On the Unique Determination of the Completely Reduced Representation of the Symmetry Group for Non-Rigid Molecules

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As already pointed out in [1–3], when studying the vibrations of non-rigid 1,4-di-X-butyne-2 molecules (X = F, Cl) belonging to the symmetry group $\boldsymbol{G}_4^+$ [1], we were unable to find a set of symmetry coordinates which factorizes the kinetic energy matrix $\mathbf{G}$ [4].

It has been moreover found [2] that the representation $\mathscr{P}_R$ of the symmetry group $\boldsymbol{G}_4^+$ in terms of the internal coordinates R defined in agreement with [4], is different from the representation $\mathscr{P}_X$ of the same group given in terms of the cartesian coordinates X.

A third still different representation $\mathscr{P}_{\bar{Q}}$ of $\boldsymbol{G}_4^+$ has been obtained for the same molecule [5] by using a method proposed by Gussoni and Zerbi [6]. This method, which allows the calculation of internal symmetry coordinates, consists in the diagonalization of the $\mathbf{G}$ matrix according to

$$\mathbf{G}\,\mathbf{D} = \mathbf{D}\,\mathbf{\Gamma}\,, \tag{1}$$

where $\mathbf{\Gamma}$ is the matrix of the eigenvalues of $\mathbf{G}$ and $\mathbf{D}$ is the eigenvector matrix.

A set of quasi-normal coordinates $\bar{Q}$ can then be defined as [6]

$$\bar{Q} = \tilde{\mathbf{D}}\,R\,, \tag{2}$$

where $\tilde{\mathbf{D}}^{-1} = \mathbf{D}$.

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The three representations $\mathscr{P}_R$, $\mathscr{P}_X$ and $\mathscr{P}_{\bar{Q}}$ do coincide only for fixed values of the torsional angle 2γ, that is for the conformers of 1,4-di-X-butyne-2, for which the symmetry group $\boldsymbol{G}_4^+$ collapses into point groups $\boldsymbol{C}_{2\mathrm{v}}$ $(\gamma = 0)$, $\boldsymbol{C}_{2\mathrm{h}}$ $(\gamma = \pi/2)$ and $\boldsymbol{C}_2$ $(\gamma \neq 0, \neq \pi/2)$ [1, 2].

In the following we wish to investigate on and clarify the different behaviour observed in rigid and non-rigid molecules, by assuming a very simple model of symmetry $\boldsymbol{G}_4^+$ (a four atom-molecule with $m_1 = m_4 = m_x$, $m_a = m_b = m$, $\overline{1a} = \overline{4b}$, $1\hat{a}b = 4\hat{b}a$).

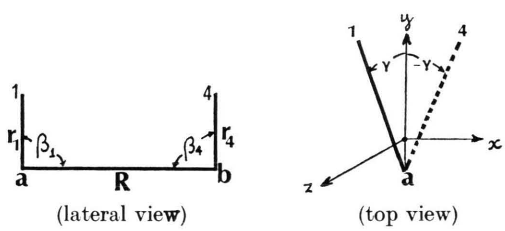


Fig. 1.

The height of the barrier to internal rotation is a function of the distance $\overline{ab}$. For the sake of simplicity the equilibrium values of the angles $1\hat{a}b = 4\hat{b}a$ have been assumed to be $\pi/2$.

For this model the following representations of $\boldsymbol{G}_4^+$ in internal and cartesian coordinates, respectively, can be derived [2]:

$$\mathscr{P}_R = 3A_{1\mathrm{s}} + 2B_{2\mathrm{s}} \tag{3}$$
$$\mathscr{P}_X = 2A_{1\mathrm{s}} + B_{2\mathrm{s}} + 2(A_{1\mathrm{d}} + A_{2\mathrm{d}} + B_{1\mathrm{d}} + B_{2\mathrm{d}}).$$

The representation $\mathscr{P}_{\bar{Q}}$ can be obtained from the $\mathbf{G}$ matrix [3]:

$$\mathbf{G} = \begin{array}{c|ccccc} & (\mathbf{r}_1) & (\mathbf{r}_4) & (\mathbf{R}) & (\beta_1) & (\beta_4) \\ (\mathbf{r}_1) & \mu+\mu_x & 0 & 0 & -\varrho'\mu & \varrho'\mu\cos 2\gamma \\ (\mathbf{r}_4) & 0 & \mu+\mu_x & 0 & \varrho'\mu\cos 2\gamma & -\varrho'\mu \\ (\mathbf{R}) & 0 & 0 & 2\mu & -\varrho_1\mu & -\varrho_1\mu \\ (\beta_1) & -\varrho'\mu & \varrho'\mu\cos 2\gamma & -\varrho_1\mu & \varrho_1^2(\mu+\mu_x)+2\mu\varrho'^2 & -2\varrho'^2\mu\cos 2\gamma \\ (\beta_4) & \varrho'\mu\cos 2\gamma & -\varrho'\mu & -\varrho_1\mu & -2\varrho'^2\mu\cos 2\gamma & \varrho_1^2(\mu+\mu_x)+2\mu\varrho'^2 \end{array} \tag{4}$$

Here r_1, r_4, R are stretching coordinates, β_1 and β_4 bending coordinates, μ and μ_x the inverses of m and m_x, respectively, ϱ' is the inverse of the distance $\overline{ab}$, ϱ_1 the inverse of the distance $\overline{1a}=\overline{4b}$, and 2γ the torsional angle. To simplify the calculations, symmetry coordinates (S), symmetric (A) or antisymmetric (B) with respect to the unique symmetry element $C_2(y)$ common to all the γ values, are used ($S=\mathbf{U}R$). They are [1]:

$$(A_{1s})\quad S_1=\frac{\mathbf{r}_1+\mathbf{r}_4}{\sqrt{2}},\quad S_2=R,\quad S_3=\frac{\beta_1+\beta_4}{\sqrt{2}},\qquad (B_{2s})\quad S_4=\frac{\mathbf{r}_1-\mathbf{r}_4}{\sqrt{2}},\quad S_5=\frac{\beta_1-\beta_4}{\sqrt{2}}. \tag{5}$$

Using these symmetry coordinates, the $\mathbf{G}$ matrix (4) factorizes into two blocks:

$$\mathbf{G}_s=\begin{matrix}(S_1)\\(S_2)\\(S_3)\\(S_4)\\(S_5)\end{matrix}\begin{pmatrix} \mu+\mu_x & 0 & -2\varrho'\mu\sin^2\gamma & 0 & 0\\ 0 & 2\mu & -\sqrt{2}\varrho_1\mu & 0 & 0\\ -2\varrho'\mu\sin^2\gamma & -\sqrt{2}\varrho_1\mu & \varrho_1^2(\mu+\mu_x)+4\mu\varrho'^2\sin^2\gamma & 0 & 0\\ 0 & 0 & 0 & \mu+\mu_x & -2\varrho'\mu\cos^2\gamma\\ 0 & 0 & 0 & -2\varrho'\mu\cos^2\gamma & \varrho_1^2(\mu+\mu_x)+4\mu\varrho'^2\cos^2\gamma \end{pmatrix} \tag{6}$$

and (1) and (2) can be replaced by

$$\mathbf{G}_s\,\mathbf{D}_s=\mathbf{D}_s\,\mathbf{\Gamma}, \tag{7}$$

$$\bar{Q}=\tilde{\mathbf{D}}_s S=\tilde{\mathbf{D}}_s\,\mathbf{U}\,R=\tilde{\mathbf{D}}\,R. \tag{8}$$

The eigenvalues of $\mathbf{G}_s$ can now be evaluated algebraically using two further simplifying assumptions:

$$\mu=\mu_x \quad\text{and}\quad \varrho_1=1. \tag{9}$$

One obtains

$$\begin{aligned}\gamma_1&=2\mu,\\ \gamma_2&=2\mu(1+\varrho'^2\sin^2\gamma)+\mu\Delta,\\ \gamma_3&=2\mu(1+\varrho'^2\sin^2\gamma)-\mu\Delta,\\ \gamma_4&=2\mu(1+\varrho'\cos^2\gamma\,\delta_1),\\ \gamma_5&=2\mu(1+\varrho'\cos^2\gamma\,\delta_2),\end{aligned} \tag{10}$$

where

$$\begin{aligned}\Delta&=(2+4\varrho'^2(1+\varrho'^2)\sin^4\gamma)^{1/2},\\ \delta_1&=\varrho'+(1+\varrho'^2)^{1/2},\\ \delta_2&=\varrho'-(1+\varrho'^2)^{1/2}.\end{aligned} \tag{11}$$

The $\tilde{\mathbf{D}}_s$ matrix is given by

$$\tilde{\mathbf{D}}_s=\begin{matrix}\\ \bar{Q}_1\\ \bar{Q}_2\\ \bar{Q}_3\\ \bar{Q}_4\\ \bar{Q}_5\end{matrix}\begin{matrix}(S_1) & (S_2) & (S_3) & (S_4) & (S_5)\\ N_1 & -\sqrt{2}\varrho'\sin^2\gamma\,N_1 & 0 & 0 & 0\\ -\sqrt{2}\varrho'\sin^2\gamma\,N_2 & -N_2 & N_2{}^{-1}/\sqrt{2}\Delta & 0 & 0\\ \sqrt{2}\varrho'\sin^2\gamma\,N_3 & N_3 & N_3{}^{-1}/\sqrt{2}\Delta & 0 & 0\\ 0 & 0 & 0 & (-\delta_2/N_4)^{1/2} & -(\delta_1/N_4)^{1/2}\\ 0 & 0 & 0 & (\delta_1/N_4)^{1/2} & (-\delta_2/N_4)^{1/2}\end{matrix} \tag{12}$$

where

$$\begin{aligned}N_1&=(1+2\varrho'^2\sin^4\gamma)^{-1/2};\\ N_2&=[\Delta(\Delta+2\varrho'^2\sin^2\gamma)]^{-1/2};\\ N_3&=[\Delta(\Delta-2\varrho'^2\sin^2\gamma)]^{-1/2};\\ N_4&=2(1+\varrho'^2)^{1/2}.\end{aligned}$$

Since the $\bar{Q}_i$ coordinates (which diagonalize $\mathbf{G}_s$) are given in terms of S_i (of species A_{1s} for the 3×3 block; of species B_{2s} for the 2×2 block) through coefficients which belong to the A_{1s} representation of the $\boldsymbol{G}_4{}^+$ group [1—2], the representation $\mathscr{P}_{\bar{Q}}$ is given by

$$\mathscr{P}_{\bar{Q}}=3A_{1s}+2B_{2s}. \tag{13}$$

We have then found that, for this particular model, $\mathscr{P}_{\bar{Q}}$ coincides with $\mathscr{P}_R$. If this were generally true, the number of irreducible representations of the symmetry group of non-rigid molecules which correspond to quasi-normal modes could be determined with the same method as used for rigid molecules [4]. We know, however, from our previous work on 1,4-di-X-butyne-2 that $\mathscr{P}_{\bar{Q}}$

Table 1.

G_4^+	E	A	B	C	E'	$E'A$	$E'B$	$E'C$	Symmetry species
$S_1' = d_{1x} + d_{4x}$	1	−1	1	−1	−1	1	−1	1	B_{1d}
$S_3' = d_{1x} - d_{4x}$	1	1	−1	−1	−1	−1	1	1	A_{2d}
$S_5' = d_{1y} + d_{4y}$	1	1	1	1	−1	−1	−1	−1	A_{1d}
$S_7' = d_{1y} - d_{4y}$	1	−1	−1	1	−1	1	1	−1	B_{2d}
$S_9' = d_{1z} + d_{4z}$	1	−1	−1	1	1	−1	−1	1	B_{2s}
$S_{11}' = d_{1z} - d_{4z}$	1	1	1	1	1	1	1	1	A_{1s}
$S_2' = d_{ax} + d_{dx}$	1	−1	1	−1	−1	1	−1	1	B_{1d}
$S_4' = d_{ax} - d_{dx}$	1	1	−1	−1	−1	−1	1	1	A_{2d}
$S_6' = d_{ay} + d_{dy}$	1	1	1	1	−1	−1	−1	−1	A_{1d}
$S_8' = d_{ay} - d_{dy}$	1	−1	−1	1	−1	1	1	−1	B_{2d}
$S_{10}' = d_{az} + d_{dz}$	1	−1	−1	1	1	−1	−1	1	B_{2s}
$S_{12}' = d_{az} - d_{dz}$	1	1	1	1	1	1	1	1	A_{1s}

generally differs from $\mathscr{P}_R$. We can then state that: *the symmetry species of the quasi-normal vibrations of non-rigid molecules can generally be determined* by using the procedure adopted in this paper, that is *through equations* (1)—(2) *or* (7)—(8).

As to the understanding of the representation $\mathscr{P}_X$ in cartesian coordinates we proceed in a few steps as follows:

I. Let us consider the representation $\mathscr{P}_X$ given in (3) and build a set of cartesian coordinates $(S_1', S_2', \ldots, S_{12}')$ which obey its structure (Table 1).

The symmetry species of the zero-frequency modes (translations, rotations and torsion (τ)) are given by [2]

$$\mathscr{P}' = A_{2s}(\tau) + B_{1s}(R_z) + B_{2s}(T_z) + A_{1d}(T_y) + A_{2d}(R_y) + B_{1d}(T_x) + B_{2d}(R_x) .$$

First of all it can be observed that, while for rigid molecules the symmetry species of the normal modes can be derived as $\mathscr{P}_{\text{vibr}} = \mathscr{P}_X - \mathscr{P}'$, for non-rigid molecules this procedure cannot be adopted. Indeed in $\mathscr{P}_X$ (3) the species A_{2s} and B_{1s} to which τ and R_z belong, do not appear. This fact can be explained as follows. Let us define the zero-frequency coordinates according to (41) of reference [1]. It can be observed (Table 2) that while translations are defined as sums of the S' coordinates, rotations and torsion are combinations of S' with coefficients which may be functions of γ. In particular, τ and R_z are combinations of S' only through functions of γ of the kind $\cos\gamma$ (A_{1d} species), $\sin\gamma$ (A_{2d} species) and $\sin 2\gamma$ (A_{2s} species). The symmetry species to which they belong can then be evaluated as direct products of the species of S' and those of the functions of γ. For this reason the symmetry species of τ and R_z may not appear in $\mathscr{P}_X$ (3).

As to the determination of the symmetry species of the quasi-normal modes starting from X coordinates, we propose here a very simple method to

Table 2.

$$T_x = S_1' + S_2' \qquad \underline{(B_{1d})}$$

$$T_y = S_5' + S_6' \qquad \underline{(A_{1d})}$$

$$T_z = S_9' + S_{10}' \qquad \underline{(B_{2s})}$$

$$R_x = -\frac{1}{2\varrho'}(S_7' + S_8') + \frac{1}{2}\cos\gamma\,(S_9' - S_{10}') \qquad \underline{(B_{2d})}$$

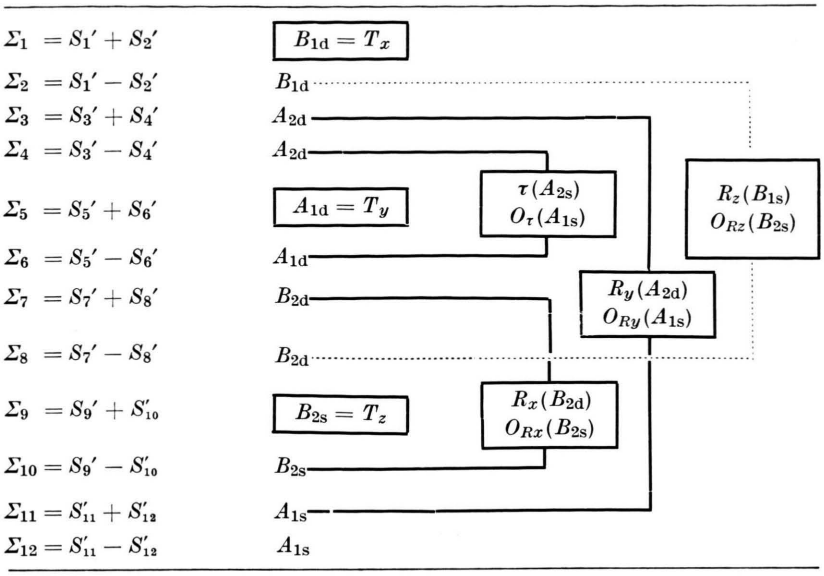
$$R_y = \frac{1}{2\varrho'}(S_3' + S_4') + \sin\gamma\, S_{11}' \qquad \underline{(A_{2d})}$$

$$R_z{}^* = -\frac{1}{2}\cos\gamma\,(S_1' - S_2') - \sin\gamma\, S_7' + \sin\gamma\left(\frac{1}{\varrho'}\right)^2 \frac{1}{2 l_2^2}(S_7' + S_8') - \sin\gamma\cos\gamma\,\frac{1}{\varrho'\, 2 l_2^2}(S_9' - S_{10}') \qquad \underline{(B_{1s})}$$

$$\tau^* = -\cos\gamma\, S_3' + \cos\gamma\left(\frac{1}{\varrho'}\right)^2 \frac{1}{2 l_1^2}(S_3' + S_4') - \frac{1}{2}\sin\gamma\,(S_5' - S_6') + \sin\gamma\cos\gamma\,\frac{1}{\varrho'\, l_1^2} S_{11}' \qquad \underline{(A_{2s})}$$

where $l_2^2 = \left(\frac{1}{\varrho'}\right)^2 + \cos^2\gamma$, $\quad l_1^2 = \left(\frac{1}{\varrho'}\right)^2 + 2\sin^2\gamma$, $\quad$ (*) = orthogonalized according to Schmidt's method [7].

Table 3.



determine them based on the requirement that quasi-normal modes must be orthogonal to the constraint equations. We refer to Appendix I for the quantitative approach. As illustrated in Table 3 where the coordinates

$$\Sigma = S_i' \pm S_j' \tag{14}$$

are reported, sets of orthogonal combinations of the type

$$\begin{cases} \cos\gamma\, \Sigma_i + \sin\gamma\, \Sigma_j \\ \sin\gamma\, \Sigma_i - \cos\gamma\, \Sigma_j \end{cases} \tag{15}$$

must be constructed. If, for instance, Σ_i and Σ_j belong to the A_{1d} and A_{2d} species, respectively, the two new coordinates should be of species A_{1s} and A_{2s}. In such a way one can determine the species of the combination orthogonal to each constraint (see Table 3). Indeed, quasi-normal modes should form an orthogonal set and be also orthogonal to all the constraints.

The species of the quasi-normal modes on a cartesian coordinates basis, determined as suggested in Table 3, are then

$$3\,A_{1s} + 2\,B_{2s}\,,$$

in agreement with the results of the previous procedures. The more detailed account given in Appendix I allows the evaluation of $\bar{Q}_x$ (quasi-normal coordinates in the cartesian space).

II. Quasi-normal coordinates $\bar{Q}_x$ can also be evaluated from (1) or (8) when the matrix $\mathbf{B}[R = \mathbf{B}X]$ is known. This procedure is described in Appendix II.

III. The quasi-normal coordinates $\bar{Q}_x$ determined with procedure I turned out to be equal to those obtained with procedure II.

As a conclusion of this first attempt to understand the symmetry species of normal coordinates in non-rigid molecules we can make the following remarks:

a) The representations of $\boldsymbol{G}_4^+$ are different on different bases because the torsional angle may enter, through its non-totally symmetric functions, in the coordinates which represent zero and non-zero frequency modes.

b) Due to the difficulty of dealing with the vibrational problem in cartesian coordinates, we think that the easiest way of determining the species of quasi-normal modes is by solving (1) or (8). For complicated systems, when an algebraic solution cannot be obtained, the species of the quasi-normal modes can be determined through a numerical solution of (1) or (8) for different γ values by plotting the resulting eigenvectors and by using the correlation Tables between $\boldsymbol{G}_4^+$, $\boldsymbol{C}_{2v}$, $\boldsymbol{C}_{2h}$ and $\boldsymbol{C}_2$ as already suggested in reference [8].

Further work on more complicated models is in progress in our Laboratory.

Appendix I

For the determination of the quasi-normal coordinates in the cartesian space we follow this procedure:

Table 4.

$\mathbf{D}_x^{-1} =$

	x_1	y_1	z_1	x_4	y_4	z_4	x_a	y_a	z_a	x_d	y_d	z_d
$\bar{Q}^*_{1x}$	$-\sigma$	η	0	σ	η	0	σ	$-\eta$	$-2\varrho'\sigma^2$	$-\sigma$	$-\eta$	$2\varrho'\sigma^2$
$\bar{Q}^*_{2x}$	$\varrho'\sigma^3$	$-\varrho'\sigma^2\eta$	$\frac{\Delta_1}{2}$	$-\varrho'\sigma^3$	$-\varrho'\sigma^2\eta$	$-\frac{\Delta_1}{2}$	$-\varrho'\sigma\Delta_3$	$\varrho'\sigma^2\eta$	$-\left(1+\frac{\Delta_1}{2}\right)$	$\varrho'\sigma\Delta_3$	$\varrho'\sigma^2\eta$	$\left(1+\frac{\Delta_1}{2}\right)$
$\bar{Q}^*_{3x}$	$-\varrho'\sigma^3$	$\varrho'\sigma^2\eta$	$\frac{\Delta_2}{2}$	$\varrho'\sigma^3$	$\varrho'\sigma^2\eta$	$-\frac{\Delta_2}{2}$	$\varrho'\sigma\Delta_4$	$-\varrho'\sigma^2\eta$	$\left(1-\frac{\Delta_2}{2}\right)$	$-\varrho'\sigma\Delta_4$	$-\varrho'\sigma^2\eta$	$-\left(1-\frac{\Delta_2}{2}\right)$
$\bar{Q}^*_{4x}$	$-\sigma$	η	$-\delta_1$	$-\sigma$	$-\eta$	$-\delta_1$	σ	$-\eta(1+2\varrho'\delta_1)$	δ_1	σ	$\eta(1+2\varrho'\delta_1)$	δ_1
$\bar{Q}^*_{5v}$	$-\sigma$	η	$-\delta_2$	$-\sigma$	$-\eta$	$-\delta_2$	σ	$-\eta(1+2\varrho'\delta_2)$	δ_2	σ	$\eta(1+2\varrho'\delta_2)$	δ_2

$\bar{Q}_{1x} = \bar{Q}^*_{1x}(2+4\varrho'^2\sin^4\gamma)^{-1/2}$, $\bar{Q}_{2x} = \bar{Q}^*_{2x}(\Delta\Delta_1)^{-1/2}$, $\bar{Q}_{3x} = \bar{Q}^*_{3x}(\Delta\Delta_2)^{-1/2}$, $\bar{Q}_{4x} = \bar{Q}^*_{4x}(1+\varrho'^2)^{-1/4}(4\delta_1)^{-1/2}$, $\bar{Q}_{5x} = \bar{Q}^*_{5x}(1+\varrho'^2)^{-1/4}(-4\delta_2)^{-1/2}$,

$\sigma = \sin\gamma$; $\Delta_1 = \Delta + 2\varrho'^2\sin^2\gamma$; $\Delta_3 = \Delta_1 + \sin^2\gamma$; $\eta = \cos\gamma$; $\Delta_2 = \Delta - 2\varrho'^2\sin^2\gamma$; $\Delta_4 = -\Delta_2 + \sin^2\gamma$.

1. The more general combinations of S' which obey the symmetry requirements (Table 3) are considered. If we restrict for instance, our attention to the two B_{2s} coordinates, two combinations such as:

$$\bar{Q}_x = a\sin\gamma\, S_1' + b\cos\gamma\, S_7' + c\, S_9' + d\sin\gamma\, S_2' + e\cos\gamma\, S_8' + f\, S_{10}' \quad (B_{2s})$$

(with $a, b, \ldots, f$ to be determined) can be studied.

2) From the orthogonality conditions with respect to T and $\mathscr{R}$ the relations $d = -a$; $f = -c$; $a = -b$; $c = (b+e)/2\varrho'$ hold.

3) Let $\bar{Q}_x(b, e)$ and $\bar{Q}_x(b', e')$ be the two B_{2s} coordinates under study. From the orthogonality condition we obtain

$$e = -b[1 + 2\varrho'^2 \mp 2\varrho'(1+\varrho'^2)^{1/2}].$$

4) From (8)

$$\bar{Q} = \tilde{\mathbf{D}}_s\,\mathbf{U}\,R = \tilde{\mathbf{D}}_s\,\mathbf{B}_s X = \mathbf{D}_x^{-1}X.$$

Since, by definition,

$$\mathbf{D}_x^{-1} = \tilde{\mathbf{D}}_s\,\mathbf{B}_s,$$

it follows that

$$\mathbf{D}_x^{-1}\,\mathbf{M}^{-1}\,\tilde{\mathbf{D}}_x^{-1} = \mathbf{\Gamma}.$$

From the last equation, b can be determined.

By proceeding in this way, the five quasi-normal coordinates in the cartesian space have been determined. The matrix $\mathbf{D}_x^{-1}(\bar{Q} = \mathbf{D}_x^{-1}X)$ is reported in Table 4.

Appendix II

Quasi-normal coordinates in the X space can be easily derived from (8):

$$\bar{Q} = \tilde{\mathbf{D}}\,R = \tilde{\mathbf{D}}\,\mathbf{B}\,X,$$

when the $\mathbf{B}(\gamma)$ matrix is known. For the model under study we have determined the $\mathbf{B}(\gamma)$ matrix as described in details in [2].

Since we are describing a non-rigid model (small ϱ'), only five internal coordinates r_1, r_4, R, β_1, β_4 have been considered. Notice that the obtained $\mathbf{B}$ matrix must obey to the relation [1—2]

$$\boldsymbol{\beta}\,\mathbf{M}^{-1}\,\tilde{\mathbf{B}} = \mathbf{0},$$

that is $\mathbf{B}$ must be orthogonal to the constraint matrix $\boldsymbol{\beta}$. The resulting $\bar{Q}_x$ are just those reported in Table 4.

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