

## Vibrations of Planar Symmetrical $XY_4$ Molecules with Application to Xenon Tetrafluoride

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A theoretical treatment is given for the harmonic vibrations of the planar (square)  $XY_4$  molecular model, including a study of Coriolis vibration-rotation interactions and the centrifugal distortion. Special emphasis has been laid on the evaluation of mean-square amplitude matrix elements and related quantities, *viz.* the mean amplitude of vibration and shrinkage effects. The theory is applied to xenon tetrafluoride, for which calculated force constants are reported, along with numerical results of the above mentioned quantities.

The planar symmetrical (square)  $XY_4$  model is of considerable interest in studies of molecular spectroscopy. Xenon tetrafluoride is a famous example of a molecule with this structure.<sup>1,2</sup> An investigation of this molecule by modern gas electron diffraction would also be of great interest, and might be undertaken in connection with the intensive studies of xenon tetrafluoride already in progress.<sup>3,4</sup> A special reason for such an investigation of xenon tetrafluoride might be the fact that the shrinkage effects are accessible from the harmonic-vibration analysis; there exist two types, and in each case the anharmonic terms vanish.<sup>5</sup> Nagarajan<sup>6</sup> has already performed a spectroscopic calculation of the mean amplitudes of vibration in xenon tetrafluoride, but has not carried the investigation further to include the mean-square perpendicular amplitudes and shrinkage effects. In the present work these quantities are included, along with additional results from a harmonic-vibration analysis, namely the Coriolis constants and constants of centrifugal stretching.

### SYMMETRY AND ORIENTATION OF COORDINATES

There are some confusing features as to the orientation of symmetry coordinates in the considered molecular model, which should be clarified. The distribution of normal modes of vibration among the symmetry species of the appropriate symmetry group ( $D_{4h}$ ) has been reported as

$$\begin{aligned} & \text{(a) } A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u \\ \text{or (b) } & A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{1u} + 2E_u \end{aligned} \quad (1)$$

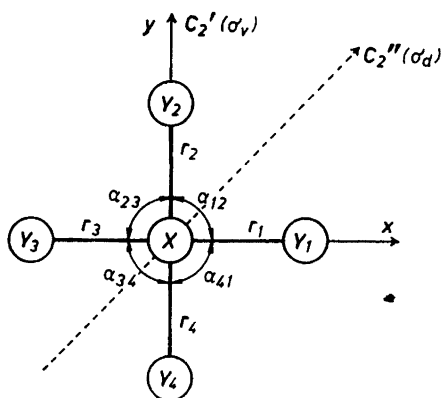


Fig. 1. Notation used for the planar symmetrical  $XY_4$  model ( $D_{4h}$ ). The symbols denote deviations from equilibrium distances and angles.

There is an ambiguity as to the label designations for  $B_{1g}$  and  $B_{2g}$  and for  $B_{1u}$  and  $B_{2u}$ , even when it is adhered strictly to the notation used in the character table of Wilson, Decius and Cross.<sup>7</sup> As a matter of fact the assignments of an asymmetric stretching and an in-plane bending deformation (in  $B_{1g}$  and  $B_{2g}$ ), and the out-of-plane ring deformation (in  $B_{1u}$  or  $B_{2u}$ ), depend on the chosen designation for the  $C_2'$  and  $C_2''$  axes (or  $\sigma_v$  and  $\sigma_d$  planes). One has the alternatives:

- $C_2'$  along an X-Y bond, and consequently  $B_{1g}$  as the stretching mode,  $B_{2g}$  as bending and the ring deformation in  $B_{2u}$ ; and
- $C_2'$  along an intersection of YXY,  $B_{1g}$  as bending,  $B_{2g}$  as the stretching and the ring deformation in  $B_{1u}$ .

The treatment of Pistorius<sup>8</sup> follows alternative (b), and the same is true for Pysh *et al.*,<sup>9</sup> Yeranov,<sup>10</sup> and Nagarajan.<sup>6,12</sup> Unfortunately all these treatments are in disagreement with the recommendations by Mulliken,<sup>13</sup> where the choice of alternative (a) is prescribed. Presently one has therefore chosen alternative (a) in spite of the cited previous work, and simultaneously it was noticed, with pleasure, that this choice agrees with the excellent book of Nakamoto.<sup>14</sup> This author, however, was apparently confused when quoting the vibrational frequencies for ions of the considered structure.<sup>15</sup>

Fig. 1 shows our orientation of a cartesian system of principal axes. The choice is consistent with the labelling of polarizability components in the character table of Wilson *et al.*,<sup>7</sup> according to which the  $(\alpha_{xx} - \alpha_{yy})$  and  $\alpha_{xy}$  terms should belong to  $B_{1g}$  and  $B_{2g}$ , respectively. Moreover, the degenerate pairs of the present symmetry coordinates ( $S_a, S_b$ ) of species  $E_u$  (see below) transform like the rigid translations ( $T_x, T_y$ ). They consequently fulfill the transformation property

$$C_4 \begin{bmatrix} S_a \\ S_b \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \begin{bmatrix} S_a \\ S_b \end{bmatrix} \quad (2)$$

where  $C_4$  is the symmetry operation of a four-fold axis, which transforms  $T_x$  into  $T_y$ . This property is consistent with the suggested convention of Boyd and Longuet-Higgins.<sup>16</sup>

As a result of the chosen orientations of symmetry coordinates with respect to the principal axes there emerge very convenient regularities for the Coriolis constants involving  $E_u$  coordinates. The constants with respect to  $x$  and  $y$  axes contain the  $b$  and  $a$  components of the normal coordinates separately. More specifically there is a coupling of  $A_{2u} \times E_u$  type, which is described by a Coriolis constant, say,  $\zeta_{46}$  or  $\zeta_{47}$  ( $\zeta_{46}^2 + \zeta_{47}^2 = 1$ ), specified by

$$\begin{aligned}\zeta_{46} &= \zeta_{46a}^y = -\zeta_{46b}^x \\ \zeta_{47} &= \zeta_{47a}^y = -\zeta_{47b}^x\end{aligned}\quad (3)$$

while  $\zeta_{4ta}^x = \zeta_{4tb}^y = 0$  for  $t = 6, 7$

Another type of Coriolis coupling, *viz.*  $B_{2u} \times E_u$ , follows the rules

$$\begin{aligned}\zeta_{56} &= \zeta_{56a}^y = \zeta_{56b}^x \\ \zeta_{57} &= \zeta_{57a}^y = \zeta_{57b}^x\end{aligned}\quad (4)$$

( $\zeta_{56}^2 + \zeta_{57}^2 = 1$ ), while  $\zeta_{5ta}^x = \zeta_{5tb}^y = 0$  for  $t = 6, 7$

Next there is a trivial Coriolis coupling of  $B_{1g} \times B_{2g}$  with respect to the  $z$  axis; it involves only one-dimensional species. The  $E_u \times E_u$  type on the other hand, is a very important kind of Coriolis coupling with respect to the  $z$  axis it involves the nonvanishing constants

$$\begin{aligned}\zeta_6 &= \zeta_{6a6b}^z & \zeta_7 &= \zeta_{7a7b}^z \\ \zeta_{67} &= \zeta_{6a7b}^z & &= \zeta_{7a6b}^z\end{aligned}\quad (5)$$

which are connected through the zeta-sum rule

$$\zeta_6 + \zeta_7 = 0 \quad \text{and} \quad \zeta_6 \zeta_7 - \zeta_{67}^2 = -1$$

#### SYMMETRY COORDINATES

$$\begin{aligned}S(A_{1g}) &= 2^{-1} (r_1 + r_2 + r_3 + r_4) \\ S(B_{1g}) &= 2^{-1} (r_1 - r_2 + r_3 - r_4) \\ S(B_{2g}) &= 2^{-1} R (\alpha_{12} - \alpha_{23} + \alpha_{34} - \alpha_{41}) \\ S(A_{2u}) &= z_1 + z_2 + z_3 + z_4 - 4z_5 \\ S(B_{2u}) &= z_1 - z_2 + z_3 - z_4 \\ S_{1a}(E_u) &= 2^{-\frac{1}{2}} (r_1 - r_3), & S_{1b}(E_u) &= 2^{-\frac{1}{2}} (r_2 - r_4) \\ S_{2a}(E_u) &= 2^{-1} R (\alpha_{12} - \alpha_{23} - \alpha_{34} + \alpha_{41}) \\ S_{2b}(E_u) &= 2^{-1} R (\alpha_{12} + \alpha_{23} - \alpha_{34} - \alpha_{41})\end{aligned}$$

Redundant:  $S_r(A_{1g}) = 2^{-1} R (\alpha_{12} + \alpha_{23} + \alpha_{34} + \alpha_{41}) \equiv 0$   
 $R$  is the equilibrium X - Y distance.

#### MEAN-SQUARE AMPLITUDES OF VIBRATION<sup>1</sup>

The parallel and perpendicular mean-square amplitudes of vibration associated with bonded and non-bonded atom pairs are expressed in terms of the  $\Sigma$ -matrix elements.

*Y—Y distance (short)*

Parallel:

$$\langle \Delta z_{12}^2 \rangle = \frac{1}{2} \Sigma(A_{1g}) + \frac{1}{8} \Sigma(B_{2g}) + \frac{1}{2} \Sigma_1(E_u) + \frac{1}{4} \Sigma_2(E_u) + 2^{-\frac{1}{2}} \Sigma_{12}(E_u)$$

Perpendicular  
in plane:

$$\langle \Delta x_{12}^2 \rangle = \frac{1}{2} \Sigma(B_{1g}) + \frac{1}{2} \Sigma_1(E_u) + \frac{1}{4} \Sigma_2(E_u) + 2^{-\frac{1}{2}} \Sigma_{12}(E_u)$$

out of plane:

$$\langle \Delta y_{12}^2 \rangle = \frac{1}{4} \Sigma(B_{2u})$$

*Y—Y distance (long)*

Parallel:

$$\langle \Delta z_{13}^2 \rangle = \Sigma(A_{1g}) + \Sigma(B_{1g})$$

Perpendicular  
in plane:

$$\langle \Delta x_{13}^2 \rangle = \frac{1}{4} \Sigma(B_{2g})$$

out of plane:

$$\langle \Delta y_{13}^2 \rangle = 0$$

*X—Y distance*

Parallel:

$$\langle \Delta z_{15}^2 \rangle = \frac{1}{4} \Sigma(A_{1g}) + \frac{1}{4} \Sigma(B_{1g}) + \frac{1}{2} \Sigma_1(E_u)$$

Perpendicular  
in plane:

$$\langle \Delta x_{15}^2 \rangle = \frac{1}{16} \Sigma(B_{2g}) + \frac{1}{4} \Sigma_2(E_u)$$

out of plane:

$$\langle \Delta y_{15}^2 \rangle = \frac{1}{16} \Sigma(A_{2u}) + \frac{1}{16} \Sigma(B_{2u})$$

Notice that the  $x$ ,  $y$ , and  $z$  directions are oriented with respect to each of the considered distances and do not conform the chosen directions of the principal system of axes; *cf.* Fig. 1.

Calculated values of the here considered quantities are found in Table 2.

## NUMERICAL COMPUTATIONS

The presently calculated force constants and  $\Sigma$ -matrix elements for xenon tetrafluoride are given in Table 1. The calculations are based on vibrational frequencies from Claassen *et al.*<sup>1</sup>

In the two-dimensional block of species  $E_u$  one adopted the  $F_{11}$  (Y-X-Y stretching) constant from the work of Nagarajan.<sup>6</sup> The force field thus produced showed general good agreement with that of the cited work.<sup>6</sup>

Table 1. Symmetrized force constants (in mdyn/Å) and  $\Sigma$  values (in Å<sup>2</sup>) for xenon tetrafluoride.

Species	$F_{ij}$	$\Sigma_{ij}$ (0°K)	$\Sigma_{ij}$ (298°K)
$A_{1g}$	$F_{11} = 3.2993$	$\Sigma_{11} = 0.0016345$	0.0018910
$B_{1g}$	$F_{11} = 2.8199$	$\Sigma_{11} = 0.0017679$	0.0021121
$B_{2g}$	$F_{11} = 0.0325$	$\Sigma_{11} = 0.0151065$	0.0294378
$A_{2u}$	$F_{11} = 0.1500$	$\Sigma_{11} = 0.0192607$	0.0317979
$B_{2u}$	$F_{11} = 0.1366$	$\Sigma_{11} = 0.0160634$	0.0329268
$E_u$	$F_{11} = 2.6534$	$\Sigma_{11} = 0.0022077$	0.0032407
	$F_{22} = 0.1211$	$\Sigma_{22} = 0.0162319$	0.0548117
	$F_{12} = -0.3397$	$\Sigma_{12} = 0.0011525$	0.0065514

Atomic masses:  $m_{Xe} = 131.3$ ,  $m_F = 19.0$   
 Equilibrium Xe—F distance:  $R = 1.953$  Å

 SHRINKAGE EFFECTS<sup>18</sup>

In the present case one will expect a linear shrinkage effect for the  $Y_1 - Y_3$  (long) distance and a non-linear shrinkage effect for the  $Y_1 - Y_2$  (short) distance.

 Table 2. Parallel and perpendicular mean square amplitudes of vibration in xenon tetrafluoride (in Å<sup>2</sup>):

Distance	Parallel		Perpendicular			
	0°K	298°K	in plane		out of plane	
	0°K	298°K	0°K	298°K	0°K	298°K
Y—Y (short)	0.008682	0.024581	0.006861	0.021012	0.004016	0.008232
Y—Y (long)	0.003402	0.004003	0.003777	0.007359	0.0	0.0
X—Y	0.001954	0.002621	0.005002	0.015543	0.002208	0.004045

By definition the linear shrinkage is given by the relation

$$-\delta_{13} = \langle r_{13} \rangle - 2 \langle r_{15} \rangle \\ = -\frac{1}{16} R^{-1} [\Sigma(A_{2u}) + \Sigma(B_{2u}) + 4 \Sigma_2(E_u)]$$

In the same way one obtains the non-linear shrinkage as follows

$$-\delta_{12} = \frac{1}{32} 2^{\ddagger} R^{-1} [4 \Sigma(B_{1g}) - \Sigma(B_{2g}) - \Sigma(A_{2u}) + \Sigma(B_{2u}) \\ + 4 \Sigma_1(E_u) - 2 \Sigma_2(E_u) + 32^{\ddagger} \Sigma_{12}(E_u)]$$

Calculated values are given in Table 3.

Table 3. Shrinkage effects in xenon tetrafluoride (in Å).

Distance	0°K	298°K
Y-Y (short)	0.000641	0.001798
Y-Y (long)	0.003208	0.009088

## CORIOLIS COUPLING CONSTANTS

One obtains the following expressions for the Coriolis coupling constants.

$$A_{2u} \times E_u(b)$$

$$\zeta_{46b}^x = -\frac{1}{2} (m_Y m_X / M)^{\frac{1}{2}} (2^{\frac{1}{2}} L_{66} - L_{76})$$

$$\zeta_{47b}^x = \frac{1}{2} (m_Y m_X / M)^{\frac{1}{2}} (L_{77} - 2^{\frac{1}{2}} L_{67})$$

$$B_{2u} \times E_u(b)$$

$$\zeta_{56b}^x = \frac{1}{2} m_Y^{\frac{1}{2}} (2^{\frac{1}{2}} L_{66} + L_{76})$$

$$\zeta_{57b}^x = \frac{1}{2} m_Y^{\frac{1}{2}} (L_{77} + 2^{\frac{1}{2}} L_{67})$$

$$E_u(a) \times E_u(b)$$

$$\zeta_{6a6b}^x = -m_Y M^{-1} [2 m_Y L_{66}^2 + m_Y L_{76}^2 + 2^{\frac{1}{2}} (m_X + 2 m_Y) L_{66} L_{76}]$$

$$\zeta_{6a7b}^x = -m_Y^2 M^{-1} (2 L_{66} L_{67} + L_{76} L_{77}) - 2^{-\frac{1}{2}} m_Y (m_X + 2 m_Y) M^{-1} (L_{66} L_{77} + L_{67} L_{76})$$

Here  $m_X$  and  $m_Y$  are atomic masses of atoms X and Y, respectively;  $M$  is the total mass of the molecule, and  $L_{ij}$  is used to denote the elements of the transformation matrix between symmetry and normal coordinates ( $S = LQ$ ).

Numerical results for the values of  $\zeta$  from the present calculations are given in Table 4.

Table 4. Coriolis coupling constants for xenon tetrafluoride.

$A_{2u} \times E_u$	$\zeta_{46a}^y = -\zeta_{46b}^x = 0.8847$ $\zeta_{47a}^y = -\zeta_{47b}^x = -0.4661$
$B_{2u} \times E_u$	$\zeta_{56a}^y = \zeta_{56b}^x = 0.4661$ $\zeta_{57a}^y = \zeta_{57b}^x = 0.8847$
$E_u(a) \times E_u(b)$	$\zeta_{6a6b}^x = -\zeta_{7a7b}^x = 0.5654$ $\zeta_{6a7b}^x = \zeta_{7a6b}^x = -0.8248$

## CENTRIFUGAL DISTORTION

Kivelson and Wilson<sup>19</sup> give the relation

$$W = W_0 - D_J J^2 (J + 1)^2 - D_{JK} J (J + 1) K^2 - D_K K^4$$

for the rotational energy  $W$  of a symmetric rotor. To obtain a more convenient unit for the constants  $D_J$ ,  $D_{JK}$ , and  $D_K$  the above equation is divided throughout by  $hc$  and rewritten as

$$W/hc = W_0/hc - D_J J^2 (J + 1)^2 - D_{JK} J (J + 1) K^2 - D_K K^4$$

The rotational constants  $D_J$ ,  $D_K$ , and  $D_{JK}$  are given by

$$\begin{aligned} D_J &= -\frac{1}{2} (3 t_{xxxx} + 3 t_{yyyy} + 2 t_{xxyy} + 4 t_{xyxy}) \\ D_K &= D_J - 4 (t_{zzzz} - t_{zzzz} - t_{yyzz} - 2 t_{zzzz} - 2 t_{yzyz}) \\ D_{JK} &= -D_J - D_K - 4 t_{zzzz} \end{aligned}$$

Here the coefficients of  $t$  are defined by

$$t_{\alpha\beta\gamma\delta} = h^2 (256\pi^4 c)^{-1} \tau_{\alpha\beta\gamma\delta}$$

where the  $\tau$  quantities are the same as those of Kivelson and Wilson.<sup>20</sup>

The expression for  $t_{\alpha\beta\gamma\delta}$  can be written as

$$t_{\alpha\beta\gamma\delta} = 2\pi^2 c h^{-1} B_{\alpha\alpha} B_{\beta\beta} B_{\gamma\gamma} B_{\delta\delta} \sum_i J_{\alpha\beta, Q^{(i)}} J_{\gamma\delta, Q^{(i)}} \omega_i^{-2}$$

Here the constants  $B_{\alpha\alpha}$ , etc. are the usual rotational constants for the equilibrium position of the molecule;

$$B_{\alpha\alpha} = h (8\pi^2 I_{\alpha\alpha})^{-1}$$

where  $I_{\alpha\alpha}$  is the moment of inertia with respect to the  $\alpha$ -axis.  $\omega_i$  denotes the  $i$ :th normal frequency ( $\text{cm}^{-1}$ ).  $J_{\alpha\beta, Q^{(i)}}$  is the first derivative of the appropriate component of the moment of inertia tensor with respect to the  $i$ :th normal coordinate ( $Q_i$ ) taken at the equilibrium position.

From the character table for the group  $D_{4h}$  one easily deduces that the only non-zero  $t_{\alpha\beta\gamma\delta}$  must be

$$t_{xxxx} = t_{yyyy}, t_{xxyy}, t_{zzzz}, t_{zzzz} = t_{yyzz} \text{ and } t_{xyxy},$$

One finds the following results.

$$\begin{aligned} t_{xxxx} &= t_{yyyy} = -8\pi^2 c h^{-1} B_{xx}^4 R^2 m_Y (\omega_1^{-2} + \omega_2^{-2}) \\ t_{xxyy} &= -8\pi^2 c h^{-1} B_{xx}^4 R^2 m_Y (\omega_1^{-2} - \omega_2^{-2}) \\ t_{xyxy} &= -8\pi^2 c h^{-1} B_{xx}^4 R^2 m_Y \omega_3^{-2} \\ t_{zzzz} &= -2\pi^2 c h^{-1} B_{xx}^4 R^2 m_Y \omega_1 \\ t_{zzzz} &= t_{yyzz} = 2 t_{zzzz} \end{aligned}$$

Subscripts 1, 2, and 3 refer to the  $A_{1g}$ ,  $B_{1g}$ , and  $B_{2g}$  species, respectively. Finally one obtains the following results for the rotational constants  $D_J$ ,  $D_K$ , and  $D_{JK}$  in the planar symmetrical  $XY_4$  molecule.

$$\begin{aligned} D_J &= -3 t_{xxxx} - t_{xxyy} - 2 t_{xyxy} \\ D_K &= D_J + 12 t_{zzzz} \\ D_{JK} &= -2 D_J - 16 t_{zzzz} \end{aligned}$$

which also gives the following relationship between the three constants

$$D_{JK} = -\frac{2}{3} (D_J + 2 D_K)$$

Numerical values for  $t_{\alpha\beta\gamma\delta}$ ,  $D_J$ ,  $D_K$ , and  $D_{JK}$  are presented in Table 5.

Experimental values of centrifugal distortion constants are often used as additional information for accurate determination of the force field of a molecule. In the present case, however, it is seen that such information would be of no use, since the two-dimensional  $E_u$  species gives no contribution to the  $\tau_{\alpha\beta\gamma\delta}$  quantities.

Table 5. Centrifugal distortion coefficients (in  $\text{cm}^{-1}$ ) for xenon tetrafluoride.

$t_{xxxx} = t_{yyyy}$	$= - 5.795 \times 10^{-9}$
$t_{xxxx} = t_{yyzz}$	$= - 1.335 \times 10^{-9}$
$t_{xyxy}$	$= \dots - 14.258 \times 10^{-9}$
$t_{zzzz}$	$= \dots - 0.668 \times 10^{-9}$
$t_{xyyy}$	$= \dots 0.454 \times 10^{-9}$
$D_J$	$= \dots 4.545 \times 10^{-8}$
$D_K$	$= \dots 3.743 \times 10^{-8}$
$D_{JK}$	$= \dots - 8.021 \times 10^{-8}$

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