ)またはねじれ(分子面がよじれる)が考えられる。いずれにせよ、立体障害の解消は隣りあうユニットに属する CH 結合の間で行われる。これによってユニットに生じる変化には、表面の上でのユニットの並び方も絡むはずである。

HCCH ユニットの対称性について考えると、 C_{2v} 対称と C_2 対称が考えられる。 C_{2v} 対称は、H 原子が立体障害を受けない場合、そして、立体障害による「逃げ」が分子面が平面のままで、表面に対する傾斜がユニットごとに互い違いになっているときのものである。これに対して C_2 対称は、「逃げ」に際して生じる左右の CH 結合のずれが、もともとの CH 面に関して反対方向になるときのものである。

 CH_2 ユニットは、3 原子分子の特性として平面のままである。そして、2 個の H 原子は等価であるから、 $C_{2\nu}$ 対称が保たれる。

2.分子固定座標系と空間固定座標系

1. 分子に固定した座標系:(abc) 系と表す。

 $\mathbf{CH_2}$ 基では、 $\mathbf{C_2}$ 対称軸に沿って外向きに \mathbf{c} 軸を取り、分子面内に \mathbf{a} 軸を取る。

HCCH 基では、 C_2 対称軸に沿って外向きに c 軸をとり、平面形 (C_{2v} 対称)では分子面内に a 軸を、ねじれ形 (C_2 対称)では 2 つの CCH 面を 2 等分する平面 (すなわち CCC 面)上に a 軸を取る。

- 2a. 表面に固定した座標系:(xyz) 系と表す。
- 2b. 空間に固定した座標系:(XYZ) 系と表す。
- **3. 分子の配向:**オイラー角 (χ, θ, ϕ) の定義を、分子固定 (abc) 系を表面固定 (xyz) 系に重ねるときのものとする。

用いる**オイラー角** (χ, θ, ϕ) は、次のように表現される。

- (1) 内部回転角 ϕ : ac 面(ここで考えている CH_2 基及び HCCH 基では分子面)の(表面に対する)ねじれ角である。c 軸まわりの回転で ac 面を表面と垂直にするために必要な回転角、あるいは a 軸が z 軸の ab 面への射影に重なるまでの回転角でもある。(a 軸に沿ったベクトルと x 軸に沿ったベクトルの内積がプラスになる方向で重ねる。)ac 面が表面に垂直なときには $\phi=0$ or π であり、ac 面が表面と向き合っているときには $\phi=\pi/2$ or $3\pi/2$ である。分子がランダムな内部回転角を取っている場合には ϕ は $0\sim2\pi$ の任意の値を等しいウェイトで取る。
- (2) **傾き角・tilt 角** θ_{tilt} : 通常の定義に合わせて、c 軸と外向きの法線 (-z) の間の角を傾き角と定義し、N 軸 (z 軸と c 軸の両方に垂直な直線、ab 面と xy 面の交線) まわりの回転で c 軸を外向きの法線に重ねる方向をプラス回転とする。z 軸は下向きの法線であるから、オイラー角 θ は π θ_{tilt} である。
- (3) 面内配向角 $\chi_{\text{in-plane}}$ (χ_{ip} と略記する): z 軸まわりの回転で c 軸の xy 面への射影を x 軸に重ねるための回転角と定義する。ここでの z 軸の向きでは、x 軸の方向に見て射影が左側にあるときがプラスになる。 z 軸を基板の内部に向けて取っているので、対応するオイラー角 χ は $\pi/2+\chi_{\text{ip}}$ である。分子の面内配向がランダムなときには、 χ_{ip} は $0\sim 2\pi$ の任意の値を等しいウェイトで取る。

3. 分子固定 (abc) 系におけるテンソル成分

対称性の考察から、ゼロ以外の値を持つテンソル成分を摘出することが出来る。 C_{2v} 分子(CH_2 基と平面形 HCCH 基)では、 β_{aac} 、 β_{bbc} 、 β_{ccc} ;、 $\beta_{caa} = \beta_{aca}$ 、 $\beta_{bbb} = \beta_{bcb}$ であり、 C_2 分子(ねじれ形 HCCH 基)では、 β_{aac} 、 β_{bbc} 、 β_{ccc} 、 $\beta_{abc} = \beta_{bac}$ 、 $\beta_{cca} = \beta_{aca}$ 、 $\beta_{bca} = \beta_{bcb}$ 、 $\beta_{cab} = \beta_{acb}$ である。それぞれの値の目安として、CH 結合のテンソル成分がそのまま転用できると仮定したときの値は、ファイル「オイラー角」と「分子固定から空間固定へ」を参照して導くことができる。

CH₂基;

ファイル「オイラー角」の Eu-5 式により、(1) 2個の CH 結合では角 χ が互いに π だけ違っているので、 $\sin\chi$ 、 $\sin3\chi$ 、 $\cos\chi$ 、 $\cos3\chi$ が掛っている項の和はゼロになる。また、 $\chi=0$ と π であるから、 $\sin2\chi=0$ 、 $\cos2\chi=+1$ となり、 $\sin2\chi$ と $(1-\cos2\chi)$ が掛る項もゼロである。 (2) 角 ϕ は ゼロ であるから、 $\sin\phi=\sin2\phi=\sin3\phi=0$ 、 $\cos\phi=\cos2\phi=\cos3\phi=+1$ となり、 $\sin\phi$ 、 $\sin2\phi$ 、 $\sin3\phi$ 、 $(1-\cos2\phi)$ が掛かる項もゼロになる。これらのことを考慮して、ファイル「分子固定から空間固定へ」により 2 個の CH 結合についてとったテンソル成分の和は、下のようになる。

$$\begin{split} \beta_{aac} &= 2\{\beta_{\xi\xi\zeta}\cos^{3}(\alpha/2) + \beta_{\zeta\zeta\zeta}[\cos(\alpha/2) - \cos^{3}(\alpha/2)]\} \\ \beta_{bbc} &= 2\beta_{\eta\eta\zeta}\cos(\alpha/2) \\ \beta_{ccc} &= 2\{\beta_{\xi\xi\zeta}[\cos(\alpha/2) - \cos^{3}(\alpha/2)] + \beta_{\zeta\zeta\zeta}\cos^{3}(\alpha/2)\} \\ \beta_{caa} &= \beta_{aca} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})[\cos(\alpha/2) - \cos^{3}(\alpha/2)] \\ \beta_{cbb} &= \beta_{bcb} = 0 \end{split} \tag{3-1a}$$

(CH 伸縮振動は b 軸方向の成分を持たないので、下付きの右端が b のテンソル成分はゼロになる。)

HCH 角を 4 面体角にとると、 $\cos\alpha = -1/3$ 、 $\sin\alpha = 2\sqrt{2}/3$ であるから、 $\cos(\alpha/2) = \sqrt{1/3}$ となり、

$$\begin{split} \beta_{aac} &= (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta}) \\ \beta_{bbc} &= (2\sqrt{3}/9)(3\beta_{\eta\eta\zeta}) \\ \beta_{ccc} &= (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta}) \\ \beta_{cas} &= \beta_{aca} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \\ \end{split} \tag{3-4a}$$

を得る。CH 基自体と違って、 $\beta_{ax} \sim \beta_{cx}$ であることに注意しよう。

HCCH基(平面形);

上と同様な筋道での導出になる。ファイル「オイラー角」の (Eu-6) 式と (Eu-5) 式の違いは、 $(\alpha/2)$ の代りに α - $\pi/2$ が入る、ということである。 (ただし、ここの α は HCC 角である) よって、下式が得られる。

$$\beta_{a\alpha} = 2[\beta_{\xi\xi\zeta}\sin^3\alpha + \beta_{\zeta\zeta\zeta}(\sin\alpha - \sin^3\alpha)] \tag{3-6a}$$

$$\beta_{\rm bbc} = 2\beta_{\rm nnr} \sin\alpha \tag{3-6b}$$

$$\beta_{cc} = 2[\beta_{\xi\xi\zeta}(\sin\alpha - \sin^3\alpha) + \beta_{\zeta\zeta\zeta}\sin^3\alpha] \tag{3-6c}$$

$$\beta_{\text{caa}} = \beta_{\text{aca}} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\alpha - \sin^3\alpha) \tag{3-7}$$

HCC 角を 4 面体角にとると、 $\cos\alpha = -1/3$ 、 $\sin\alpha = 2\sqrt{2}/3$ であるから、

$$\beta_{ax} = (4\sqrt{2}/37)(8\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta}) \tag{3-8a}$$

$$\beta_{\rm phc} = (4\sqrt{2}/37)(9\beta_{\rm nn'}) \tag{3-8b}$$

$$\beta_{cc} = (4\sqrt{2}/37)(\beta_{\xi\xi\zeta} + 8\beta_{\zeta\zeta\zeta}) \tag{3-8c}$$

$$\beta_{caa} = \beta_{aca} = -(4\sqrt{2}/37)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})$$
 (3-9)

ここでは、 $\beta_{aac} < \beta_{coc}$, β_{caa} であることに注意しよう。

HCCH 基 (ねじれ形);

ファイル「オイラー角」の (Eu-8) 式、(Eu-10) 式、(Eu-10) 式により、オイラー角を使った表式がまず得られる。次に、オイラー角を HCC 角および 2 面角と結び付ける、という面倒な手続きが必要である。ファイル「分子固定から空間固定へ」により得られるオイラー角を使った表式は、下のようになる。

$$\begin{split} \beta_{aac} &= (\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta})cos\theta \\ &- (1/2)(\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta} - 2\beta_{\zeta\zeta\zeta})(cos\theta - cos^3\theta)(1 + cos2\chi) \\ &- (1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})\{[cos\theta(1 - cos2\chi) - cos^3\theta(1 + cos2\chi)]cos2\varphi + 2cos^2\theta sin2\chi sin2\varphi\} \\ \beta_{bbc} &= (\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta})cos\theta \end{split} \tag{3-10a}$$

$$-\ (1/2)(\beta_{\xi\xi\zeta}+\beta_{\eta\eta\zeta}-2\beta_{\zeta\zeta\zeta})(cos\theta-cos^3\theta)(1-cos2\chi)$$

$$-(1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})\{[\cos\theta(1 + \cos2\chi) - \cos^3\theta(1 - \cos2\chi)]\cos2\phi - 2\cos^2\theta\sin2\chi\sin2\phi\}$$
 (3-10b)

 $\beta_{\rm ccc} = (\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta})cos\theta$

$$-(\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta} - 2\beta_{\zeta\zeta\zeta})\cos^3\theta$$

$$+ (\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})(\cos\theta - \cos^3\theta)\cos 2\phi \qquad \qquad 1 \tag{3-10c}$$

 $\beta_{abc} = \beta_{bac} = (1/2)(\beta_{\xi\xi\zeta} + \beta_{nn\zeta} - 2\beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)\sin 2\chi$

$$-(1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})[(\cos\theta + \cos^3\theta)\sin2\chi\cos2\phi + 2\cos^2\theta\cos2\chi\sin2\phi]$$
 (3-10d)

$$\beta_{\text{caa}} = \beta_{\text{aca}} = \text{-}(1/2)(\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta} - 2\beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)(1 + \cos2\chi)$$

$$-(1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})[(\cos\theta - \cos^3\theta)(1 + \cos2\chi)\cos2\phi - \sin^2\theta\sin2\chi\sin2\phi]$$
 (3-11a)

$$\beta_{bca} = \beta_{cba} = (1/2)(\beta_{\xi\xi\zeta} + \beta_{nn\zeta} - 2\beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)\sin 2\chi$$

$$+ (1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi + \sin^2\theta (1 + \cos2\chi)\sin2\phi] \tag{3-11b}$$

$$\beta_{cbb} = \beta_{bcb} = -(1/2)(\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta} - 2\beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)$$

$$\begin{split} &-(1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\cos2\phi + \sin^2\theta\sin2\chi\sin2\phi] \\ \beta_{cab} &= \beta_{acb} = (1/2)(\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta} - 2\beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)\sin2\chi \\ &+ (1/2)(\beta_{\xi\xi\zeta} - \beta_{\eta\eta\zeta})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi - \sin^2\theta \ (1 - \cos2\chi)\sin2\phi] \end{split} \tag{3-12b}$$

これを α と τ による表式に変えるにあたり、単純な置き換えをしてから式を整理すると、下記のようになる。

$$\begin{split} \beta_{aac} &= 2(\beta_{\xi\xi\zeta}\sin^2\alpha + \beta_{\zeta\zeta\zeta}\cos^2\alpha)\sin\alpha\cos(\tau/2) & (3\text{-}13a) \\ \beta_{bbc} &= 2[\beta_{\xi\xi\zeta}\cos^2\alpha\sin^2(\tau/2) + \beta_{\eta\eta\zeta}\cos^2(\tau/2) + \beta_{\zeta\zeta\zeta}\sin^2\alpha\sin^2(\tau/2)]\sin\alpha\cos(\tau/2) & (3\text{-}13b) \\ \beta_{ccc} &= 2[\beta_{\xi\xi\zeta}\cos^2\alpha\cos^2(\tau/2) + \beta_{\eta\eta\zeta}\sin^2(\tau/2) + \beta_{\zeta\zeta\zeta}\sin^2\alpha\cos^2(\tau/2)]\sin\alpha\cos(\tau/2) & (3\text{-}13c) \\ \beta_{abc} &= \beta_{bac} &= 2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})[\sin\alpha\cos\alpha\sin(\tau/2)]\sin\alpha\cos(\tau/2) & (3\text{-}13d) \\ \beta_{caa} &= \beta_{aca} &= -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\alpha\cos^2\alpha\cos(\tau/2) & (3\text{-}14a) \\ \beta_{bca} &= \beta_{cba} &= -2[\beta_{\xi\xi\zeta}\cos^2\alpha - \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta}\sin^2\alpha]\cos\alpha\sin(\tau/2)\cos(\tau/2) & (3\text{-}14b) \\ \beta_{cbb} &= \beta_{bcb} &= +2[\beta_{\xi\xi\zeta}\cos^2\alpha - \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta}\sin^2\alpha]\sin\alpha\sin^2(\tau/2)\cos(\tau/2) & (3\text{-}15a) \\ \beta_{cab} &= \beta_{acb} &= -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin^2\alpha\cos\alpha\cos(\tau/2) & (3\text{-}15b) \\ \end{split}$$

HCC 角を四面体角にとると、 $\cos\alpha = -1/3$ 、 $\sin\alpha = 2\sqrt{2}/3$ であるから、

$$\begin{array}{lll} \beta_{aac} &= (4\sqrt{2} \, / \, 27)(8\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos(\tau/2) & (3\text{-}16a) \\ \beta_{bbc} &= (4\sqrt{2} \, / \, 27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin^2(\tau/2) + 9\beta_{\eta\eta\zeta}]\cos(\tau/2) & (3\text{-}16b) \\ \beta_{ccc} &= (4\sqrt{2} \, / \, 27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\cos^2(\tau/2) + 9\beta_{\eta\eta\zeta}]\cos(\tau/2) & (3\text{-}16c) \\ \beta_{abc} &= \beta_{bac} = -(4\sqrt{2} \, / \, 27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(2\sqrt{2})\sin(\tau/2)\cos(\tau/2) & (3\text{-}16d) \\ \beta_{caa} &= \beta_{aca} = -(4\sqrt{2} \, / \, 27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos(\tau/2) & (3\text{-}17a) \\ \beta_{bca} &= \beta_{cba} = +(2/27)[\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}]\sin(\tau/2)\cos(\tau/2) & (3\text{-}17b) \\ \beta_{cbb} &= \beta_{bcb} = +(4\sqrt{2} \, / \, 27)[\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}]\sin^2(\tau/2)\cos(\tau/2) & (3\text{-}18a) \\ \beta_{cab} &= \beta_{acb} = +(8/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos(\tau/2) & (3\text{-}18b) \end{array}$$

4 . 表面固定 (xyz) 系における HCCH 基のテンソル成分

典型的な配向について、表面固定系でのテンソル成分を求めておこう。なお、一般的な配向に対する表式を**付録** A に記してあるので、個別のオイラー角を当てはめれば以下で示す表式が求まる。

なお、下で出てくる τ は、分子面 (α c 面)と表面 (α xy 面)の間の α 2 面角である。

4a. 傾いた平面形 HCCH 基

分子面 [ac 面] が表面から角 τ だけ傾いているとして、2 つある傾き方に対するオイラー角は (ファイル「オイラー角」の (Eu-4) 式を参照して)次のようになる。 α は CCH 結合角である。

$$R_z(\chi = -\pi/2) \ R_b \cdot (\theta = -\tau) \ R_c(\phi = \pi/2)$$
、 $R_z(\chi = -\pi/2) \ R_b \cdot (\theta = +\tau) \ R_c(\phi = \pi/2)$ 、 $\tau = \pi/2 - \theta$ $\sin \chi = -1$ 、 $\sin 2\chi = 0$ 、 $\sin 3\chi = +1$ $\cos \chi = 0$ 、 $\cos 2\nu = -1$ 、 $\cos 3\chi = 0$ $\sin \phi = +1$ 、 $\sin 2\phi = 0$ 、 $\sin 3\nu = -1$ $\cos \phi = 0$ 、 $\cos 2\phi = -1$ 、 $\cos 3\phi = 0$ $\sin \theta = -(\pm)\sin \tau$ 、 $\cos \theta = \cos \tau$ (4a-1) (隣り合う HCCH 基は交互に $-\tau \, \succeq \, +\tau \,$ を取る。)

により、

[対称伸縮振動]

$$\begin{aligned} (\text{ppp}) & \quad \chi_{xxz} = \beta_{aac} \text{cost} \\ & \quad \chi_{zzz} = -(\beta_{bbc} - \beta_{ccc}) \text{cos}^3 \tau + \beta_{bbc} \text{cos} \tau \\ (\text{spp}) & \quad \chi_{yzz} = \pm (\beta_{bbc} - \beta_{ccc}) (\text{sin}\tau - \text{sin}^3 \tau) \\ (\text{ssp}) & \quad \chi_{yyz} = (\beta_{bbc} - \beta_{ccc}) \text{cos}^3 \tau + \beta_{ccc} \text{cos} \tau \\ (\text{psp}) & \quad \chi_{zyz} = \pm (\beta_{bbc} - \beta_{ccc}) (\text{sin}\tau - \text{sin}^3 \tau) \\ (\text{sps}) & \quad \chi_{yzy} = -(\beta_{bbc} - \beta_{ccc}) (\text{cos}\tau - \text{cos}^3 \tau) \\ (\text{pps}) & \quad \chi_{xxy} = -(\pm) \beta_{aac} \text{sin} \tau \\ & \quad \chi_{zzy} = -(\pm) \beta_{bbc} \text{sin}^3 \tau - (\pm) \beta_{ccc} (\text{sin}\tau - \text{sin}^3 \tau) \\ (\text{pss}) & \quad \chi_{zyy} = -(\beta_{bbc} - \beta_{ccc}) (\text{cos}\tau - \text{cos}^3 \tau) \end{aligned}$$

(sss) $\chi_{yyy} = -(\pm)\beta_{bbc}(\sin\tau - \sin^3\tau) - (\pm)\beta_{ccc}\sin^3\tau$

「逆対称伸縮振動]

(ppp)
$$\chi_{zxx} = \beta_{caa} \cos \tau$$

$$\chi_{xzx} = \beta_{caa} \cos \tau$$
(spp) $\chi_{yxx} = -(\pm)\beta_{caa} \sin \tau$
(ssp) none
(psp) $\chi_{xyx} = -(\pm)\beta_{caa} \sin \tau$
(sps) none
(psp) $\chi_{xyx} = -(\pm)\beta_{caa} \sin \tau$
(sps) none
(psp) none

(4a-2)

(sss) none (4a-3)

CH 基のテンソル成分による表式 (3-6) 式に Td 角を仮定した (3-8) 式を使用すると、下記の表式を得る。

「対称伸縮振動)

(ppp)
$$\chi_{xxz} = (4\sqrt{2}/27)(8\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos\tau$$

 $\chi_{zzz} = (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\cos^3\tau$
(spp) $\chi_{yzz} = -(\pm)(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\sin\tau - \sin^3\tau)$
(ssp) $\chi_{yyz} = (4\sqrt{2}/27)[-(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\cos\tau - \cos^3\tau) + 9\beta_{\eta\eta\zeta}\cos\tau]$
(psp) $\chi_{zyz} = -(\pm)(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\sin\tau - \sin^3\tau)$
(sps) $\chi_{yzy} = (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\cos\tau - \cos^3\tau)$
(pps) $\chi_{xxy} = -(\pm)(4\sqrt{2}/27)(9\beta_{\eta\eta\zeta})\sin\tau$
 $\chi_{zzy} = -(\pm)(4\sqrt{2}/27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\sin\tau - \sin^3\tau) - 9\beta_{\eta\eta\zeta}\sin\tau]$
(pss) $\chi_{zyy} = (4\sqrt{2}/27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\cos\tau - \cos^3\tau)$
(sss) $\chi_{yyy} = -(\pm)(4\sqrt{2}/27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})(\cos\tau - \cos^3\tau)$

[逆対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{zxx} = \text{-}(~4\sqrt{2}~/~27~)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\tau \\ \chi_{xzx} = \text{-}(~4\sqrt{2}~/~27~)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\tau \\ (spp) \qquad & \chi_{yxx} = (\pm)(~4\sqrt{2}~/~27~)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})sin\tau \end{split}$$

(ssp) none

(psp)
$$\chi_{xxx} = -(\pm)(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\tau$$

- (sps) none
- (pps) none
- (pss) none

4b. ねじれ形 HCCH 基

ねじれ形 HCCH 基の ac 面は xz 面と重なっていると見なせるから、上の (3-10) 式 $\sim (3-18)$ 式で左辺の下付き (abc) を (xyz) に読み替えたものがそのまま当てはまる。 α は CCH 結合角、 τ は 2 個の CCH 面の間の 2 面角である。

$$R_{\tau}(\chi = 0) R_{b'}(\theta = 0) R_{c}(\phi = 0), \quad \tau = 0$$
 (4b-1)

により、下記の表式を得る。なお、CH 基のテンソル成分による表式 (3-13) 式を使って整理したものも示す。

[対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{xxz} = \beta_{aac} = 2(\beta_{\xi\xi\zeta} sin^2\alpha + \beta_{\zeta\zeta\zeta} cos^2\alpha) sin\alpha cos(\tau/2) \\ \chi_{zzz} = \beta_{ccc} = 2[\beta_{\xi\xi\zeta} cos^2\alpha cos^2(\tau/2) + \beta_{\eta\eta\zeta} sin^2(\tau/2) + \beta_{\zeta\zeta\zeta} sin^2\alpha cos^2(\tau/2)] sin\alpha cos(\tau/2) \end{split}$$

(spp)
$$\chi_{vxz} = \beta_{abc} = 2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})[\sin\alpha\cos\alpha\sin(\tau/2)]\sin\alpha\cos(\tau/2)$$

$$(ssp) \qquad \chi_{yyz} = \beta_{bbc} = 2[\beta_{\xi\xi\zeta} cos^2 \alpha sin^2 (\tau/2) + \beta_{\eta\eta\zeta} cos^2 (\tau/2) + \beta_{\zeta\zeta\zeta} sin^2 \alpha sin^2 (\tau/2)] sin\alpha cos(\tau/2)$$

(psp)
$$\chi_{xyz} = \beta_{abc} = 2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})[\sin\alpha\cos\alpha\sin(\tau/2)]\sin\alpha\cos(\tau/2)$$

- (sps) none
- (pps) none
- (pss) none

[逆対称伸縮振動]

$$\begin{split} \text{(ppp)} \qquad & \chi_{zxx} = \beta_{caa} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin\alpha\cos^2\!\alpha\cos(\tau/2) \\ & \chi_{xzx} = \beta_{caa} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin\alpha\cos^2\!\alpha\cos(\tau/2) \end{split}$$

(spp)
$$\chi_{vzx} = \beta_{bca} = -2(\beta_{\xi\xi\zeta}\cos^2\alpha - \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta}\sin^2\alpha)\cos\alpha\sin(\tau/2)\cos(\tau/2)$$

- (ssp) none
- (psp) $\chi_{zvx} = \beta_{bca} = -2(\beta_{\xi\xi\zeta}\cos^2\alpha \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta}\sin^2\alpha)\cos\alpha\sin(\tau/2)\cos(\tau/2)$

$$(sps) \qquad \chi_{yzy} = \beta_{cbb} = +2(\beta_{\xi\xi\zeta}cos^2\alpha - \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta}sin^2\alpha)sin\alpha sin2(\tau/2)cos(\tau/2)$$

$$\begin{split} (pps) \qquad & \chi_{zxy} = \beta_{cab} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin^2 \alpha cos\alpha cos(\tau/2) \\ & \chi_{xzy} = \beta_{cab} = -2(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin^2 \alpha cos\alpha cos(\tau/2) \\ (pss) \qquad & \chi_{zyy} = \beta_{cbb} = +2(\beta_{\xi\xi\zeta} cos^2 \alpha - \beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta} sin^2 \alpha) sin\alpha sin^2(\tau/2) cos(\tau/2) \end{split}$$

さらに、Td 角を仮定すると $cos\alpha = -1/3$, $sin\alpha = 2\sqrt{2}/3$ であるから、

[対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{xxz} = \beta_{a\infty} = (\,4\sqrt{2}\,\,/\,\,27\,)(\,8\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta})cos(\tau/2) \\ \chi_{zzz} = \beta_{ccc} = (\,4\sqrt{2}\,\,/\,\,27\,)[(\,\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})cos^2(\tau/2) + 9\beta_{\eta\eta\zeta}]cos(\tau/2) \end{split}$$

(spp)
$$\chi_{vxz} = \beta_{abc} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(2\sqrt{2})\sin(\tau/2)\cos(\tau/2)$$

$$(ssp) \qquad \chi_{yyz} = \beta_{bbc} = (\,4\sqrt{2}\,/\,27)[\,(\beta_{\xi\xi\zeta}\,-\,9\beta_{\eta\eta\zeta}\,+\,8\beta_{\zeta\zeta\zeta})sin^2(\tau/2)\,+\,9\beta_{\eta\eta\zeta}]cos(\tau/2)$$

(psp)
$$\chi_{xvz} = \beta_{abc} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(2\sqrt{2})\sin(\tau/2)\cos(\tau/2)$$

- (sps) none
- (pps) none
- (pss) none

[逆対称伸縮振動]

$$\begin{split} \text{(ppp)} \qquad & \chi_{zxx} = \beta_{caa} = \text{-(} \ 4\sqrt{2} \ / \ 27) (\beta_{\xi\xi\zeta} \ \text{-} \ \beta_{\zeta\zeta\zeta}) cos(\tau/2) \\ \chi_{xzx} = & \beta_{caa} = \text{-(} \ 4\sqrt{2} \ / \ 27) (\beta_{\xi\xi\zeta} \ \text{-} \ \beta_{\zeta\zeta\zeta}) cos(\tau/2) \end{split}$$

$$(spp) \qquad \chi_{vzx} = \beta_{bca} = (2/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})sin(\tau/2)cos(\tau/2)$$

- (ssp) none
- $(psp) \qquad \chi_{zvx} = \beta_{bca} = (2/27)(\beta_{\xi\xi\zeta} 9\beta_{nn\zeta} + 8\beta_{\zeta\zeta\zeta})\sin(\tau/2)\cos(\tau/2)$

(sps)
$$\chi_{yzy} = \beta_{cbb} = (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin^2(\tau/2)\cos(\tau/2)$$

$$\begin{split} (pps) \qquad \chi_{zxy} &= \beta_{cab} = (8/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos(\tau/2) \\ \chi_{xzy} &= \beta_{cab} = (8/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos(\tau/2) \end{split}$$

(pss)
$$\chi_{\text{zyy}} = \beta_{\text{cbb}} = (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin^2(\tau/2)\cos(\tau/2)$$

5. 表面固定 (xyz) 系における CH₂ 基のテンソル成分

5a. ねじれた CH, 基

立体障害を解消するために C_2 軸まわりで角 γ だけねじれるとき、ファイル「オイラー角」の (Eu-1) 式により下式が得られる。 α は HCH 結合角である。

$$\begin{split} R_z(\chi=\gamma) \; R_{b'}(\theta=0) \; R_c(\varphi=0), \quad R_z(\chi=-\gamma) \; R_{b'}(\theta=0) \; R_c(\varphi=0), \quad \tau=\pi/2 \\ \sin\chi = \sin\gamma, \quad \sin2\chi = \sin2\gamma, \quad \sin3\chi = \sin3\gamma \qquad \cos\chi = \cos\gamma, \quad \cos2\chi = -\cos2\gamma, \quad \cos3\chi = \cos3\gamma \\ \sin\varphi=0, \quad \sin2\varphi=0, \quad \sin3\varphi=0 \qquad \qquad \cos\varphi=1, \quad \cos2\varphi=1, \quad \cos3\varphi=1 \\ (\sin\gamma/-\sin\gamma), \quad (\sin2\gamma/-\sin2\gamma), \quad (\sin3\gamma/-\sin3\gamma) \quad pairs \end{split}$$

(隣り合う CH_2 基はともに $+\gamma$ または $-\gamma$ のどちらかを取り、互い違いにはならない。) により、

[対称伸縮振動]

(ppp)
$$\chi_{xxz} = (1/2)[\beta_{aac}(1 + \cos 2\chi) + \beta_{bbc}(1 - \cos 2\chi)]$$
$$\chi_{xzz} = \beta_{coc}$$

(spp)
$$\chi_{vxz} = -(1/2)(\beta_{aac} - \beta_{bbc})\sin 2\chi$$

$$(ssp) \qquad \chi_{yyz} = (1/2)[\left(\beta_{aac}(1 \text{ -} cos2\chi) + \beta_{bbc}(1 + cos2\chi)\right]$$

(psp)
$$\chi_{xyz} = -(1/2)(\beta_{aac} - \beta_{bbc})\sin 2\chi$$

- (sps) none
- (pps) none

[逆対称伸縮振動]

(ppp)
$$\chi_{zxx} = (1/2)\beta_{cas}(1 + \cos 2\chi)$$

 $\chi_{xzx} = (1/2)\beta_{cas}(1 + \cos 2\chi)$
(spp) $\chi_{xxy} = -(1/2)\beta_{xy}\sin 2\chi$

(spp)
$$\chi_{yzx} = -(1/2)\beta_{caa}\sin 2\chi$$

(ssp)

(psp)
$$\chi_{zvx} = -(1/2)\beta_{caa}\sin 2\chi$$

(sps)
$$\chi_{vzv} = (1/2)\beta_{caa}(1 - \cos 2\chi)$$

(pps)
$$\chi_{zxy} = -(1/2)\beta_{caa} \sin 2\chi$$
$$\chi_{xzy} = -(1/2)\beta_{caa} \sin 2\chi$$

(pss)
$$\chi_{zyy} = (1/2)\beta_{caa}(1 - \cos 2\chi)$$

CH 基のテンソル成分による表式に Td 角を仮定すると、(3-4) 式と (3-5) 式によりさらに整理される。

「対称伸縮振動]

$$\begin{split} \text{(ppp)} \qquad & \chi_{xxz} = (\sqrt{3} \ / 9 \) [\ (\beta_{\xi\xi\zeta} + 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta}) + (\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta}) \cos 2\chi] \\ \chi_{zzz} = (2\sqrt{3} \ / 9 \) (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta}) \end{split}$$

(spp)
$$\chi_{yxz} = -(\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\sin 2\chi$$

(ssp)
$$\chi_{yyz} = (\sqrt{3}/9)[(\beta_{\xi\xi\zeta} + 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta}) - (\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos 2\chi]$$

(psp)
$$\chi_{xyz} = -(\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\sin 2\chi$$

(sps) none

(pps) none

(pss) none

「逆対称伸縮振動]

$$\begin{array}{ll} \text{(ppp)} & \chi_{zxx} = -(\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(1 + \cos2\chi) \\ \chi_{xzx} = -(\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(1 + \cos2\chi) \end{array}$$

(spp)
$$\chi_{yzx} = (\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\beta_{cas}\sin 2\chi$$

(ssp)

(psp)
$$\chi_{\text{zyx}} = (\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin 2\chi$$

$$(sps) \qquad \chi_{yzy} = \text{-}(\sqrt{3} \ / 9 \) (\beta_{\xi\xi\zeta} \ \text{-} \ \beta_{\zeta\zeta\zeta}) (1 \ \text{-} \ cos2\chi)$$

(pps)
$$\chi_{zxy} = (\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin 2\chi$$
$$\chi_{xzy} = (\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin 2\chi$$

(pss)
$$\chi_{\text{zyy}} = -(\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(1 - \cos 2\chi)$$

5b. のけぞった CH, 基

分子面が xz 面から角 θ だけ $\pm y$ 軸方向にのけぞることで立体障害を解消しているときには、ファイル

「オイラー角」の (Eu-2a) 式により下しきが得られる。 α は HCH 結合角である。

$$R_z(\chi = -\pi/2) R_{b'}(-\theta) R_c(\phi = \pi/2)$$
、 $R_z(\chi = -\pi/2) R_{b'}(\theta) R_c(\phi = \pi/2)$ 、 $\tau = \pi/2 - \theta$ $\sin \chi = -1$ 、 $\sin 2\chi = 0$ 、 $\sin 3\chi = +1$ $\cos \chi = 0$ 、 $\cos 2\chi = -1$ 、 $\cos 3\chi = 0$ $\sin \phi = +1$ 、 $\sin 2\phi = 0$ 、 $\sin 3\phi = -1$ $\cos \phi = 0$ 、 $\cos 2\phi = -1$ 、 $\cos 3\phi = 0$ $\sin \theta = -(\pm)\cos \tau$ 、 $\cos \theta = \sin \tau$ (5b-1) $(\sin \theta / -\sin \theta)$ pair (隣り合う CH_2 基は交互に $+\theta$ と $-\theta$ をとる。)

により、

「対称伸縮振動]

$$\begin{aligned} (ppp) & \quad \chi_{xxz} = \beta_{aac} cos\theta \\ & \quad \chi_{zzz} = \beta_{bbc} (cos\theta - cos^3\theta) + \beta_{ccc} cos^3\theta \\ (spp) & \quad \chi_{yzz} = (\beta_{bbc} - \beta_{ccc}) (sin\theta - sin^3\theta) \\ (ssp) & \quad \chi_{yyz} = (\beta_{bbc} - \beta_{ccc}) cos^3\theta + \beta_{ccc} cos\theta \\ (psp) & \quad \chi_{zyz} = (\beta_{bbc} - \beta_{ccc}) (sin\theta - sin^3\theta) \\ (sps) & \quad \chi_{yzy} = -(\beta_{bbc} - \beta_{ccc}) (cos\theta - cos^3\theta) \\ (pps) & \quad \chi_{xxy} = -\beta_{aac} sin\theta \\ & \quad \chi_{zzy} = -(\beta_{bbc} - \beta_{ccc}) sin^3\theta - \beta_{ccc} sin\theta \\ (pss) & \quad \chi_{zyy} = -(\beta_{bbc} - \beta_{ccc}) (cos\theta - cos^3\theta) \\ (sss) & \quad \chi_{vyv} = -\beta_{bbc} sin\theta + (\beta_{bbc} - \beta_{ccc}) sin^3\theta \end{aligned}$$
 (5b-2)

[逆対称伸縮振動] (ppp)

 $\chi_{\rm zxx} = \beta_{\rm caa} \cos \theta$

 $\chi_{xzx} = \beta_{caa} cos\theta$

none

$$(spp) \qquad \chi_{yxx} = -\beta_{cas} sin\theta$$

$$(ssp) \qquad none$$

$$(psp) \qquad \chi_{xyx} = -\beta_{cas} sin\theta$$

$$(sps) \qquad none$$

$$(pps) \qquad none$$

$$(pss) \qquad none$$

$$(sss) \qquad none$$

CH 基のテンソル成分による表式に Td 角を仮定すると、(3-4) 式と(3-5) 式によりさらに整理される。

[対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{xxz} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta})cos\theta \\ & \chi_{zzz} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})cos^3\theta + 3\beta_{\eta\eta\zeta}cos\theta] \\ (spp) & \chi_{yzz} = -(2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(sin\theta - sin^3\theta) \\ (ssp) & \chi_{yyz} = (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(cos\theta - cos^3\theta) + 3\beta_{\eta\eta\zeta}cos\theta] \\ (psp) & \chi_{zyz} = -(2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(sin\theta - sin^3\theta) \\ (sps) & \chi_{yzy} = (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(cos\theta - cos^3\theta) \\ \end{array}$$

(pps)
$$\chi_{xxy} = -(2\sqrt{3}/9)(\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta})\sin\theta$$

 $\chi_{zzy} = -(2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta) + 3\beta_{\eta\eta\zeta}\sin\theta]$
(pss) $\chi_{zyy} = (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)$
(sss) $\chi_{vvy} = -(2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^3\theta + 3\beta_{\eta\eta\zeta}\sin\theta]$ (5b-4)

[逆対称伸縮振動]

(ppp)
$$\chi_{zxx} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\theta$$
$$\chi_{xzx} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\theta$$

(spp)
$$\chi_{yxx} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\theta$$

(ssp) none

(psp)
$$\chi_{xyx} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\theta$$

- (sps) none
- (pps) none
- (pss) none

5c. 横ざまにかしいだ CH₂基

分子面が xz 面内で角 θ だけ $\pm x$ 軸方向に横ざまにかしぐことで立体障害を解消しているとき、ファイル「オイラー角」の (Eu-2b) 式により下式が得られる。 α は HCH 結合角である。

$$\begin{split} R_z(\chi=\pi) \; R_{b}\cdot(\theta) \; R_c(\phi=\pi) & \text{ $\pm t$ it } \quad R_z(\chi=-\pi) \; R_{b}\cdot(-\theta) \; R_c(\phi=\pi), \quad \tau=\pi/2 \\ \sin\chi=0, & \sin2\chi=0, & \sin3\chi=0 & \cos\chi=-1, & \cos2\chi=+1, & \cos3\chi=-1 \\ \sin\phi=0, & \sin2\phi=0, & \sin3\phi=0 & \cos\phi=-1, & \cos2\phi=+1, & \cos3\phi=-1 \\ & \sin\theta=\pm\sin\theta, & \cos\theta=\cos\theta \end{split} \tag{5c-1}$$

either $\sin\theta$ /or - $\sin\theta$

(隣り合う CH_0 基は、交互に $+\theta$ または $-\theta$ のどちらかをとり、逆符号のものが隣り合わせにはならない。)

により、

[対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{xxx} = \beta_{aac}(sin\theta - sin^3\theta) + \beta_{coc}sin^3\theta \\ \chi_{xzz} = -(\beta_{aac} - \beta_{coc})(sin\theta - sin^3\theta) \\ \chi_{zxz} = -(\beta_{aac} - \beta_{coc})(sin\theta - sin^3\theta) \\ \chi_{zzx} = \beta_{aac}sin^3\theta + \beta_{coc}(sin\theta - sin^3\theta) \\ \chi_{xzx} = -(\beta_{aac} - \beta_{coc})(cos\theta - cos^3\theta) \\ \chi_{zxx} = -(\beta_{aac} - \beta_{coc})(cos\theta - cos^3\theta) \\ \chi_{xxz} = \beta_{aac}cos^3\theta + \beta_{coc}(cos\theta - cos^3\theta) \\ \chi_{zzz} = \beta_{aac}(cos\theta - cos^3\theta) + \beta_{coc}cos^3\theta \end{split}$$

(spp) none

$$\begin{aligned} (ssp) \qquad & \chi_{yyx} = \beta_{bbc} sin\theta \\ \chi_{yyz} &= \beta_{bbc} cos\theta \end{aligned}$$

(psp) none

(sps)
$$\chi_{yzy} = -(\beta_{aac} - \beta_{ccc})(\cos\theta - \cos^3\theta)$$

(pps) none

$$(pss) \qquad \chi_{zyy} = -(\beta_{aac} - \beta_{ccc})(cos\theta - cos^3\theta)$$

$$(sss) \quad none \qquad (5c-2)$$

[逆対称伸縮振動]

$$\begin{aligned} \text{(ppp)} \qquad \chi_{zxx} &= \beta_{caa} cos \theta \\ \chi_{xzx} &= \beta_{caa} cos \theta \end{aligned}$$

- (spp) none
- (ssp) none
- (psp) none
- (sps) $\chi_{yxy} = \beta_{caa} sin\theta$
- (pps) none
- (pss) $\chi_{xyy} = \beta_{caa} \sin \theta$

(sss) none (5c-3)

CH 基のテンソル成分による表式に Td 角を仮定すると、(3-4) 式と (3-5) 式によりさらに整理される。

[対称伸縮振動]

$$\begin{aligned} (\text{ppp}) \qquad & \chi_{xxx} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta) - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\sin\theta] \\ & \chi_{xzz} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta) \\ & \chi_{zxz} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta) \\ & \chi_{zzx} = (2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta) - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\sin\theta] \\ & \chi_{xzx} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta) \\ & \chi_{zxx} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta) \\ & \chi_{zxx} = (2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta) - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos\theta] \\ & \chi_{xzz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta) - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos\theta] \\ & \chi_{zzz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta) - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos\theta] \end{aligned}$$

(spp) none

(ssp)
$$\chi_{yyx} = (6\sqrt{3}/9)\beta_{\eta\eta\zeta}\sin\theta$$
$$\chi_{yyz} = (6\sqrt{3}/9)\beta_{\eta\eta\zeta}\cos\theta$$

(psp) none

$$(sps) \qquad \chi_{yzy} = (2\sqrt{3} \ / 9\) (\beta_{\xi\xi\zeta} \ \text{--} \ \beta_{\zeta\zeta\zeta}) (cos\theta \ \text{--} \ cos^3\theta)$$

(pps) none

(pss)
$$\chi_{\text{zyy}} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\cos\theta - \cos^3\theta)$$

[逆対称伸縮振動]

(ppp)
$$\begin{aligned} \chi_{zxx} &= -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\theta \\ \chi_{xzx} &= -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\theta \end{aligned}$$

- (spp) none
- (ssp) none
- (psp) none

(sps)
$$\chi_{yxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\theta$$

(pps) none

(pss)
$$\chi_{xyy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\theta$$

5d. z 軸まわりにねじれてからうしろにのけぞった CH, 基

分子面が z 軸まわりに γ だけねじれると同時に xz 面から角 θ だけ $\pm y$ 軸方向にのけぞっているとき、ファイル「オイラー角」の (Eu-3a) 式により下式が得られる。 α は HCH 結合角である。

$$\sin \chi = -1, \quad \sin 2\chi = 0, \quad \sin 3\chi = -1 \qquad \cos \chi = 0, \quad \cos 2\chi = -1, \quad \cos 3\chi = 0,$$

$$\sin \varphi = \cos \gamma = \cos \tau / \sin \theta, \qquad \sin 2\varphi = \sin 2\gamma = 2\cos \tau \quad \sqrt{\sin^2 \theta - \cos^2 \tau} / \sin^2 \theta,$$

$$\cos \varphi = \sin \gamma = \sqrt{\sin^2 \theta - \cos^2 \tau} / \sin \theta, \qquad \cos 2\varphi = -\cos 2\gamma = (\sin^2 \theta - 2\cos^2 \tau) / \sin^2 \theta,$$

$$1 + \cos 2\varphi = 1 - \cos 2\gamma = 2(\sin^2 \theta - \cos^2 \tau) / \sin^2 \theta, \qquad 1 - \cos \varphi = 1 + \cos 2\gamma = 2\cos^2 \tau / \sin^2 \theta$$

$$= \sinh \gamma + \sin 2\gamma, \quad -\sin 2\gamma, \quad -\cos 2\gamma = \cos^2 \tau / \sin^2 \theta,$$

(隣り合う CH, 基は同じく $+\gamma$ または $-\gamma$ のどちらかを取り、 θ の符号が交互に交代する。)

により、

「対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{xxx} = -(1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin12\varphi \\ & \chi_{xzz} = (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin12\varphi \\ & \chi_{xzz} = (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin12\varphi \\ & \chi_{xzz} = (1/2)[\beta_{ax}(1-\cos2\varphi) + \beta_{bbc}(1+\cos2\varphi)]\cos\theta \\ & \chi_{zzz} = (1/2)[\beta_{ax}(1-\cos2\varphi) + \beta_{bbc}(1+\cos2\varphi)](\cos\theta - \cos^3\theta) + \beta_{ccc}\cos^3\theta \\ & (spp) & \chi_{yxz} = (1/4)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta + (1/2)\beta_{ccc}\sin^3\theta - (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos2\varphi \\ & \chi_{yzz} = (1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\sin\theta - \sin^3\theta) - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{yxz} = (1/2)(\beta_{ax} - \beta_{bbc})\cos^2\theta\sin2\theta \\ & (spp) & \chi_{yyz} = (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\varphi \\ & \chi_{yyz} = (1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\cos^3\theta + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ & (psp) & \chi_{xyx} = (1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta + (1/2)\beta_{ccc}\sin^3\theta - (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos2\varphi \\ & \chi_{zyz} = (1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\sin\theta - \sin^3\theta) - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & (sps) & \chi_{yzy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ & (pps) & \chi_{xxy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ & (pps) & \chi_{xxy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zzy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{xyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - \beta_{ccc}(\sin\theta - \sin^3\theta) \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - (1/2)(\beta_{ax} + \beta_{bbc})\sin\theta - (1/2)\beta_{ccc}\sin^3\theta \\ & \chi_{zyy} = -(1/2)[\beta_{ax}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)]\sin^3\theta - (1/2)(\beta_{ax} + \beta_{bbc})\sin\theta - (1/2)\beta_{ccc}\sin^3\theta \\ \end{pmatrix}$$

[逆対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{xxx} = -\beta_{caa} sin\theta cos\theta sin2\varphi \\ & \chi_{zxx} = \beta_{caa} cos\theta \\ & \chi_{xzx} = \beta_{caa} cos\theta \\ (spp) & \chi_{yzz} = (1/2)\beta_{caa} (sin\theta - 2sin^3\theta)(1 + cos2\varphi) \\ (ssp) & none \\ (psp) & none \\ (sps) & \chi_{yxy} = (1/2)\beta_{caa} sin\theta cos\theta sin2\varphi \\ (pps) & none \\ (psp) & none \\$$

(sss) $\chi_{yyy} = -(1/2)\beta_{caa}[(\sin\theta - \sin^3\theta)(1 + \cos2\phi) + \sin\theta (1 - \cos2\phi)]$ (5d-3)

CH 基のテンソル成分による表式に Td 角を仮定すると、(3-4) 式と (3-5) 式によりさらに整理される。

 $\gamma_{xxx} = -(2\sqrt{3}/9)[(\beta_{EET} - 3\beta_{nnT} + 2\beta_{TTT})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}]\cos\theta$

「対称伸縮振動)

$$\chi_{xzz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}]\cos\theta$$

$$\chi_{zxz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}]\cos\theta$$

$$\chi_{zxz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta]\cos\theta$$

$$\chi_{zzz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta + 3\beta_{\eta\eta\xi}](\cos\theta - \cos^3\theta)$$

$$+ (2\beta_{\xi\xi\xi} + \beta_{\xi\xi\xi})\cos^3\theta$$
(spp)
$$\chi_{yxz} = (\sqrt{3}/9)[-(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})(1 + \cos^2\tau - 2\cos^2\tau/\sin^2\theta)$$

$$+ 3(\beta_{\xi\xi\xi} + \beta_{\xi\xi\xi})\sin^2\theta]\sin\theta$$

$$\chi_{yzz} = (2\sqrt{3}/9)[-(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$- (\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi})](\sin\theta - \sin^3\theta)]$$

$$\chi_{yxz} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}]\cos^2\theta/\sin\theta$$
(ssp)
$$\chi_{yyx} = (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}]\cos\theta$$

$$\chi_{yyz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$- (\beta_{\xi\xi\xi} + 2\beta_{\xi\xi\xi})]\cos^3\theta$$

$$- (2\beta_{\xi\xi\xi} + 2\beta_{\xi\xi\xi})(\cos\theta - \cos^3\theta)\}$$
(psp)
$$\chi_{xyz} = -(\sqrt{3}/9)[(\beta_{\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$- 3(\beta_{\xi\xi\xi} + \beta_{\xi\xi\xi})\sin\theta$$
(spo)
$$\chi_{yzy} = -(2\sqrt{3}/9)[(\beta_{\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$+ (\beta_{\xi\xi\xi} + 2\beta_{\xi\xi\xi})](\sin\theta - \sin^3\theta)$$
(spo)
$$\chi_{xyz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$+ (\beta_{\xi\xi\xi} + 2\beta_{\xi\xi\xi})](\sin\theta - \sin^3\theta)$$
(spo)
$$\chi_{xyz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$- 3(\beta_{\xi\xi\xi} + \beta_{\xi\xi\xi})](\sin\theta - \sin^3\theta)$$
(spo)
$$\chi_{xyz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\xi\xi\xi})\cos^2\tau/\sin^2\theta$$

$$- 3(\beta_{\xi\xi\xi} + \beta_{\xi\xi\xi})](\cos\theta - \cos^3\theta)$$

$$\begin{split} \chi_{zzy} &= (2\sqrt{3}/9)[(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\zeta\zeta\zeta})\cos^2\tau\sin\theta \\ &\quad + (\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta})\sin^3\theta \\ &\quad + (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta)] \\ (pss) \qquad \chi_{zyy} &= (2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos^2\tau/\sin^2\theta \\ &\quad - 3(\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})](\cos\theta - \cos^3\theta) \\ (sss) \qquad \chi_{yyy} &= -(\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(\sin\theta + \cos^2\tau\sin\theta) \\ &\quad + (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin^3\theta \\ &\quad + 6\beta_{\eta\eta'}\sin\theta] \end{split}$$

[逆対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{xxx} = (8\,\sqrt{3}\,/9\,)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\tau\sqrt{\sin^2\theta - \cos^2\tau}\,\cos\theta \\ \qquad & \chi_{zxx} = -(4\,\sqrt{3}\,/9\,)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\theta \\ \qquad & \chi_{xzx} = -(4\,\sqrt{3}\,/9\,9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\theta \\ (spp) \qquad & \chi_{yzz} = -(4\,\sqrt{3}\,/9\,)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(sin\theta - 2sin^3\tau)(1-cos^2\tau/sin^2\theta) \\ (ssp) \qquad & none \end{split}$$

- none (psp)

(sps)
$$\chi_{yxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}\cos\theta$$

(pps)

$$\chi_{xyy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sqrt{\sin^2\theta - \cos^2\tau}\cos\theta$$
(sss)
$$\chi_{vvy} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})[(\sin\theta - \sin^3\theta) + \cos^2\tau\sin\theta]$$
(5d-5)

5e. z 軸まわりにねじれてから横ざまにかしいだ CH₂ 基

分子面が z 軸まわりに γ だけねじれると同時に xz 面内で角 θ だけ $\pm x$ 軸方向に横ざまにかしいでいる とき、ファイル「オイラー角」の (Eu-3b) 式により下式が得られる。α は HCH 結合角である。

により、

[対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{xxx} = (1/2)[\beta_{aac}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\sin\theta-\sin^3\theta) + \beta_{ccc}\sin^3\theta \\ & \chi_{xzz} = -(1/2)[\beta_{aac}(1+\cos2\varphi) + \beta_{bbc}(1-\cos2\varphi)](\sin\theta-\sin^3\theta) + \beta_{ccc}(\sin\theta-\sin^3\theta) \end{split}$$

$$\begin{array}{lll} \chi_{xzz} = -(1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\sin\theta - \sin^3\theta) + \beta_{ccc}(\sin\theta - \sin^3\theta) \\ \chi_{zzx} = -(1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)]\sin^3\theta + \beta_{ccc}(\sin\theta - \sin^3\theta) \\ \chi_{xzx} = -(1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ \chi_{zxx} = -(1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ \chi_{xxz} = (1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ \chi_{zzz} = (1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\cos\theta - \cos^3\theta) + \beta_{ccc}(\cos\theta - \cos^3\theta) \\ \chi_{yzz} = (1/2)[\beta_{ax}(1+\cos2\phi) + \beta_{bbc}(1-\cos2\phi)](\cos\theta - \cos^3\theta) + \beta_{ccc}\cos^3\theta \\ (spp) & \chi_{yxx} = -(1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\phi \\ \chi_{yzz} = (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\phi \\ \chi_{yzz} = (1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\phi \\ \chi_{yyz} = (1/2)[\beta_{ax}(1-\cos2\phi) + \beta_{bbc}(1+\cos2\phi)]\sin\theta \\ \chi_{yyz} = (1/2)[\beta_{ax}(1-\cos2\phi) + \beta_{bbc}(1+\cos2\phi)]\sin\theta \\ \chi_{yyz} = (1/2)[\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\phi \\ \chi_{xyz} = -(1/2)(\beta_{ax} - \beta_{bbc})\sin\theta\cos\theta\sin2\phi \\ \chi_{xyz} = (1/2)(\beta_{ax} - \beta_{bbc})\cos\theta\sin2\phi \\ \chi_{xyz} = (1/2)(\beta_{ax} - \beta_{bbc})\cos\theta\sin2\phi \\ \chi_{xyz} = (1/2)(\beta_{ax} - \beta_{bb$$

「逆対称伸縮振動]

(ppp)
$$\chi_{xxx} = \beta_{caa}(\sin\theta - \sin^3\theta)(1 + \cos 2\phi)$$

 $\chi_{xzz} = -(1/2)\beta_{caa}(\sin\theta - \sin^3\theta)(1 + \cos 2\phi)$
 $\chi_{zxz} = -(1/2)\beta_{caa}(\sin\theta - \sin^3\theta)(1 + \cos 2\phi)$
 $\chi_{zxx} = -\beta_{caa}(\sin\theta - \sin^3\theta)(1 + \cos 2\phi)$
 $\chi_{zxx} = -(1/2)\beta_{caa}(\cos\theta - 2\cos^3\theta)(1 + \cos 2\phi)$
 $\chi_{xzz} = -(1/2)\beta_{caa}(\cos\theta - 2\cos^3\theta)(1 + \cos 2\phi)$
 $\chi_{xzz} = -\beta_{caa}(\cos\theta - \cos^3\theta)(1 + \cos 2\phi)$
 $\chi_{xzz} = \beta_{caa}(\cos\theta - \cos^3\theta)(1 + \cos 2\phi)$
(spp) $\chi_{yxz} = -(1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{yzz} = (1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{yzz} = (1/2)\beta_{caa}\sin^2\theta\sin2\phi$
(ssp) none
(psp) $\chi_{xyz} = -(1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{xyz} = (1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{xyz} = (1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
(ssp) $\chi_{xyz} = -(1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{xyz} = (1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
 $\chi_{xyz} = (1/2)\beta_{caa}\sin\theta\cos\theta\sin2\phi$
(sps) $\chi_{xyz} = -(1/2)\beta_{caa}\sin^2\theta\sin2\phi$
(sps) $\chi_{xyz} = -(1/2)\beta_{caa}\sin^2\theta\sin2\phi$
(sps) $\chi_{yxy} = (1/2)\beta_{caa}\cos^2\theta\sin2\phi$
(sps) $\chi_{yxy} = (1/2)\beta_{caa}\cos\theta(1 - \cos2\phi)$
 $\chi_{yzy} = (1/2)\beta_{caa}\cos\theta(1 - \cos2\phi)$
(pps) $\chi_{xxy} = -\beta_{caa}\sin\theta\cos\theta\sin2\phi$

$$\begin{split} \chi_{zxy} &= \beta_{cas} sin\theta cos\theta sin2\varphi \\ \chi_{zxy} &= (1/2)\beta_{cas} (1 - 2cos^2\theta) sin2\varphi \\ \chi_{xzy} &= (1/2)\beta_{cas} (1 - 2cos^2\theta) sin2\varphi \\ (pss) \qquad \chi_{xyy} &= (1/2)\beta_{cas} sin\theta (1 - cos2\varphi) \\ \chi_{zyy} &= (1/2)\beta_{cas} cos\theta (1 - cos2\varphi) \\ (sss) \qquad none \end{split}$$

CH 基のテンソル成分による表式に Td 角を仮定すると、(3-4) 式と(3-5) 式によりさらに整理される。

「対称伸縮振動]

(ppp)
$$\chi_{xxx} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + 3\beta_{\eta\eta\zeta}]\cos^2\theta + (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\theta\}\sin\theta$$
 $\chi_{xzz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin\theta\cos^2\theta$
 $\chi_{zxz} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin\theta\cos^2\theta$
 $\chi_{zzx} = -(2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + 3\beta_{\eta\eta\zeta}]\sin^2\theta - (2\beta_{\xi\xi\zeta} + \beta_{\zeta\zeta\zeta})\cos^2\theta\}\sin\theta$
 $\chi_{xzx} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) - (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin^2\theta\cos\theta$
 $\chi_{xxx} = -(2\sqrt{3}/9)[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) - (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin^2\theta\cos\theta$
 $\chi_{xxz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin^2\theta\cos\theta$
 $\chi_{xzz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin^2\theta\cos\theta$
 $\chi_{xzz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})]\sin^2\theta\cos\theta$
 $\chi_{xzz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\theta\}\cos\theta$
 $\chi_{xzz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\zeta\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\theta\}\cos\theta$
 $\chi_{xzz} = (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})(1 - \cos^2\tau/\sin^2\theta) + (2\beta_{\xi\zeta\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\theta\}\cos\theta$
 $\chi_{yxx} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos\tau\sqrt{1 - \cos^2\tau/\sin^2\theta}\cos\theta}$

$$\chi_{yxz} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos\tau\sqrt{1 - \cos^2\tau/\sin^2\theta}\cos^2\theta/\sin\theta$$

(ssp)
$$\begin{aligned} \chi_{yyx} &= (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos^2\tau/\sin^2\theta + 3\beta_{\eta\eta\zeta}]\sin\theta \\ \chi_{yyz} &= (2\sqrt{3}/9)\{[(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos^2\tau/\sin^2\theta + 3\beta_{\eta\eta\zeta}]\cos\theta \end{aligned}$$

$$(psp) \qquad \chi_{xyx} = (2\sqrt{3}/9)(\beta_{\xi\xi\xi} - 3\beta_{\eta\eta\xi} + 2\beta_{\zeta\zeta\zeta})\cos\tau\sqrt{1-\cos^2\tau/\sin^2\theta}\,\cos\theta$$

$$\chi_{\rm zyz} = -(2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos\tau\sqrt{1-\cos^2\tau/\sin^2\theta}\cos\theta$$

$$\chi_{xyz} = (2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})\cos\tau\sqrt{1-\cos^2\tau/\sin^2\theta}\cos^2\theta/\sin\theta$$

$$\chi_{\rm zyx} = -(2\sqrt{3}/9)(\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta}) cos\tau \sqrt{1-cos^2\tau/\sin^2\theta} \, sin\theta$$

- (sps) none
- (pps) none
- (pss) none

$$(sss)$$
 none $(5e-4)$

[逆対称伸縮振動]

(ppp)
$$\begin{aligned} \chi_{xxx} &= -(8\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - \sin^3\theta)(1 - \cos^2\tau/\sin^2\theta) \\ \chi_{xzz} &= (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})(\sin\theta - 2\sin^3\theta)(1 - \cos^2\tau/\sin^2\theta) \end{aligned}$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\sin\theta - 2\sin^3\theta)(1 - \cos^2\tau / \sin^3\theta)$$

$$\chi_{xx} = (8\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\cos\theta - 2\cos^3\theta)(1 - \cos^2\tau / \sin^2\theta)$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\cos\theta - 2\cos^3\theta)(1 - \cos^2\tau / \sin^2\theta)$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\cos\theta - 2\cos^3\theta)(1 - \cos^2\tau / \sin^2\theta)$$

$$\chi_{xx} = (8\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\cos\theta - \cos^3\theta)(1 - \cos^2\tau / \sin^2\theta)$$

$$\chi_{xx} = (8\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) (\cos\theta - \cos^3\theta)(1 - \cos^2\tau / \sin^2\theta)$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{yxx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{yxx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$
(ssp) none

$$(psp) \quad \chi_{xyx} = (4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xyx} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xyx} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xyx} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$
(sps)
$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos^2\theta / \sin\theta$$
(sps)
$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\theta\cos^2\tau / \sin^2\theta}$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\theta\cos^2\tau / \sin^2\theta}$$
(sps)
$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\theta\cos^2\tau / \sin^2\theta}$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\theta\cos^2\tau / \sin^2\theta}$$
(sps)
$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\theta\cos^2\tau / \sin^2\theta}$$
(sps)
$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} \cos\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy} = -(4\sqrt{3}/9)(\beta_{\xi\xi\xi} - \beta_{\xi\xi\xi}) \cos\tau\sqrt{1 - \cos^2\tau} / \sin^2\theta} / \sin\theta$$

$$\chi_{xxy}$$

5f. ねじれと傾きの両方を持つ CH2 基

(sss)

分子軸が z 軸から角 $\pm \theta$ だけ倒れ、さらに分子面が表面と 2 面角 τ で傾くことで立体障害を解消しているときには、ファイル「オイラー角」の (Eu-3c) 式により下式がを得られる。 α は HCH 結合角である。

(5e-5)

 $R_z(\chi) R_{b'}(\theta) R_c(\phi), \quad R_z(\chi) R_{b'}(-\theta) R_c(\phi)$

$$\begin{split} \sin\chi &= \sin\chi^*, \quad \sin2\chi = -\sin2\chi^*, \quad \sin3\chi = \sin3\chi^* & \cos\chi = -\cos\chi^*, \quad \cos2c = +\cos2\chi^*, \quad \cos3\chi = -\cos3\chi^*, \\ \sin\varphi &= \sin\gamma = \cos\tau/\sin\theta, & \sin2\varphi = -\sin2\gamma = -2\cos\tau\sqrt{(\sin^2\theta - \cos^2\tau)/\sin^2\theta}, \\ \cos\varphi &= -\cos\gamma = -\sqrt{(\sin^2\theta - \cos^2\tau)/\sin\theta}, & \cos2\varphi = \cos2\gamma = (\sin^2\theta - 2\cos^2\tau)/\sin^2\theta, \\ 1 + \cos2\varphi &= 1 + \cos2\gamma = 2(\sin^2\theta - \cos^2\tau)/\sin^2\theta, & 1 - \cos2\varphi = 1 - \cos2\gamma = 2\cos^2\tau/\sin^2\theta & (5f-1) \\ \text{for either one of the } (+\gamma, +\theta) \text{ set, } (+\gamma, -\theta) \text{ set, } (-\gamma, +\theta) \text{ set, } \text{ or } (-\gamma, -\theta) \text{ set} \end{split}$$

(隣り合う CH_2 基は同じく $+\gamma$ または $-\gamma$ のどちらかを取り、 θ も同じ符号を取る。 χ^* の符号が交代する。)

により、

[対称伸縮振動]

 $\chi_{\rm vzz} = -(1/2)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\sin\theta - \sin^3\theta)\sin\chi^*$

```
-(1/2)(\beta_{ax} - \beta_{bbc})[(\sin\theta - \sin^3\theta)\sin\chi^*\cos 2\phi - \sin\theta\cos\theta\cos\chi^*\sin 2\phi]
                \chi_{\rm vzx} = -(1/4)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         -(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin 2\chi * \cos 2\phi - \sin^2\theta(1 + \cos 2\chi *)\sin 2\phi]
                 \chi_{yxz} = -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         + (1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta + \cos^3\theta)\sin2\chi * \cos2\varphi - 2\cos^2\theta\cos2\chi * \sin2\varphi]
                \chi_{yyx} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\cos\chi^*
(ssp)
                        -(1/8)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})\sin^3\theta(\cos\chi^* - \cos3\chi^*)
                         -(1/8)(\beta_{ax} - \beta_{bbc})\{[\sin\theta(3\cos\chi^* + \cos3\chi^*) - (\sin\theta - \sin^3\theta)(\cos\chi^* - \cos3\chi^*)]\cos2\phi\}
                                              + 2\sin\theta\cos\theta(\sin\chi^* + \sin3\chi^*)\sin2\phi
                 \chi_{\rm vyz} = (1/2)(\beta_{\rm aac} + \beta_{\rm bbc})\cos\theta
                         -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})(\cos\theta - \cos^3\theta)(1 - \cos2\chi^*)
                         -(1/4)(\beta_{aac} - \beta_{bbc})\{[(\cos\theta - \cos^3\theta) + (\cos\theta + \cos^3\theta)\cos 2\chi^*]\cos 2\phi + 2\cos^2\theta\sin 2\chi^*\sin 2\phi\}
                \chi_{xvx} = -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})\sin^3\theta(\sin\chi^* + \sin3\chi^*)
(psp)
                         +(1/8)(\beta_{aac} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\sin\chi^* + \sin3\chi^*)\cos2\phi - 2\sin\theta\cos\theta(\cos\chi^* + \cos3\chi^*)\sin2\phi]
                 \chi_{\rm zyz} = -(1/2)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\sin\theta - \sin^3\theta)\sin\chi^*
                         -(1/2)(\beta_{ax} - \beta_{bbc})[(\sin\theta - \sin^3\theta)\sin\chi^*\cos 2\phi - \sin\theta\cos\theta\cos\chi^*\sin 2\phi]
                \chi_{xvz} = -(1/4)(\beta_{ax} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         +(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta + \cos^3\theta)\sin2\chi \cos2\phi - 2\cos^2\theta\cos2\chi \sin2\phi]
                \chi_{\text{zvx}} = -(1/4)(\beta_{\text{ac}} + \beta_{\text{bbc}} - 2\beta_{\text{cc}})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         -(1/4)(\beta_{aac}-\beta_{bbc})[(cos\theta-cos^3\theta)sin2\chi*cos2\phi-sin^2\theta(1+cos2\chi*)sin2\phi]
                \chi_{yxy} = -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})\sin^3\theta(\cos\chi^* - \cos3\chi^*)
(sps)
                         + (1/8)(\beta_{aac} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\cos\chi^* - \cos3\chi^*)\cos2\phi + 2\sin\theta\cos\theta (\sin\chi^* - \sin3\chi^*)\sin2\phi]
                 \chi_{\rm vzv} = -(1/4)(\beta_{\rm aac} + \beta_{\rm bbc} - 2\beta_{\rm ccc})(\cos\theta - \cos^3\theta)(1 - \cos2\chi^*)
                         -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi^*)\cos2\phi - \sin^2\theta\sin2\chi^*\sin2\phi]
                \chi_{xxy} = (1/2)(\beta_{aac} + \beta_{bbc}) \sin q \sin \chi^*
(pps)
                         -(1/8)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})\sin^3\theta(\sin c^* + \sin 3\chi^*)
                         +(1/8)(\beta_{ax} - \beta_{bbc})\{[(\sin\theta - \sin^3\theta)(\sin c^* + \sin 3\chi^*) - \sin\theta(3\sin \chi^* - \sin 3\chi^*)\cos 2\phi]\}
                \chi_{zzy} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\sin\chi^*
                         -(1/2)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})(\sin\theta - \sin^3\theta)\sin\chi^*
                         + (1/2)(\beta_{aac} - \beta_{bbc})\sin^3\theta\sin\chi*\cos2\phi
                \chi_{xzy} = -(1/4)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin 2\chi \cos 2\phi + \sin^2\theta(1 - \cos 2\chi \sin 2\phi)]
                 \chi_{\text{zxy}} = -(1/4)(\beta_{\text{aac}} + \beta_{\text{bbc}} - 2\beta_{\text{ccc}})(\cos\theta - \cos^3\theta)\sin 2\chi^*
                         -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin 2\chi \cos 2\phi + \sin^2\theta(1 - \cos 2\chi \sin 2\phi)]
                \chi_{xyy} = -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})\sin^3\theta(\cos\chi^* - \cos3\chi^*)
(pss)
                         + (1/8)(\beta_{ax} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\cos\chi^* - \cos3\chi^*)\cos2\phi + 2\sin\theta\cos\theta (\sin\chi^* - \sin3\chi^*)\sin2\phi]
                \chi_{\text{zyy}} = -(1/4)(\beta_{\text{ax}} + \beta_{\text{bbc}} - 2\beta_{\text{cx}})(\cos\theta - \cos^3\theta)(1 - \cos2\chi^*)
                         -(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi^*)\cos2\phi - \sin^2\theta\sin2\chi^*\sin2\phi]
```

$$\begin{split} (sss) & \chi_{yyy} = (1/2)(\beta_{aac} + \beta_{bbc}) sin\theta sin\chi^* \\ & - (1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) sin^3\theta \; (3sin\chi^* - sin3\chi^*) \\ & - (1/8)(\beta_{aac} - \beta_{bbc}) \{ [sin\theta (sin\chi^* + sin3\chi^*) - (sin\theta - sin^3\theta) (3sin\chi^* - sin3\chi^*)] cos2\phi \\ & + 2sin\theta cos\theta \; (cos\chi^* - cos3\chi^*) sin2\phi \} \end{split}$$

「逆対称伸縮振動]

$$\begin{array}{ll} (pps) & \chi_{xxy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(1 + cos2\phi) - sin\theta(1 - cos2\phi)](sin\chi^* + sin3\chi^*) \\ & - 2sin\theta cos\theta \ (cos\chi^* + cos3\chi^*)sin2\phi \} \\ & \chi_{zzy} = -\beta_{cm} [(sin\theta - sin^3\theta)sin\chi^*(1 + cos2\phi) - sin\theta cos\theta cos\chi^*sin2\phi] \\ & \chi_{zxy} = -(1/4)\beta_{cm} \{ 2[(cos\theta - cos^3\theta)(1 + cos2\phi) - cos\theta cos2\phi]sin2\chi^* \\ & - [sin^2\theta + (1 - 3cos^2\theta)cos2\chi^*]sin2\phi \} \\ & \chi_{xzy} = -(1/4)\beta_{cm} \{ 2[(cos\theta - cos^3\theta)(1 + cos2\phi) - cos\theta cos2\phi]sin2\chi^* \\ & - [sin^2\theta + (1 - 3cos^2\theta)cos2\chi^*]sin2\phi \} \\ & (pss) & \chi_{xyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(cos\chi^* - cos3\chi^*)(1 + cos2\phi) + sin\theta(cos\chi^* + cos3\chi^*)(1 - cos2\phi)] \\ & - 2sin\theta cos\theta sin3\chi^*sin2\phi \} \\ & \chi_{zyy} = (1/4)\beta_{cm} \{ 2[cos\theta(1 - cos2\phi cos2\chi^*) - (cos\theta - cos^3\theta)(1 - cos2\chi^*)(1 + cos2\phi)] \\ & + (1 - 3cos^2\theta)sin2\chi^*sin2\phi \} \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi)] \\ & (sss) & \chi_{yyy} = (1/4)\beta_{cm} \{ [(sin\theta - sin^3\theta)(3sin\chi^* - sin3\chi^*)(1 + cos2\phi) + sin\theta(sin\chi^* + sin3\chi^*)(1 - cos2\phi) \} \\ \end{cases}$$

上の結果も、 $1 \pm \cos 2\phi$ と θ , τ を結びつける式及び CH 基のテンソル成分による表式に Td 角を仮定する と、(3-4) 式と (3-5) 式によりさらに整理されるが、あまり実りがなさそうなのでやめておく。

(5f-3)

 $-2\sin\theta\cos\theta(\cos\chi^* - \cos3\chi^*)\sin2\phi$

6. 実験室固定(XYZ)系におけるテンソル成分

光の光路にあわせて定義される実験室固定 (XYZ) 座標系におけるテンソル成分を導く。(XYZ) 座標系は表面固定 (xyz) 座標系を z 軸のまわりに角 χ だけ回転したものであるとして、ファイル「表面の回転」を参照している。

6a. 傾いた平面形 HCCH 基

「対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{XXX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau - \beta_{bbc}] sin t sin^3 \chi - \beta_{acc} sin t sin \chi cos^2 \chi \\ & \chi_{XZZ} = (\beta_{bbc} - \beta_{ccc}) sin t cos^2 t sin \chi \\ & \chi_{ZXZ} = (\beta_{bbc} - \beta_{ccc}) sin t cos^2 t sin \chi \\ & \chi_{ZXX} = -[(\beta_{bbc} - \beta_{ccc}) sin t cos^2 \tau + \beta_{ccc} sin t] sin \chi \\ & \chi_{ZXX} = -(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin^2 \chi \\ & \chi_{XZX} = -(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin^2 \chi \\ & \chi_{XXZ} = [(\beta_{bbc} - \beta_{ccc}) cos^2 \tau + \beta_{ccc}] cos t sin^2 \chi + \beta_{acc} cos t cos^2 \chi \\ & \chi_{ZZZ} = -[(\beta_{bbc} - \beta_{ccc}) cos^2 \tau - \beta_{bbc}] cos \tau \\ & (spp) & \chi_{YXX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & \chi_{YZZ} = (\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin \chi cos \chi \\ & \chi_{YZZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin \chi cos \chi \\ & \chi_{YXZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bcc})] cos t sin \chi cos \chi \\ & \chi_{YYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos^2 \chi - \beta_{acc} sin t sin \chi \\ & \chi_{YYZ} = [(\beta_{bbc} - \beta_{ccc}) cos^2 \tau + \beta_{ccc}] cos t sin^2 \chi + \beta_{acc} cos t cos^2 \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi \\ & (psp) & \chi_{XYX} = [(psp) + (psp) +$$

$$\begin{split} \chi_{ZYZ} &= (\beta_{bbc} - \beta_{ccc}) sintcos^2 t cos \chi \\ \chi_{XYZ} &= [(\beta_{bbc} - \beta_{ccc}) cos^2 \tau - (\beta_{aac} - \beta_{ccc})] cost sin \chi cos \chi \\ \chi_{ZYX} &= (\beta_{bbc} - \beta_{ccc}) sin^2 t cost sin \chi cos \chi \\ (sps) \qquad \chi_{YXY} &= [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{aac} - \beta_{bbc})] sint sin \chi cos^2 \chi \\ \chi_{YZY} &= -(\beta_{bbc} - \beta_{ccc}) sin^2 t cost cos^2 \chi \\ (pps) \qquad \chi_{XXY} &= [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{aac} - \beta_{bbc})] sint sin^2 \chi cos \chi - \beta_{aac} sint cos \chi \\ \chi_{ZZY} &= -[(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + \beta_{ccc}] sint cos \chi \\ \chi_{ZXY} &= -(\beta_{bbc} - \beta_{ccc}) sin^2 t cost sin \chi cos \chi \\ \chi_{XZY} &= -(\beta_{bbc} - \beta_{ccc}) sin^2 t cost sin \chi cos \chi \\ \chi_{XYY} &= [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{aac} - \beta_{bbc})] sint sin \chi cos^2 \chi \\ \chi_{ZYY} &= -(\beta_{bbc} - \beta_{ccc}) sin^2 t cost cos^2 \chi \\ (sss) \qquad \chi_{YYY} &= [(\beta_{bbc} - \beta_{ccc}) sin^2 t cost cos^2 \chi \\ (sss) \qquad \chi_{YYY} &= [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau - \beta_{bbc}] sin \tau cos^3 \chi - \beta_{aac} sin \tau sin^2 \chi cos \chi \end{aligned} \tag{6a-1}$$

「逆対称伸縮振動]

$$\begin{array}{ll} \text{(ppp)} & \chi_{XXX} = 0 \\ & \chi_{XZZ} = 0 \\ & \chi_{ZXZ} = 0 \\ & \chi_{ZXX} = 0 \\ & \chi_{ZXX} = \beta_{caa} costcos^2 \chi \\ & \chi_{XZX} = \beta_{caa} costcos^2 \chi \\ & \chi_{XXZ} = 0 \\ & \chi_{ZZZ} = 0 \end{array}$$

$$\begin{split} (spp) & \chi_{YXX} = 2\beta_{caa} sintsin^2 \chi cos \chi \\ \chi_{YZZ} &= 0 \\ \chi_{YZX} = -\beta_{caa} costsin \chi cos \chi \\ \chi_{YXZ} &= 0 \\ (ssp) & \chi_{YYX} = 2\beta_{caa} sintsin \chi cos^2 \chi \\ \chi_{YYZ} &= 0 \\ (psp) & \chi_{XYX} = 2\beta_{caa} sintsin^2 \chi cos \chi \\ \chi_{ZYZ} &= 0 \\ \chi_{ZYZ} &= 0 \\ \chi_{ZYZ} &= 0 \\ \chi_{ZYX} &= -\beta_{caa} costsin \chi cos \chi \end{split}$$

$$\begin{split} \chi_{YZY} &= \beta_{\text{caa}} \text{costsin}^2 \chi \\ (pps) &\quad \chi_{XXY} &= 2\beta_{\text{caa}} \text{sintsin}^2 \chi \text{cos} \chi \\ \chi_{ZZY} &= 0 \\ \chi_{ZXY} &= -\beta_{\text{caa}} \text{costsin} \chi \text{cos} \chi \\ \chi_{XZY} &= -\beta_{\text{caa}} \text{costsin} \chi \text{cos} \chi \end{split}$$

$$(pss) &\quad \chi_{XYY} &= 2\beta_{\text{caa}} \text{sintsin} \chi \text{cos}^2 \chi \end{split}$$

(sps)

 $\chi_{\rm YXY} = 2\beta_{\rm cas} {\rm sin} \tau {\rm sin} \chi {\rm cos}^2 \chi$

 $\chi_{\rm ZYY} = \beta_{\rm cas} {\rm cos} \tau {\rm sin}^2 \chi$ (sss) $\chi_{\rm YYY} = -2\beta_{\rm cas} {\rm sin} \tau {\rm sin}^2 \chi {\rm cos} \chi$

 $\chi_{YYY} = -2\beta_{caa}\sin\tau\sin^2\chi\cos\chi \tag{6a-2}$

(3-8) 式を使うと、

[対称伸縮振動]

(ppp)
$$\chi_{\text{XXX}} = -(4\sqrt{2}/27)\{[(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\tau - 9\beta_{\text{trig}}]\sin\sin^2\gamma + (8\beta_{\text{ESC}} + \beta_{\text{CCC}})\sin\sin\cos^2\gamma\}$$
 $\chi_{\text{CZZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\tau - 9\beta_{\text{trig}}]\sin\sin^2\gamma + (8\beta_{\text{ESC}} + \beta_{\text{CCC}})\sin\sin\sin\gamma\cos^2\gamma\}$
 $\chi_{\text{ZZZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\tau\cos^2\gamma$
 $\chi_{\text{ZZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\tau\cos^2\gamma$
 $\chi_{\text{ZZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\gamma\cos^2\gamma$
 $\chi_{\text{XZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\gamma\cos^2\gamma$
 $\chi_{\text{XZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\sin^2\gamma\cos^2\gamma$
 $\chi_{\text{XZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\cos^2\tau - (\beta_{\text{ESC}} + 8\beta_{\text{CCC}})]\cos\sin^2\gamma$
 $\chi_{\text{XZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{CCC}})\cos^2\tau - (\beta_{\text{ESC}} + 8\beta_{\text{CCC}})]\sin\sin^2\gamma$
(spp) $\chi_{\text{XZZ}} = (4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau - (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{CCC}})]\sin\sin\sin^2\gamma\cos\gamma$
 $\chi_{\text{YZZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau - (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}})]\sin\sin\sin^2\gamma\cos\gamma$
(spp) $\chi_{\text{YXZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau + (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\sin\sin\sin^2\gamma\cos\gamma$
 $\chi_{\text{YZZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau + (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\cos\sin\sin\gamma\cos\gamma$
(spp) $\chi_{\text{YYZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau + (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\cos\sin\sin\gamma\cos\gamma$
 $\chi_{\text{YYZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}}})\sin^2\tau + (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\cos\sin\sin\gamma\alpha\cos\gamma$
(pp) $\chi_{\text{YYZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau - (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\sin\sin\gamma\alpha\cos^2\gamma$
 $\chi_{\text{YZZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau - (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\sin\sin\gamma\alpha\cos\gamma$
(pp) $\chi_{\text{YYZ}} = -(4\sqrt{2}/27)(\beta_{\text{ESC}} - 9\beta_{\text{trig}} + 8\beta_{\text{ECC}})\sin^2\tau - (8\beta_{\text{ESC}} - 9\beta_{\text{trig}} + \beta_{\text{ECC}}})]\sin\sin\gamma\alpha\cos\gamma\alpha$
(pp) $\chi_{\text{YZZ}} = -(4\sqrt{2}/27)(\beta_{\text{$

[逆対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{XXX} = 0 \\ & \chi_{XZZ} = 0 \\ & \chi_{ZXZ} = 0 \\ & \chi_{ZZX} = 0 \\ & \chi_{ZXX} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costcos^2\chi \\ & \chi_{XZX} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costcos^2\chi \end{array}$$

$$\chi_{XXZ} = 0$$
$$\chi_{ZZZ} = 0$$

$$\begin{split} \text{(spp)} \qquad & \chi_{YXX} = \text{-(8}\,\sqrt{2}\,/\,27\,) (\beta_{\xi\xi\zeta} \,\text{-}\,\,\beta_{\zeta\zeta\zeta}) sintsin^2\chi cos\chi \\ \chi_{YZZ} &= 0 \\ \chi_{YZX} &= (4\,\sqrt{2}\,/\,27\,) (\beta_{\xi\xi\zeta} \,\text{-}\,\,\beta_{\zeta\zeta\zeta}) costsin\chi cos\chi \\ \chi_{YXZ} &= 0 \end{split}$$

(ssp)
$$\chi_{YYX} = -(8\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sintsin\chi cos^2\chi$$

$$\chi_{YYZ} = 0$$

$$\begin{array}{ll} (psp) & \chi_{XYX} = \text{-}(8\sqrt{2} \ / \ 27)(\beta_{\xi\xi\zeta} \ \text{-} \ \beta_{\zeta\zeta\zeta}) sintsin^2\chi cos\chi \\ & \chi_{ZYZ} = 0 \\ & \chi_{XYZ} = 0 \\ & \chi_{ZYX} = (4\sqrt{2} \ / \ 27)(\beta_{\xi\xi\zeta} \ \text{-} \ \beta_{\zeta\zeta\zeta}) costsin\chi cos\chi \end{array}$$

(sps)
$$\chi_{YXY} = -(8\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\tau\sin\chi\cos^2\chi$$
$$\chi_{YZY} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sin^2\chi$$

(pps)
$$\begin{split} \chi_{XXY} &= -(8\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sintsin^2\chi cos\chi \\ \chi_{ZZY} &= 0 \\ \chi_{ZXY} &= (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costsin\chi cos\chi \\ \chi_{XZY} &= (4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costsin\chi cos\chi \end{split}$$

(pss)
$$\chi_{XYY} = -(6\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \sin t \sin \chi \cos^2 \chi$$
$$\chi_{ZYY} = -(4\sqrt{2}/27)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \cos t \sin^2 \chi$$

(sss)
$$\chi_{\text{YYY}} = (8\sqrt{2}/27)(\beta_{\xi\xi\xi} - \beta_{\zeta\zeta\zeta})\sin\tau\sin^2\chi\cos\chi$$
 (6a-4)

6b. ねじれ形 HCCH 基

「対称伸縮振動]

$$\begin{split} \text{(ppp)} \qquad & \chi_{XXZ} = \beta_{aac} cos^2 \chi + \beta_{bbc} sin^2 \chi + 2\beta_{abc} sin\chi cos \chi \\ \chi_{ZZZ} = \beta_{ccc} \end{split}$$

(spp)
$$\chi_{YXZ} = -(\beta_{aac} - \beta_{bbc}) \sin \chi \cos \chi + \beta_{abc} (\cos^2 \chi - \sin^2 \chi)$$

(ssp)
$$\chi_{yyz} = \beta_{aac} \sin^2 \chi + \beta_{bbc} \cos^2 \chi - 2\beta_{abc} \sin \chi \cos \chi$$

(psp)
$$\chi_{XYZ} = -(\beta_{aac} - \beta_{bbc}) \sin \chi \cos \chi + \beta_{abc} (\cos^2 \chi - \sin^2 \chi)$$

(sps) none

(pps) none

(pss) none

(sss) none (6b-1)

[逆対称伸縮振動]

$$\begin{split} \text{(ppp)} \qquad & \chi_{ZXX} = \beta_{caa} cos^2 \chi + \beta_{cbb} sin^2 \chi + (\beta_{cab} + \beta_{bca}) sin\chi cos \chi \\ & \chi_{XZX} = \beta_{caa} cos^2 \chi + \beta_{cbb} sin^2 \chi + (\beta_{cab} + \beta_{bca}) sin\chi cos \chi \end{split}$$

(spp)
$$\chi_{YZX} = -(\beta_{caa} - \beta_{cbb}) \sin \chi \cos \chi + (\beta_{bca} \cos^2 \chi - \beta_{cab} \sin^2 \chi)$$

(ssp) none

(psp)
$$\chi_{ZYX} = -(\beta_{caa} - \beta_{cbb}) \sin \chi \cos \chi + (\beta_{bca} \cos^2 \chi - \beta_{cab} \sin^2 \chi)$$

(sps)
$$\chi_{YZY} = \beta_{caa} sin^2 \chi + \beta_{cbb} cos^2 \chi - (\beta_{cab} + \beta_{bca}) sin \chi cos \chi$$

$$\begin{split} \text{(pps)} \qquad \chi_{\text{ZXY}} &= \text{-}(\beta_{\text{caa}} - \beta_{\text{cbb}}) \text{sin}\chi \text{cos}\chi + (\beta_{\text{bca}} \text{cos}^2 \chi - \beta_{\text{cab}} \text{sin}^2 \chi) \\ \chi_{\text{XZY}} &= \text{-}(\beta_{\text{caa}} - \beta_{\text{cbb}}) \text{sin}\chi \text{cos}\chi + (\beta_{\text{bca}} \text{cos}^2 \chi - \beta_{\text{cab}} \text{sin}^2 \chi) \end{split}$$

(pss)
$$\chi_{ZYY} = \beta_{can} \sin^2 \chi + \beta_{cbb} \cos^2 \chi - (\beta_{cab} + \beta_{bca}) \sin \chi \cos \chi$$

$$\chi_{\text{YYY}} = 0 \tag{6b-2}$$

(3-16) 式 ~ (3-18) 式を使うと、

「対称伸縮振動]

(ppp)
$$\chi_{XXZ} = (4\sqrt{2}/27)\{(8\beta_{\xi\xi\xi} + \beta_{\eta\eta\xi})\cos^2\chi + [(\beta_{\xi\xi\xi} - 9\beta_{\eta\eta\xi} + 8\beta_{\zeta\zeta\xi})\sin^2(\tau/2) + 9\beta_{\eta\eta\xi}]\sin^2\chi \\ - 4\sqrt{2} (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin(\tau/2)\sin\chi\cos\chi\}\cos(\tau/2)$$

$$\chi_{ZZZ} = (4\sqrt{2}/27)[(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\cos^2(\tau/2) + 9\beta_{\eta\eta\zeta}]\cos(\tau/2)$$

$$\begin{split} (spp) \qquad \chi_{YXZ} &= -(4\sqrt{2}/27) \{ [(8\beta_{\xi\xi\zeta} - 8\beta_{\eta\eta\zeta}) - (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin^2(\tau/2)] \sin\chi \cos\chi \\ &- 2\sqrt{2} \ (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \sin(\tau/2) (\cos^2\chi - \sin^2\chi) \} \cos(\tau/2) \end{split}$$

$$\begin{split} (ssp) \qquad \chi_{YYZ} &= (4\sqrt{2}/27)\{(8\beta_{\xi\xi\zeta} + \beta_{\eta\eta\zeta})sin^2\chi + [(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})sin^2(\tau/2) + 9\beta_{\eta\eta\zeta}]cos^2\chi \\ &+ 4\sqrt{2} \quad (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})sin(\tau/2)sin\chi cos\chi\}cos(\tau/2) \end{split}$$

$$\begin{split} (psp) \qquad & \chi_{XYZ} = -(4\sqrt{2}/27) \{ [(8\beta_{\xi\xi\zeta} - 8\beta_{\eta\eta\zeta}) - (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin^2(\tau/2)] \sin\chi \cos\chi \\ & - 2\sqrt{2} \ \ (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \sin(\tau/2) (\cos^2\chi - \sin^2\chi) \} \cos(\tau/2) \end{split}$$

- (sps) none
- (pps) none
- (pss) none

「逆対称伸縮振動]

$$\begin{split} (ppp) \qquad & \chi_{ZXX} = (4\,\sqrt{2}\,/\,27) \{ -(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \cos^2\!\chi + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin^2\!(\tau/2) \sin^2\!\chi \\ & + [(\,\sqrt{2}\,/4) (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin(\tau/2) + \,\, \sqrt{2} \,\, (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})] \sin\!\chi\!\cos\!\chi \} \cos(\tau/2) \\ & \chi_{XZX} = (4\,\sqrt{2}\,/\,27) \{ -(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \cos^2\!\chi + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin^2\!(\tau/2) \sin^2\!\chi \\ & + [(\,\sqrt{2}\,/4) (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin(\tau/2) + \,\, \sqrt{2} \,\, (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})] \sin\!\chi\!\cos\!\chi \} \cos(\tau/2) \end{split}$$

$$\begin{aligned} \text{(spp)} \qquad & \chi_{YZX} = (4\sqrt{2}/27)\{ [(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin^2(\tau/2)] \sin\chi \cos\chi \\ & - [(\sqrt{2}/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) \sin(\tau/2) \cos^2\chi - \sqrt{2} (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \sin^2\chi] \} \cos(\tau/2) \end{aligned}$$

(ssp) none

$$\begin{split} (psp) \qquad \chi_{ZYX} &= (4\sqrt{2}/27)\{[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin^2(\tau/2)]\sin\chi\cos\chi \\ &- [(\sqrt{2}/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin(\tau/2)\cos^2\chi - \sqrt{2}(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin^2\chi]\}\cos(\tau/2) \end{split}$$

$$\begin{split} (sps) \qquad & \chi_{YZY} = (4\,\sqrt{2}\,/\,27) \{ -(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin^2\chi + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin^2(\tau/2) cos^2\chi \\ & - [(\,\sqrt{2}\,/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin(\tau/2) + \sqrt{2}\,\,(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})] sin\chi cos\chi \} cos(\tau/2) \end{split}$$

$$\begin{array}{ll} (pps) & \chi_{ZXY} = (4\sqrt{2}/27)\{[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \! + \! (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin^2(\tau/2)] sin\chi cos\chi \\ & - [(\sqrt{2}/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin(\tau/2) cos^2\chi - \sqrt{2} (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin^2\chi]\} cos(\tau/2) \\ \chi_{XZY} = (4\sqrt{2}/27)\{[(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) \! + \! (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin^2(\tau/2)] sin\chi cos\chi \\ & - [(\sqrt{2}/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta}) sin(\tau/2) cos^2\chi - \sqrt{2} (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sin^2\chi]\} cos(\tau/2) \\ \end{array}$$

$$\begin{aligned} \text{(pss)} \qquad & \chi_{ZYY} = (4\sqrt{2}/27)\{-(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin^2\!\chi + (\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin^2\!(\tau/2)\cos^2\!\chi \\ & - [(\sqrt{2}/4)(\beta_{\xi\xi\zeta} - 9\beta_{\eta\eta\zeta} + 8\beta_{\zeta\zeta\zeta})\sin(\tau/2) + \sqrt{2} - (\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})]\sin\chi\cos\chi\}\cos(\tau/2) \end{aligned}$$

6c. のけぞった CH, 基

分子固定座標で表したものは (6a-1) 式および (6a-2) 式と同じ方式になる。CH 固定テンソルで近似する段階で違いが出る。

[対称伸縮振動]

$$(ppp) \quad \chi_{CXX} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau - \beta_{bbc}] sin t sin^3 \chi - \beta_{acc} sin t sin \chi cos^2 \chi$$

$$\chi_{ZZZ} = (\beta_{bbc} - \beta_{ccc}) sin t cos^2 t sin \chi$$

$$\chi_{ZXZ} = (\beta_{bbc} - \beta_{ccc}) sin t cos^2 t sin \chi$$

$$\chi_{ZXZ} = -[(\beta_{bbc} - \beta_{ccc}) sin t cos^2 \tau + \beta_{ccc} sin \tau] sin \chi$$

$$\chi_{ZXX} = -(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin^2 \chi$$

$$\chi_{ZXZ} = -(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin^2 \chi$$

$$\chi_{ZXZ} = -(\beta_{bbc} - \beta_{ccc}) sin^2 t cos t sin^2 \chi$$

$$\chi_{ZXZ} = -[(\beta_{bbc} - \beta_{ccc}) cos^2 \tau + \beta_{bcc}] cos \tau$$

$$(spp) \quad \chi_{YXX} = (1/4)[(\beta_{bbc} - \beta_{ccc}) cos^2 \tau - \beta_{bbc}] cos \tau$$

$$\chi_{YZZ} = (\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{YZZ} = (\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{YXZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{YYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{YYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{YYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{YYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{ZYZ} = (\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin^2 \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZYZ} = [(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZZY} = -(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZZY} = -(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin t sin \chi cos \chi$$

$$\chi_{ZZY} = -(\beta_{bbc} - \beta_{ccc}) sin^2 \tau + (\beta_{acc} - \beta_{bbc})] sin$$

[逆対称伸縮振動]

$$\begin{array}{ll} \text{(ppp)} & \chi_{XXX} = 0 \\ & \chi_{XZZ} = 0 \\ & \chi_{ZXZ} = 0 \\ & \chi_{ZZX} = 0 \\ & \chi_{ZXX} = \beta_{\text{can}} \text{costcos}^2 \chi \\ & \chi_{XZX} = \beta_{\text{can}} \text{costcos}^2 \chi \\ & \chi_{XXZ} = 0 \end{array}$$

$$\chi_{ZZZ} = 0$$

$$\begin{split} (spp) & \chi_{YXX} = 2\beta_{caa} sintsin^2 \chi cos \chi \\ \chi_{YZZ} &= 0 \\ \chi_{YZX} = -\beta_{caa} costsin \chi cos \chi \\ \chi_{YXZ} &= 0 \\ (ssp) & \chi_{YYX} = 2\beta_{caa} sintsin \chi cos^2 \chi \end{split}$$

$$\begin{array}{ll} (psp) & \chi_{XYX} = 2\beta_{cas} sintsin^2 \chi cos \chi \\ & \chi_{ZYZ} = 0 \\ & \chi_{XYZ} = 0 \\ & \chi_{ZYX} = -\beta_{cas} cost sin \chi cos \chi \end{array}$$

$$\chi_{YXY} = 2\beta_{cm} sintsin\chi cos^2 \chi$$

$$\chi_{YZY} = \beta_{cm} cos\tau sin^2 \chi$$

$$\begin{array}{ll} (pps) & \chi_{XXY} = 2\beta_{caa} sin\tau sin^2 \chi cos \chi \\ & \chi_{ZZY} = 0 \\ & \chi_{ZXY} = -\beta_{caa} cos \tau sin \chi cos \chi \\ & \chi_{XZY} = -\beta_{caa} cos \tau sin \chi cos \chi \end{array}$$

$$\begin{split} \text{(pss)} \qquad & \chi_{XYY} = 2\beta_{\text{cas}}\text{sintsin}\chi\text{cos}^2\chi \\ & \chi_{ZYY} = \beta_{\text{cas}}\text{costsin}^2\chi \end{split}$$

$$\chi_{YYY} = -2\beta_{cas} \sin \tau \sin^2 \chi \cos \chi \tag{6c-2}$$

(3-4) 式と (3-5) 式を使うと、

「対称伸縮振動]

(ppp)
$$χ_{XXX} = (2\sqrt{3}/9) \{ [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ - 3β_{ηηξ}] sintsin^3χ - (β_{ξξξ} + 2β_{ζξξ}) sintsinχcos^2χ \}$$
 $χ_{XZZ} = (2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sintcos^2τ sinχ$
 $χ_{ZXZ} = (2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sintcos^2τ sinχ$
 $χ_{ZZX} = -(2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sinτcos^2τ + (2β_{ξξξ} + β_{ζξξ}) sinτ$
 $χ_{ZXX} = -(2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sin^2χ$
 $χ_{XZX} = -(2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sin^2χ$
 $χ_{XZX} = -(2\sqrt{3}/9) (2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sin^2χ$
 $χ_{XZX} = -(2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) cos^2τ + (2β_{ξξξ} + β_{ζξξ})] cosτ sin^2χ + (β_{ξξξ} + 2β_{ζξξ}) cosτ cos^2χ \}$
 $χ_{ZZZ} = -(2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sin^2χ cosχ$
 $χ_{YZZ} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sinχ cosχ$
 $χ_{YZZ} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sinχ cosχ$
 $χ_{YZZ} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ cosτ sinχ cosχ$
 $χ_{YYZ} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sinχ cosχ$
(ssp)
 $χ_{YYX} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sinχ cos^2χ$
 $- (β_{ξξξ} + 2β_{ζξξ}) sinτ sinχ \}$
 $χ_{YYX} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sinχ cos^2χ$
(psp)
 $χ_{XYX} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - β_{ζξξ})] cosτ sin^2χ + (β_{ξξξ} + 2β_{ζξξ}) cosτ cos^2χ \}$
(psp)
 $χ_{XYX} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sin^2χ cosχ$
 $χ_{XYX} = (2\sqrt{3}/9) [(2β_{ξξξ} - 3β_{ηηξ} + β_{ζξξ}) sin^2τ + (β_{ξξξ} - 3β_{ηηξ} + 2β_{ζξξ})] sinτ sin^2χ cosχ$

$$\chi_{XYZ} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\cos^2\tau - (\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})]\cos\tau\sin\chi\cos\chi$$

$$\chi_{ZYX} = (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\sin\chi\cos\chi$$
(sps)
$$\chi_{YXY} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau + (\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})]\sin\tau\sin\chi\cos^2\chi$$

$$\chi_{YZY} = -(2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\cos^2\chi$$
(pps)
$$\chi_{XXY} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau + (\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + 2\beta_{\zeta\zeta\zeta})]\sin\tau\sin^2\chi\cos\chi$$

$$- (\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta})\sin\tau\cos\chi\}$$

$$\chi_{ZZY} = -(2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau + (2\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})]\sin\tau\cos\chi$$

$$\chi_{ZXY} = -(2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\sin\chi\cos\chi$$
(pss)
$$\chi_{XYY} = (2\sqrt{3}/9)(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\sin\chi\cos\chi$$
(pss)
$$\chi_{XYY} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\sin\chi\cos\chi$$
(sss)
$$\chi_{YYY} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\cos^2\chi$$
(sss)
$$\chi_{YYY} = (2\sqrt{3}/9)[(2\beta_{\xi\xi\zeta} - 3\beta_{\eta\eta\zeta} + \beta_{\zeta\zeta\zeta})\sin^2\tau\cos\tau\cos^2\chi - [(\beta_{\xi\xi\zeta} + 2\beta_{\zeta\zeta\zeta})\sin\tau\sin^2\chi\cos\chi]$$

[逆対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{XXX} = 0 \\ & \chi_{XZZ} = 0 \\ & \chi_{ZXZ} = 0 \\ & \chi_{ZXX} = 0 \\ & \chi_{ZXX} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costcos^2\chi \\ & \chi_{XZX} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) costcos^2\chi \\ & \chi_{XXZ} = 0 \\ & \chi_{ZZZ} = 0 \end{array}$$

(spp)
$$\begin{split} \chi_{YXX} &= \text{-}(8\,\sqrt{3}\,/9\,)(\beta_{\xi\xi\zeta}\,\text{-}\,\beta_{\zeta\zeta\zeta})\text{sintsin}^2\chi\text{cos}\chi\\ \chi_{YZZ} &= 0\\ \chi_{YZX} &= (4\,\sqrt{3}\,/9\,)(\beta_{\xi\xi\zeta}\,\text{-}\,\beta_{\zeta\zeta\zeta})\text{costsin}\chi\text{cos}\chi\\ \chi_{YXZ} &= 0 \end{split}$$

$$(ssp) \qquad \chi_{YYX} = -(8\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta}) sintsin\chi cos^2\chi$$

$$\chi_{YYZ} = 0$$

$$\begin{array}{ll} (psp) & \chi_{xyx} = -(8\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})sintsin^2\chi cos\chi \\ & \chi_{zyz} = 0 \\ & \chi_{xyz} = 0 \\ & \chi_{zyx} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})costsin\chi cos\chi \end{array}$$

(sps)
$$\chi_{YXY} = -(8\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\tau\sin\chi\cos^2\chi$$
$$\chi_{YZY} = -(4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sin^2\chi$$

(pps)
$$\chi_{XXY} = -(8\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\sin\tau\sin^2\chi\cos\chi$$
$$\chi_{ZZY} = 0$$
$$\chi_{ZXY} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sin\chi\cos\chi$$
$$\chi_{XZY} = (4\sqrt{3}/9)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})\cos\tau\sin\chi\cos\chi$$

$$\begin{array}{ll} (pss) & \chi_{XYY} = \text{-}(8\,\sqrt{\!\!\!/}3\,/9\,)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})sin\tau sin\chi cos^2\chi \\ & \chi_{ZYY} = \text{-}(4\,\sqrt{\!\!\!/}3\,/9\,)(\beta_{\xi\xi\zeta} - \beta_{\zeta\zeta\zeta})cos\tau sin^2\chi \end{array}$$

6d. z軸まわりにねじれてからうしろにのけぞった CH2 基

未着手である。

付録 A C(100) 面の dihydride および monohydride pair の SFG テンソル

分子固定 (abc) 系がオイラー角 (χ, θ, ϕ) によって空間固定 (XYZ) 系に重なるものとして、(XYZ) 系でのテンソル成分を求めると下のようになる。

CH₂ 基および平面 HCCH 基 (C_{2v} 対称)

[対称伸縮振動]

(ppp)
$$\chi_{XXX} = -(1/2)(\beta_{aac} + \beta_{abc})\sin \theta \cos xy + (1/8)(\beta_{aic} + \beta_{abc} - 2\beta_{ccc})\sin^3\theta(3\cos xy + \cos 3y) + (1/8)(\beta_{aic} + \beta_{abc})[\sin \theta(\cos xy - \cos 3y) - (\sin \theta - \sin^3\theta)(3\cos xy + \cos 3y)]\cos 2\phi + (1/8)(\beta_{aic} - \beta_{abc})[\sin \theta(\cos xy - \cos 3y) - (\sin \theta - \sin^3\theta)(3\cos xy + \cos 3y)]\cos 2\phi + 2\sin \theta \cos \theta(\sin xy + \sin^3\theta)\cos xy + (1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\sin \theta - \sin^3\theta)\cos xy + (1/2)(\beta_{aac} - \beta_{abc})[(\sin \theta - \sin^3\theta)\cos xy\cos 2\phi - \sin \theta \cos \theta\sin xy\sin 2\phi] \\ \chi_{ZXZ} = (1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\sin \theta - \sin^3\theta)\cos xy + (1/2)(\beta_{aac} - \beta_{abc})[(\sin \theta - \sin^3\theta)\cos xy\cos 2\phi - \sin \theta \cos \theta\sin xy\sin 2\phi] \\ \chi_{ZXZ} = (-1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\sin \theta - \sin^3\theta)\cos xy + (1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\sin \theta - \sin^3\theta)\cos xy + (1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\sin \theta - \sin^3\theta)\cos xy + (1/2)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) \\ - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) \\ - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos 2y) - (1/4)(\beta_{aac} + \beta_{abc} - 2\beta_{ccc})(\cos \theta - \cos^3\theta)(1 + \cos^3\theta)\cos 2x + 2\sin \theta \cos \theta \cos x + \cos^3\theta \cos$$

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(ssp)
               \chi_{YYX} = -(1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\cos\chi
                          +\ (1/8)(\beta_{a\alpha}+\beta_{bbc}\ \text{-}\ 2\beta_{c\alpha})sin^3\theta(cos\chi\ \text{-}\ cos3\chi)
                          +(1/8)(\beta_{aac} - \beta_{bbc})\{[\sin\theta(3\cos\chi + \cos3\chi) - (\sin\theta - \sin^3\theta)(\cos\chi - \cos3\chi)]\cos2\phi\}
                                                                -2\sin\theta\cos\theta(\sin\chi+\sin3\chi)\sin2\phi
                \chi_{YYZ} = (1/2)(\beta_{aac} + \beta_{bbc})\cos\theta
                          -(1/4)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)
                          -(1/4)(\beta_{ax} - \beta_{bbc})\{[(\cos\theta - \cos^3\theta) + (\cos\theta + \cos^3\theta)\cos 2\chi]\cos 2\phi - 2\cos^2\theta\sin 2\chi\sin 2\phi\}
                \chi_{XYX} = -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{cac})\sin^3\theta(\sin\chi + \sin3\chi)
(psp)
                          + (1/8)(\beta_{aac} - \beta_{bbc})[(2sin\theta - sin^3\theta)(sin\chi + sin3\chi)cos2\phi + 2sin\theta cos\theta(cos\chi + cos3\chi)sin2\phi]
                \chi_{\rm ZYZ} = -(1/2)(\beta_{\rm aac} + \beta_{\rm bbc} - 2\beta_{\rm ccc})(\sin\theta - \sin^3\theta)\sin\chi
                          -\ (1/2)(\beta_{aac}\ -\ \beta_{bbc})[\ (sin\theta\ -\ sin^3\theta)sin\chi cos2\varphi\ +\ sin\theta cos\theta cos\chi sin2\varphi]
                \chi_{XYZ} = (1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta + \cos^3\theta)\sin2\chi\cos2\phi + 2\cos^2\theta\cos2\chi\sin2\phi]
                \chi_{\rm ZYX} = (1/4)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          +(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi + \sin^2\theta(1 + \cos2\chi)\sin2\phi]
                \chi_{\rm YXY} = (1/8)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})\sin^3\theta(\cos\chi - \cos3\chi)
(sps)
                          -(1/8)(\beta_{aac}-\beta_{bbc})[(2sin\theta-sin^3\theta)(cos\chi-cos3\chi)cos2\phi-2sin\theta cos\theta(sin\chi-sin3\chi)sin2\phi]
                \chi_{yzy} = -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{coc})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)
                          -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\cos2\phi + \sin^2\theta\sin2\chi\sin2\phi]
                \chi_{XXY} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\sin\chi
(pps)
                          -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})\sin^3\theta(\sin\chi + \sin3\chi)
                          + \, (1/8)(\beta_{aac} - \beta_{bbc}) \{ [(sin\theta - sin^3\theta)(sin\chi + sin3\chi) - sin\theta(3sin\chi - sin3\chi)cos2\varphi]
                \chi_{ZZY} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\sin\chi
                          -(1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})(\sin\theta - \sin^3\theta)\sin\chi
                        + (1/2)(\beta_{ax} - \beta_{bbc})\sin^3\theta \sin\chi\cos 2\phi
                \chi_{XZY} = (1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          +(1/4)(\beta_{asc} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi - \sin^2\theta(1 - \cos2\chi)\sin2\phi]
                \chi_{\rm ZXY} = (1/4)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          +(1/4)(\beta_{asc} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi - \sin^2\theta(1 - \cos2\chi)\sin2\phi]
                \chi_{XYY} = (1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})\sin^3\theta(\cos\chi - \cos3\chi)
(pss)
                          -(1/8)(\beta_{aac}-\beta_{bbc})[(2sin\theta-sin^3\theta)(cos\chi-cos3\chi)cos2\phi-2sin\theta cos\theta(sin\chi-sin3\chi)sin2\phi]
                \chi_{\text{ZYY}} = -(1/4)(\beta_{\text{ax}} + \beta_{\text{bbc}} - 2\beta_{\text{cx}})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)
                          -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\cos2\phi + \sin^2\theta\sin2\chi\sin2\phi]
                \chi_{YYY} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\sin\chi
(sss)
                          -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{coc})\sin^3\theta(3\sin\chi - \sin3\chi)
                          -(1/8)(\beta_{ax}-\beta_{bbc})\{[\sin\theta(\sin\chi+\sin3\chi)-(\sin\theta-\sin^3\theta)(3\sin\chi-\sin3\chi)]\cos2\phi\}
                                                                -2\sin\theta\cos\theta(\cos\chi-\cos3\chi)\sin2\phi
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「逆対称伸縮振動 ]
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$$\begin{aligned} & (\text{ppp}) \quad \chi_{\text{XXX}} = -(14)\beta_{\text{km}} [[(\sin\theta - \sin^3\theta)(3\cos\chi + \cos3\chi)(1 + \cos2\phi) + \sin\theta(\cos\chi - \cos3\chi)(1 - \cos2\phi)] \\ & - 2\sin\theta\cos(\sin\chi + \sin3\chi)\sin2\phi] \\ & \chi_{\text{XZZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - 2\sin^3\theta)\cos\chi(1 + \cos2\phi) - \sin\theta\cos\theta\sin\chi\sin2\phi] \\ & \chi_{\text{XZZ}} = \beta_{\text{km}} [(\sin\theta - \sin^3\theta)\cos\chi(1 + \cos2\phi) - \sin\theta\cos\theta\sin\chi\sin2\phi] \\ & \chi_{\text{XZZ}} = \beta_{\text{km}} [(\sin\theta - \sin^3\theta)\cos\chi(1 + \cos2\phi) - \sin\theta\cos\theta\sin\chi\sin2\phi] \\ & \chi_{\text{XZZ}} = (1/4)\beta_{\text{km}} [2[\cos\theta(1 + \cos2\phi\cos2\chi) - (\cos\theta - \cos^3\theta)(1 + \cos2\chi)(1 + \cos2\phi)] \\ & + (1 - 3\cos^3\theta)\sin2\chi\sin2\phi) \\ & \chi_{\text{XZZ}} = (1/4)\beta_{\text{km}} [2[\cos\theta(1 + \cos2\phi\cos2\chi) - (\cos\theta - \cos^3\theta)(1 + \cos2\chi)(1 + \cos2\phi)] \\ & + (1 - 3\cos^3\theta)\sin2\chi\sin2\phi] \\ & \chi_{\text{XZZ}} = (1/2)\beta_{\text{km}} [(\cos\theta - \cos^3\theta)(1 + \cos2\chi)(1 + \cos2\phi) - \sin^3\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{XZZ}} = (1/2)\beta_{\text{km}} [(\cos\theta - \cos^3\theta)(1 + \cos2\chi)(1 + \cos2\phi) + \sin^3\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YZZ}} = (1/2)\beta_{\text{km}} [(\cos\theta - \cos^3\theta)(1 + \cos2\phi) + \sin\theta(\sin\chi - \sin3\chi)(1 - \cos2\phi)] \\ & + 2\sin\theta\cos\theta\cos3\chi\sin2\phi] \\ & \chi_{\text{YZZ}} = (1/4)\beta_{\text{km}} [2[(\cos\theta - \cos^3\theta)(1 + \cos2\phi) - \cos\theta\cos2\phi]\sin2\chi + [- \sin^2\theta + (1 - 3\cos^2\theta)\cos2\chi]\sin2\phi] \\ & \chi_{\text{YZZ}} = (1/2)\beta_{\text{km}} [(\cos\theta - \cos^3\theta)(1 + \cos2\phi) + \sin^2\theta\cos2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\cos\theta - \cos^3\theta)(1 + \cos2\phi) + \sin^2\theta\cos2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)((1 + \cos2\phi) + \sin^2\theta\cos2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\sin\chi - \sin^3\chi)(1 + \cos2\phi) + \sin^2\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\sin\chi - \sin^3\chi)(1 + \cos2\phi) + \sin^2\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\sin\chi - \sin^3\chi)(1 + \cos2\phi) + \sin^2\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)(1 + \cos2\phi) + \sin^2\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/2)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\sin\chi - \sin^3\chi)(1 + \cos2\phi) + \sin^2\theta\sin2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos2\phi) + \sin^2\theta\cos2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos2\phi) + \sin^2\theta\cos2\chi\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos2\phi) + \sin^2\theta(\cos\chi + \cos^3\chi)(1 - \cos^2\theta)(1 - \cos^2\chi)(1 + \cos^2\theta)) \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos^2\theta)\sin2\chi + [\sin^3\theta + (1 - 3\cos^3\theta)\cos2\chi]\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos^2\theta)]\sin2\chi + [\sin^3\theta + (1 - 3\cos^3\theta)\cos2\chi]\sin2\phi] \\ & \chi_{\text{YYZ}} = (1/4)\beta_{\text{km}} [(\sin\theta - \sin^3\theta)(\cos\chi - \cos^3\chi)(1 + \cos^2\theta)]\sin2\chi + [\sin^3\theta +$$

$$\begin{split} &+2sin\theta cos\theta sin3\chi sin2\varphi\}\\ &\chi_{ZYY}=(1/4)\beta_{caa}\{2[cos\theta(1-cos2\varphi cos2\chi)-(cos\theta-cos^3\theta)(1-cos2\chi)(1+cos2\varphi)]\\ &-(1-3cos^2\theta)sin2\chi sin2\varphi\}\\ (sss) &\chi_{YYY}=(1/4)\beta_{caa}\{[(sin\theta-sin^3\theta)(3sin\chi-sin3\chi)(1+cos2\varphi)+sin\theta(sin\chi+sin3\chi)(1-cos2\varphi)]\\ &+2sin\theta cos\theta(cos\chi-cos3\chi)sin2\varphi\} \end{split}$$

ねじれ HCCH 基 (C2 対称)

[対称伸縮振動]

$$\begin{array}{ll} (ppp) & \chi_{XXX} = -(1/2)(\beta_{ax} + \beta_{bbc}) sin\theta cos \chi \\ & + (1/8)(\beta_{abc} + \beta_{bbc} - 2\beta_{ccc}) sin^3\theta (3cos \chi + cos 3\chi) \\ & + (1/8)(\beta_{abc} + \beta_{bbc} - 2\beta_{ccc}) sin^3\theta (3cos \chi + cos 3\chi) \\ & + (1/8)(\beta_{abc} + \beta_{bbc}) [sin\theta (cos \chi - cos 3\chi) - (sin\theta - sin^3\theta) (3cos \chi + cos 3\chi)] cos 2\phi \\ & + 2sin\theta cos \theta (sin\chi + sin 3\chi) sin 2\phi \\ & + (1/4)\beta_{abc} [sin\theta (cos \chi - cos 3\chi) - (sin\theta - sin^3\theta) (3cos \chi + cos 3\chi)] sin 2\phi \\ & - 2sin\theta cos \theta (sin\chi + sin 3\chi) cos 2\phi \} \\ \chi_{XZZ} = (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & + (1/2)(\beta_{aac} - \beta_{bbc}) ((sin\theta - sin^3\theta) cos \chi cos 2\phi - sin\theta cos \theta sin \chi sin 2\phi] \\ & + \beta_{abc} (sin\theta - sin^3\theta) cos \chi sin 2\phi + sin\theta cos \theta sin \chi cos 2\phi] \\ \chi_{ZXZ} = (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & + (1/2)(\beta_{aac} - \beta_{bbc}) (sin\theta - sin^3\theta) cos \chi cos 2\phi - sin\theta cos \theta sin \chi sin 2\phi] \\ & + \beta_{abc} (sin\theta - sin^3\theta) cos \chi sin 2\phi + sin\theta cos \theta sin \chi cos 2\phi] \\ \chi_{ZZZ} = -(1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & + (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & - (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & - (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) cos \chi \\ & - (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (sin\theta - sin^3\theta) (sin 2\chi) \\ & \chi_{ZZZ} = -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (cos\theta - cos^3\theta) (1 + cos 2\chi) \\ & - (1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (cos\theta - cos^3\theta) (1 + cos 2\chi) \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) (1 + cos 2\chi) cos 2\phi - sin^3\theta sin 2\chi sin 2\phi] \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) (1 + cos 2\chi) sin 2\phi + sin^3\theta sin 2\chi sin 2\phi] \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) (1 + cos 2\chi) sin 2\phi + sin^3\theta sin 2\chi sin 2\phi] \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) - (cos\theta + cos^3\theta) cos 2\chi] sin 2\phi - 2cos^2\theta sin 2\chi sin 2\phi] \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) - (cos\theta + cos^3\theta) cos 2\chi] sin 2\phi - 2cos^2\theta sin 2\chi sin 2\phi] \\ & - (1/2)\beta_{abc} [(cos\theta - cos^3\theta) - (cos\theta + cos^3\theta) cos 2\chi] sin 2\phi - 2cos^2\theta sin 2\chi sin 2\phi] \\ & - (1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) cos^3\theta - (cos\theta + cos^3\theta) cos 2\chi] sin 2\phi - 2cos^2\theta sin 2\chi sin 2\phi] \\ & - (1/$$

(spp)
$$\chi_{YXX} = -(1/8)(\beta_{ax} + \beta_{bbc} - 2\beta_{cx})\sin^3\theta(\sin\chi + \sin3\chi)$$

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+(1/8)(\beta_{aac} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\cos2\phi + 2\sin\theta\cos\theta(\cos\chi + \cos3\chi)\sin2\phi]
                          +(1/2)\beta_{abc}[2(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\sin2\phi - \sin\theta\cos\theta(\cos\chi + \cos3\chi)\cos2\phi]
                \chi_{YZZ} = -(1/2)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})(\sin\theta - \sin^3\theta)\sin\chi
                         -(1/2)(\beta_{aac} - \beta_{bbc})[(\sin\theta - \sin^3\theta)\sin\chi\cos 2\phi + \sin\theta\cos\theta\cos\chi\sin 2\phi]
                          - \beta_{abc}[(\sin\theta - \sin^3\theta)\sin\chi\sin2\phi - \sin\theta\cos\theta\cos\chi\cos2\phi]
                \chi_{YZX} = (1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          +(1/4)(\beta_{ac} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi + \sin^2\theta(1 + \cos2\chi)\sin2\phi]
                          +(1/2)\beta_{abc}[(\cos\theta - \cos^3\theta)\sin2\gamma\sin2\phi - \sin^2\theta(1 + \cos2\gamma)\cos2\phi]
                \chi_{\rm YXZ} = (1/4)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          -(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta + \cos^3\theta)\sin2\chi\cos2\phi + 2\cos^2\theta\cos2\chi\sin2\phi]
                          - (1/2)\beta_{abc}[(\cos\theta + \cos^3\theta)\sin2\chi\sin2\phi - 2\cos^2\theta\cos2\chi\cos2\phi]
               \chi_{YYX} = -(1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\cos\chi
(ssp)
                          +(1/8)(\beta_{aac}+\beta_{bbc}-2\beta_{ccc})\sin^3\theta(\cos\chi-\cos3\chi)
                          +(1/8)(\beta_{ax}-\beta_{bbc})\{[\sin\theta(3\cos\chi+\cos3\chi)-(\sin\theta-\sin^3\theta)(\cos\chi-\cos3\chi)]\cos2\phi\}
                                              -2\sin\theta\cos\theta(\sin\chi+\sin3\chi)\sin2\phi
                          + (1/4)\beta_{abc} \{ [4 \sin\theta \cos\chi - (2\sin\theta - \sin^3\theta)] \sin 2\phi + 2\sin\theta \cos\theta (\sin\chi + \sin3\chi) \cos 2\phi \}
                \chi_{\rm YYZ} = (1/2)(\beta_{\rm agc} + \beta_{\rm bbc})\cos\theta
                          -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)
                          -(1/4)(\beta_{soc} - \beta_{bbc})\{[(\cos\theta - \cos^3\theta) + (\cos\theta + \cos^3\theta)\cos 2\chi]\cos 2\phi - 2\cos^2\theta\sin 2\chi\sin 2\phi\}
                          -(1/2)\beta_{abc}\{[(\cos\theta - \cos^3\theta) + (\cos\theta + \cos^3\theta)\cos 2\chi]\sin 2\phi + \cos^2\theta\sin 2\chi\cos 2\phi\}
                \chi_{XYX} = -(1/8)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})\sin^3\theta(\sin\chi + \sin3\chi)
(psp)
                         +(1/8)(\beta_{aac} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\cos2\phi + 2\sin\theta\cos\theta(\cos\chi + \cos3\chi)\sin2\phi]
                          +(1/4)\beta_{abc}[(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\sin2\phi - 2\sin\theta\cos\theta(\cos\chi + \cos3\chi)\cos2\phi]
                \chi_{\rm ZYZ} = -(1/2)(\beta_{\rm aac} + \beta_{\rm bbc} - 2\beta_{\rm ccc})(\sin\theta - \sin^3\theta)\sin\chi
                          -(1/2)(\beta_{aac} - \beta_{bbc})[(\sin\theta - \sin^3\theta)\sin\chi\cos2\phi + \sin\theta\cos\theta\cos\chi\sin2\phi]
                          -\beta_{abc}[(\sin\theta - \sin^3\theta)\sin\chi\sin2\phi - \sin\theta\cos\theta\cos\chi\cos2\phi]
                \chi_{XYZ} = (1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          -(1/4)(\beta_{ax} - \beta_{bbc})[(\cos\theta + \cos^3\theta)\sin2\chi\cos2\phi + 2\cos^2\theta\cos2\chi\sin2\phi]
                          -(1/2)\beta_{abc}[(\cos\theta + \cos^3\theta)\sin2\gamma\sin2\phi - 2\cos^2\theta\cos2\gamma\cos2\phi]
                \chi_{\rm ZYX} = (1/4)(\beta_{\rm ac} + \beta_{\rm bbc} - 2\beta_{\rm cc})(\cos\theta - \cos^3\theta)\sin 2\chi
                          +(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi + \sin^2\theta(1 + \cos2\chi)\sin2\phi]
                          +(1/2)\beta_{abc}[(\cos\theta - \cos^3\theta)\sin2\chi\sin2\phi - \sin^2\theta(1 + \cos2\chi)\cos2\phi]
                \chi_{\rm YXY} = (1/8)(\beta_{\rm aac} + \beta_{\rm bbc} - 2\beta_{\rm cc})\sin^3\theta(\cos\chi - \cos3\chi)
(sps)
                          -(1/8)(\beta_{aac} - \beta_{bbc})[(2\sin\theta - \sin^3\theta)(\cos\chi - \cos3\chi)\cos2\phi - 2\sin\theta\cos\theta(\sin\chi - \sin3\chi)\sin2\phi]
                          -(1/4)\beta_{abc}[(2\sin\theta - \sin^3\theta)(\cos\chi - \cos3\chi)\sin2\phi + 2\sin\theta\cos\theta(\sin\chi + \sin3\chi)\cos2\phi]]
                \chi_{YZY} = -(1/4)(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)
                         -(1/4)(\beta_{aac} - \beta_{bbc})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\cos2\phi + \sin^2\theta\sin2\chi\sin2\phi]
                          -(1/2)\beta_{abc}[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\sin2\phi - \sin^2\theta\sin2\chi\cos2\phi]
(pps)
               \chi_{XXY} = (1/2)(\beta_{aac} + \beta_{bbc})\sin\theta\sin\chi
```

$$-(1/8)(β_{ax} + β_{bx} - 2β_{ax})\sin^{2}(siny + sin^{2}y) - sin^{2}(3siny - sin^{2}y)\cos 2\phi]$$

$$+(1/8)(β_{ax} - β_{ax})[[(sin\theta - sin^{2}\theta)(siny + sin^{2}y) - sin^{2}(3siny - sin^{2}y)\cos 2\phi]$$

$$+(1/4)β_{ax}[\{(2sin\theta - sin^{2}\theta)(siny + sin^{2}y) - 4sin^{2}cos^{2}y]\sin 2\phi]$$

$$+(1/2)(β_{ax} + β_{ax} - 2β_{ax})\sin 6yiny$$

$$-(1/2)(β_{ax} + β_{ax} - 2β_{ax})\sin 6yiny$$

$$-(1/2)(β_{ax} + β_{ax} - 2β_{ax})\sin 6yiny$$

$$+(1/2)(β_{ax} - β_{ax})\sin 6yiny\cos 2\phi$$

$$+ β_{ax}\sin^{2}\theta\sin y\sin 2\phi$$

$$2χ_{ZZY} = (1/4)(β_{ax} + β_{ax} - 2β_{ax})(cos\theta - cos^{2}\theta)\sin 2y$$

$$+(1/4)(β_{ax} + β_{ax}) - 2β_{ax})(cos\theta - cos^{2}\theta)\sin 2y$$

$$+(1/2)β_{ax}[(cos\theta - cos^{2}\theta)\sin 2y\cos 2\phi - sin^{2}\theta(1 - cos 2y)\cos 2\phi]$$
(pss)
$$2χ_{YYY} = (1/8)(β_{ax} + β_{ax} - 2β_{ax})\sin^{2}\theta(cosy - cos^{2}y)\cos 2\phi - 2sin^{2}\theta\cos \theta(siny - sin^{2}y)\sin 2\phi$$

$$-(1/8)(β_{ax} + β_{ax}) - 2β_{ax}(sin\theta - sin^{2}\theta)(cosy - cos^{2}y)\cos 2\phi - 2sin^{2}\theta\cos \theta(siny - sin^{2}y)\cos 2\phi]$$

$$2χ_{YYY} = (-1/4)(β_{ax} + β_{ax} - 2β_{ax})\sin^{2}\theta(cosy - cos^{2}y)\sin 2\phi + 2sin^{2}\theta\cos \theta(siny - sin^{2}y)\cos 2\phi]$$

$$2χ_{YYY} = (-1/4)(β_{ax} + β_{ax}) - 2β_{ax}(sin\theta - sin^{2}\theta)(cosy - cos^{2}y)\cos 2\phi - 2sin^{2}\theta\cos \theta(siny - sin^{2}y)\cos 2\phi]$$

$$2χ_{YYY} = (-1/4)(β_{ax} + β_{ax}) - 2β_{ax}(sin\theta - sin^{2}\theta)(cosy - cos^{2}y)\cos 2\phi + sin^{2}\theta\sin 2y\sin 2\phi]$$

$$-(1/8)(β_{ax} + β_{ax}) - 2β_{ax}(sin\theta - sin^{2}\theta)(siny - cos^{2}\theta)(siny - sin^{2}$$

+ $(\beta_{caa} - \beta_{cbb})[(\sin\theta - 2\sin^3\theta)\cos\chi\cos2\phi - \sin\theta\cos\theta\sin\chi\sin2\phi]]$ + $(\beta_{bca} + \beta_{cab})[(\sin\theta - 2\sin^3\theta)\cos\chi\sin2\phi + \sin\theta\cos\theta\sin\chi\cos2\phi]$

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+ (\beta_{bca} - \beta_{cab})sin\theta cos\theta sin\chi\}
                 \chi_{ZZX} = (\beta_{caa} + \beta_{cbb})(\sin\theta - \sin^3\theta)\cos\chi
                          + (\beta_{can} - \beta_{cbb})[(\sin\theta - \sin^3\theta)\cos\chi\cos2\phi - \sin\theta\cos\theta\sin\chi\sin2\phi]
                          +\ (\beta_{bca}+\beta_{cab})[(sin\theta-sin^3\theta)cos\chi sin2\varphi+sin\theta cos\theta sin\chi cos2\varphi]
                          - (β<sub>bca</sub> - β<sub>cab</sub>)sinθcosθsinχsin2φ
                 \chi_{ZXX} = (1/4)\{(\beta_{caa} + \beta_{cbb})[2cos\theta - (cos\theta - cos^3\theta)(1 + cos2\chi)]
                          + (\beta_{caa} - \beta_{cbb})[2cos\theta cos2\phi cos2\phi cos2\chi - (cos\theta - cos^3\theta)(1 + cos2\chi)cos2\phi + (1 - 3cos^2\theta)sin2\chi sin2\phi]
                          -(\beta_{bca} + \beta_{csb})[2(\cos\theta - \cos^3\theta) - \cos^3\theta\cos2\chi]\sin2\phi + (1 - 3\cos^2\theta)\cos2\phi\sin2\chi]
                          + (\beta_{bca} - \beta_{cab})\sin^2\theta\sin2\chi
                \chi_{XZX} = (1/4)\{(\beta_{caa} + \beta_{cbb})[2cos\theta - (cos\theta - cos^3\theta)(1 + cos2\chi)]
                          +\left(\beta_{\text{\tiny Caa}} - \beta_{\text{\tiny Cbb}}\right) [2cos\theta\cos2\phi\cos2\chi - (cos\theta - cos^3\theta)(1 + cos2\chi)\cos2\varphi + (1 - 3cos^2\theta)\sin2\chi\sin2\varphi]
                          -(\beta_{bca}+\beta_{cab})[2(cos\theta-cos^3\theta)-cos^3\theta cos2\chi]sin2\varphi+(1-3cos^2\theta)cos2\varphi sin2\chi]
                          + (\beta_{bca} - \beta_{cab})\sin^2\theta\sin2\chi
                 \chi_{XXZ} = -(1/2)\{(\beta_{cso} + \beta_{cbb})(\cos\theta - \cos^3\theta)(1 + \cos2\chi)\}
                          + (\beta_{caa} - \beta_{cbb})[(\cos\theta - \cos^3\theta)(1 + \cos2\chi)\cos2\phi - \sin^2\theta\sin2\chi\sin2\phi]
                          +(\beta_{bca}+\beta_{cab})[(\cos\theta-\cos^3\theta)(1+\cos2\chi)\sin2\phi+\sin^2\theta\sin2\chi\cos2\phi]
                          + (\beta_{bca} - \beta_{cab})\sin^2\theta\sin2\chi
                 \chi_{ZZZ} = (\beta_{caa} + \beta_{cbb})(cos\theta - cos^3\theta)
                          + (\beta_{caa} - \beta_{cbb})(\cos\theta - \cos^3\theta)\cos 2\phi
                          + (\beta_{bca} + \beta_{cab})(\cos\theta - \cos^3\theta)\sin 2\phi
                \chi_{\rm YXX} = (1/4)\{(\beta_{\rm can} + \beta_{\rm cbb})[2\sin\theta\sin\chi - \sin^3\theta(\sin\chi + \sin3\chi)]
(spp)
                          +(\beta_{caa} - \beta_{cbb})[(2\sin\theta\sin3\chi - \sin^3\theta(\sin\chi + \sin3\chi))\cos2\phi + 2\sin\theta\cos\theta\cos3\chi\sin2\phi]
                          -(\beta_{bca} + \beta_{cab})[\sin\theta(\sin\chi - \sin3\chi)\sin2\phi + 2\sin\theta\cos\theta\cos3\chi\cos2\phi]
                          -(\beta_{bca} - \beta_{cab})[(\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\sin2\phi + 2\sin\theta\cos\theta\cos\chi\cos2\phi]\}
                 \chi_{YZZ} = -(1/2) \{ (\beta_{can} + \beta_{cbb}) (\sin\theta - 2\sin^3\theta) \sin\chi \}
                          + (\beta_{caa} - \beta_{cbb})[(\sin\theta - 2\sin^3\theta)\cos 2\phi + \sin\theta\cos\theta\cos\chi\sin 2\phi]
                          + (\beta_{bca} + \beta_{cab})[(\sin\theta - 2\sin^3\theta)\sin2\chi\sin2\phi - \sin\theta\cos\theta\cos\chi\cos2\phi]
                          - (\beta_{bca} - \beta_{cab})\sin\theta\cos\theta\cos\chi
                 \chi_{YZX} = (1/4)\{(\beta_{caa} + \beta_{cbb})[2(\cos\theta - \cos^3\theta)\sin 2\chi]\}
                          + (\beta_{con} - \beta_{cbb})[-2\cos^3\theta\sin2\chi\cos2\phi - (\sin^2\theta - (1 - 3\cos^2\theta)\cos2\chi)\sin2\phi]
                          + (\beta_{bca} + \beta_{csb})[2\cos^3\theta \cos 2\phi \sin 2\chi \cos 2\phi - \sin^2\theta(1 - \cos 2\chi) + 2\cos^2\theta]
                          + (\beta_{bca} - \beta_{cab})[\sin^2\theta(1 - \cos 2\chi) + 2\cos^2\theta\cos 2\chi]\cos 2\phi
                \chi_{YXZ} = (1/2)\{(\beta_{caa} + \beta_{cbb})(\cos\theta - \cos^3\theta)\sin 2\chi
                          + (\beta_{caa} - \beta_{cbb})[(\cos\theta - \cos^3\theta)\cos2\chi\sin2\phi + \sin^2\theta\sin2\chi\cos2\phi]
                          + (\beta_{bca} + \beta_{cab})[(cos\theta - cos^3\theta)sin2\chi sin2\varphi - sin^2\theta cos2\chi cos2\varphi]
                          - (\beta_{bca} - \beta_{cab})\sin^2\theta\cos 2\chi
                \chi_{YYX} = (1/4)\{(\beta_{caa} + \beta_{cbb})\sin^3\theta(\cos\chi - \cos3\chi)\}
(ssp)
                          +\left(\beta_{\rm caa}-\beta_{\rm cbb}\right)\left[-(2sin\theta-sin^3\theta)(cos\chi-cos3\chi)cos2\varphi+2sin\theta cos\theta(sin\chi-sin3\chi)sin2\varphi\right]
                          - (\beta_{bca} + \beta_{cab})(2sin\theta - sin^3\theta)(cos\chi - cos3\chi)sin2\phi
                          + (\beta_{bca} - \beta_{cab})[2\sin 2\theta(\sin \chi + \sin 3\chi)\cos 2\phi]
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\chi_{YYZ} = -(1/2)\{(\beta_{caa} + \beta_{cbb})(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\}
                          + (\beta_{con} - \beta_{cbb})[(\cos\theta - \cos^3\theta)(1 - \cos2\chi)\cos2\phi + \sin^2\theta\sin2\chi\sin2\phi]
                          +(\beta_{bca}+\beta_{cab})[(\cos\theta-\cos^3\theta)(1-\cos2\chi)\sin2\phi-\sin^2\theta\sin2\chi\cos2\phi]
                          - (\beta_{bca} - \beta_{cab})\sin^2\theta\sin 2\chi
(psp)
                \chi_{XYX} = (1/4)\{(\beta_{can} + \beta_{cbb})[2\sin\theta\sin\chi - \sin^3\theta(\sin\chi + \sin3\chi)]
                          +(\beta_{caa} - \beta_{cbb})[(-2\sin\theta\sin3\chi + \sin^3\theta(\sin\chi + \sin3\chi))\cos2\phi + 2\sin\theta\cos\theta\cos3\chi\sin2\phi]
                          -(\beta_{bca} + \beta_{csb})[(2\sin\theta\sin\chi - (2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi))\sin2\phi + 2\sin\theta\cos\theta\cos3\chi\cos2\phi]
                          -(\beta_{bca} - \beta_{cab})[2\sin\theta\cos\theta\cos\chi]
                 \chi_{\rm ZYZ} = -(1/2) \{ (\beta_{\rm caa} + \beta_{\rm cbb}) (\sin\theta - 2\sin^3\theta) \sin\chi
                          + (\beta_{caa} - \beta_{cbb})[(\sin\theta - 2\sin^3\theta)\sin\chi\cos2\phi + \sin\theta\cos\theta\cos\chi\sin2\phi]
                          + (\beta_{bca} + \beta_{cab})[(sin\theta - 2sin^3\theta)sin\chi sin2\varphi - sin\theta cos\theta cos\chi cos2\varphi]
                          - (\beta_{bca} - \beta_{cab})\sin\theta\cos\theta\cos\chi
                \chi_{XYZ} = (1/2)\{(\beta_{can} + \beta_{cbb})(\cos\theta - \cos^3\theta)\sin 2\chi
                          + (\beta_{caa} - \beta_{cbb})[(\cos\theta - \cos^3\theta)\sin2\chi\cos2\phi + \sin^2\theta\cos2\chi\sin2\phi]
                          +(\beta_{bca}+\beta_{cab})[(\cos\theta-\cos^3\theta)\sin2\chi\sin2\phi-\sin^2\theta\cos2\chi\cos2\phi]
                          - (\beta_{bca} - \beta_{cab})\sin^2\theta\cos 2\chi
                 \chi_{\text{ZYX}} = (1/4)\{(\beta_{\text{CM}} + \beta_{\text{cbb}})[2(\cos\theta - \cos^3\theta)\sin 2\chi]\}
                          +(\beta_{caa} - \beta_{cbb})[-2\cos^3\theta\sin2\chi\cos2\phi + (-\sin^2\theta + (1 - 3\cos^2\theta)\cos2\chi)\sin2\phi]
                          + (\beta_{bca} + \beta_{cab})[2cos^3\theta sin2\chi sin2\varphi - sin^2\theta (1 - cos2\chi) + 2cos^2\theta]
                \chi_{\rm YXY} = -(1/4) \{ (\beta_{\rm caa} + \beta_{\rm cbb}) [2\sin\theta\cos\chi - \sin^3\theta(\cos\chi - \cos3\chi)] \}
(sps)
                          +(\beta_{caa} - \beta_{cbb})[(-2\sin\theta\cos3\chi - \sin^3\theta(\cos\chi - \cos3\chi))\cos2\phi + 2\sin\theta\cos\theta\sin3\chi\sin2\phi]
                          -(\beta_{bca} + \beta_{cab})[(2\sin\theta\cos\chi - (2\sin\theta - \sin^3\theta)(\cos\chi - \cos3\chi))\sin2\phi - 2\sin\theta\cos\theta\sin3\chi\cos2\phi]
                          + (\beta_{bca} - \beta_{cab})[2sin\theta cos\theta sin\chi]
                 \chi_{YZY} = (1/4) \{ (\beta_{cap} + \beta_{cbb}) [2\cos\theta - 2(\cos\theta - \cos^3\theta)(1 - \cos2\chi)] \}
                          +\left(\beta_{caa}-\beta_{cbb}\right)\left[-2(cos\theta cos2\chi+(cos\theta-cos^3\theta)(1-cos2\chi))cos2\varphi-(1-3cos^2\theta)sin2\chi sin2\varphi\right]
                          - (\beta_{bca} + \beta_{cab})[2(\cos\theta - \cos^3\theta)\sin 2\phi - (1 - 3\cos^2\theta)\sin 2\chi\cos 2\phi]
                          -(\beta_{bca} - \beta_{csb})[-2\cos^3\theta\cos2\chi\sin2\phi + \sin^2\theta\sin2\chi\cos2\phi]
(pps)
                \chi_{XXY} = (1/4)\{(\beta_{caa} + \beta_{cbb})[-\sin^3\theta(\sin\chi + \sin3\chi)]
                          +(\beta_{caa} - \beta_{cbb})[(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\cos2\phi + 2\sin\theta\cos\theta(\cos\chi + \cos3\chi)\sin2\phi]
                          + (\beta_{bca} + \beta_{cab})[(2\sin\theta - \sin^3\theta)(\sin\chi + \sin3\chi)\sin2\phi]
                          + (\beta_{bca} - \beta_{cab})[2sin\theta cos\theta(cos\chi - cos3\chi)cos2\phi]
                 \chi_{ZZY} = \{ (\beta_{caa} + \beta_{cbb}) [-(\sin\theta - \sin^3\theta)\sin\chi] \}
                          + (\beta_{\text{ca}} - \beta_{\text{cbb}})[\text{-}(sin\theta - sin^3\theta)sin\chi cos2\phi - sin\theta cos\theta cos\chi sin2\phi]
                          +\ (\beta_{bca}+\beta_{cab})[\ -(sin\theta\ -\ sin^3\theta)sin\chi sin2\varphi\ +\ sin\theta cos\theta cos\chi cos2\varphi]
                         + (\beta_{bca} - \beta_{cab})\sin\theta\cos\theta\cos\chi
                 \chi_{\text{ZXY}} = (1/4)\{(\beta_{\text{caa}} + \beta_{\text{cbb}})[2(\cos\theta - \cos^3\theta)1\sin2\chi]
                          +(\beta_{con} - \beta_{cbb})[-2\cos^3\theta\sin2\chi\cos2\phi + (\sin^2\theta + (1 - 3\cos^2\theta)\cos2\chi)\sin2\phi]
                          +(\beta_{bca}+\beta_{cab})[-\sin^2\theta(1+\cos2\chi)\cos2\phi+2\cos^2\theta\cos2\chi\cos2\phi]
                          + (\beta_{bca} - \beta_{cab})[-2\cos^2\theta + 2\cos^3\theta\sin2\chi\sin2\phi + \sin^2\theta(1 + \cos2\chi)]
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\chi_{XZY} = (1/4)\{(\beta_{caa} + \beta_{cbb})[2(\cos\theta - \cos^3\theta)1\sin2\chi]
                           + (\beta_{caa} - \beta_{cbb})[-2\cos^3\theta\sin2\chi\cos2\phi + (\sin^2\theta + (1 - 3\cos^2\theta)\cos2\chi)\sin2\phi]
                          +(\beta_{bca}+\beta_{cab})[-sin^2\theta(1+cos2\chi)cos2\varphi+2cos^2\theta cos2\chi cos2\varphi]
                          + (\beta_{bca} - \beta_{cab})[-2\cos^2\theta + 2\cos^3\theta\sin2\chi\sin2\phi + \sin^2\theta (1 + \cos2\chi)]
                \chi_{xyy} = \text{-}(1/4) \left\{ (\beta_{\text{caa}} + \beta_{\text{cbb}}) [2 \text{sin}\theta \text{cos}\chi - \text{sin}^3\theta (\text{cos}\chi - \text{cos}3\chi)] \right.
(pss)
                          +(\beta_{caa} - \beta_{cbb})[-2\sin\theta\cos3\chi - \sin^3\theta(\cos\chi - \cos3\chi)\cos2\phi + 2\sin\theta\cos\theta\sin3\chi\sin2\phi]
                          -(\beta_{bca} + \beta_{cab})[(2sin\theta cos\chi - (2sin\theta - sin^3\theta)(cos\chi - cos3\chi))sin2\phi - 2sin\theta cos\theta sin3\chi cos2\phi]
                          + (\beta_{bca} - \beta_{cab})[2\sin\theta\cos\theta\sin\chi]
                \chi_{\text{ZYY}} = (1/4)\{(\beta_{\text{caa}} + \beta_{\text{cbb}})[2\cos\theta - 2(\cos\theta - \cos^3\theta)(1 - \cos2\chi)]
                          +(\beta_{caa}-\beta_{cbb})[-2(\cos\theta\cos2\chi+(\cos\theta-\cos^3\theta)(1-\cos2\chi))\cos2\phi-(1-3\cos^2\theta)\sin2\chi\sin2\phi]
                          -(\beta_{bca} + \beta_{cab})[2(\cos\theta - \cos^3\theta)\sin 2\phi - (1 - 3\cos^2\theta)\sin 2\chi\cos 2\phi]
                          - (\beta_{bca} - \beta_{cab})[-2cos^3\theta cos2\chi sin2\varphi + sin^2\theta sin2\chi cos2\varphi]\}
                \chi_{\rm YYY} = (1/4)\{(\beta_{\rm caa} + \beta_{\rm cbb})[(\sin\theta - \sin^3\theta)(3\sin\chi - \sin3\chi) + \sin\theta(\sin\chi + \sin3\chi)]
(sss)
                          + (\beta_{caa} - \beta_{cbb})[(2\sin\theta(\sin\chi - \sin3\chi) - \sin^3\theta(3\sin\chi - \sin3\chi))\cos2\phi]
                                               +2\sin\theta\cos\theta(\cos\chi-\cos3\chi)\sin2\phi]
                          +\ (\beta_{bca}+\beta_{cab})[4(sin\theta\text{ - }sin^3\theta)sin\chi\text{ - }(2sin\theta\text{ - }sin^3\theta)(sin\chi+sin3\chi)]sin2\varphi
                                               -2\sin\theta\cos\theta(\cos\chi-\cos3\chi)\cos2\phi]
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