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Spectroscopic Studies on Metal Carbonyls

IV. Coriolis Coupling for Metal Hexacarbonyls

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Further studies on the octahedral $W(XY)_6$ molecular model are reported. Algebraic expressions are given for the Coriolis C^{α} matrix elements. The large variety of quantities of ζ^{α} have been systematized, and numerical values are given for the hexacarbonyls of chromium and molybdeneum.

This is a continuation of the previous work [1] on the vibrations of metal hexacarbonyl type molecules. A precise definition of a complete set of symmetry coordinates is given in that paper,[1] being Part I of the present series. It is adhered to the same notation and definitions in the present work.

TYPES OF CORIOLIS COUPLING

The Coriolis coupling of rotation-vibration is described in terms of a ζ matrix.[2] It contains blocks with nonvanishing elements corresponding to certain combinations of symmetry species, which may be predicted by the methods of group theory.[3] In the present case, considering the $W(XY)_6$ model of O_h symmetry, there will be some arbitrariness in the definition of ζ^{α} ($\alpha = x, y, z$), depending on the orientation of degenerate coordinates. The given scheme (Table 1) applies to the previously adopted definitions.[1]

For each type (i)—(ix) of ζ^{α} it is sufficient to specify one single block, say (i) $A_{1g} \times F_{1ga}$, (ii) $E_{ga} \times F_{1ga}$, *etc.* Then any value of ζ^{α} may easily be found with the aid of Table 1, taking account of the factors given in parentheses. One has, for instance, in the first case (i) $A_{1g} \times F_{1g}$:

$$\zeta_{i\ ja}^{x} = \zeta_{i\ jb}^{x} = -\zeta_{i\ ja}^{y} = \zeta_{i\ jb}^{y} = -2^{\frac{1}{2}}\zeta_{i\ jc}^{z}$$

($i = 1, 2, j = 5$). Precisely the same relations hold for the C_{ij}^{α}, which will be specified in the next section.

CORIOLIS C^{α} MATRICES

A sufficient number of C_{i}^{α} elements to define the skew-symmetric C^{α} matrices ($\alpha = x,y,z$),[4] are specified in the following. To evaluate any other nonvanishing C_{ij}^{α} element, Table 1 should be consulted (see above).

Table 1. Types of Coriolis coupling in octahedral $W(XY)_6$ type molecules.

Type	x	y	z
(i) $A_{1g} \times F_{1g}$	$A_{1g} \times F_{1ga}$ $A_{1g} \times F_{1gb}$	$A_{1g} \times F_{1ga}(-1)$ $A_{1g} \times F_{1gb}$	$A_{1g} \times F_{1gc}(-2^{\frac{1}{2}})$
(ii) $E_{g} \times F_{1g}$	$E_{ga} \times F_{1ga}$ $E_{ga} \times F_{1gb}(-\frac{1}{2})$ $E_{gb} \times F_{1gb}(-\frac{1}{2}3^{\frac{1}{2}})$	$E_{ga} \times F_{1ga}(-1)$ $E_{ga} \times F_{1gb}(-\frac{1}{2})$ $E_{gb} \times F_{1gb}(-\frac{1}{2}3^{\frac{1}{2}})$	$E_{ga} \times F_{1gc}(2^{-\frac{1}{2}})$ $E_{gb} \times F_{1gc}(-\frac{1}{2}6^{\frac{1}{2}})$
(iii) $E_{g} \times F_{2g}$	$E_{ga} \times F_{2gb}$ $E_{gb} \times F_{2ga}(\frac{2}{3}3^{\frac{1}{2}})$ $E_{gb} \times F_{2gb}(-3^{-\frac{1}{2}})$	$E_{ga} \times F_{2gb}$ $E_{gb} \times F_{2ga}(-\frac{2}{3}3^{\frac{1}{2}})$ $E_{gb} \times F_{2gb}(-3^{-\frac{1}{2}})$	$E_{ga} \times F_{2gc}(-2^{\frac{1}{2}})$ $E_{gb} \times F_{2gc}(-\frac{1}{3}6^{\frac{1}{2}})$
(iv) $F_{1g} \times F_{1g}$	$F_{1ga} \times F_{1gc}$ $F_{1gb} \times F_{1gc}(-1)$	$F_{1ga} \times F_{1gc}$ $F_{1gb} \times F_{1gc}$	$F_{1ga} \times F_{1gb}(2^{\frac{1}{2}})$
(v) $F_{1g} \times F_{2g}$	$F_{1ga} \times F_{2gc}$ $F_{1gb} \times F_{2gc}$ $F_{1gc} \times F_{2ga}(-1)$ $F_{1gc} \times F_{2gb}(-1)$	$F_{1ga} \times F_{2gc}$ $F_{1gb} \times F_{2gc}(-1)$ $F_{1gc} \times F_{2ga}(-1)$ $F_{1gc} \times F_{2gb}$	$F_{1ga} \times F_{2gb}(2^{\frac{1}{2}})$ $F_{1gb} \times F_{2ga}(2^{\frac{1}{2}})$
(vi) $F_{1u} \times F_{1u}$	$F_{1ua} \times F_{1ub}$ $F_{1ua} \times F_{1uc}(-1)$	$F_{1ua} \times F_{1ub}(-1)$ $F_{1ua} \times F_{1uc}(-1)$	$F_{1ub} \times F_{1uc}(-2^{\frac{1}{2}})$
(vii) $F_{1u} \times F_{2u}$	$F_{1ua} \times F_{2ua}$ $F_{1ua} \times F_{2uc}$ $F_{1ub} \times F_{2ub}(-1)$ $F_{1uc} \times F_{2ub}(-1)$	$F_{1ua} \times F_{2ua}$ $F_{1ua} \times F_{2uc}(-1)$ $F_{1ub} \times F_{2ub}$ $F_{1uc} \times F_{2ub}(-1)$	$F_{1ub} \times F_{2ua}(-2^{\frac{1}{2}})$ $F_{1uc} \times F_{2uc}(-2^{\frac{1}{2}})$
(viii) $F_{2g} \times F_{2g}$	$F_{2ga} \times F_{2gc}$ $F_{2gb} \times F_{2gc}(-1)$	$F_{2ga} \times F_{2gc}$ $F_{2gb} \times F_{2gc}$	$F_{2ga} \times F_{2gb}(-2^{\frac{1}{2}})$
(ix) $F_{2u} \times F_{2u}$	$F_{2ua} \times F_{2ub}$ $F_{2ub} \times F_{2uc}$	$F_{2ua} \times F_{2ub}$ $F_{2ub} \times F_{2uc}(-1)$	$F_{2ua} \times F_{2uc}(-2^{\frac{1}{2}})$

Notation

μ_W, μ_X and μ_Y denote the inverse masses of the W, X and Y atoms, respectively.

$R =$ W—X equilibrium distance.

$D =$ X—Y equilibrium distance.

$\gamma = (R + D)\ (RD)^{-\frac{1}{2}}$

$\varkappa = (R/D)^{\frac{1}{2}}$

(i) $A_{1g} \times F_{1g}$

$C_{1}{}^{x}{}_{5a} = -\frac{1}{3}\, 6^{\frac{1}{2}}(\gamma\mu_X + \varkappa\mu_Y),\; C_{2}{}^{x}{}_{5a} = \frac{1}{3}\, 6^{\frac{1}{2}}\gamma\mu_X$

(ii) $E_g \times F_{1g}$

$C_{3a}{}^{x}{}_{5a} = 3^{-\frac{1}{2}}(\gamma\mu_X + \varkappa\mu_Y),\; C_{4a}{}^{x}{}_{5a} = -3^{-\frac{1}{2}}\gamma\mu_X$

(iii) $E_g \times F_{2g}$

$C_{3a}{}^{x}{}_{10b} = -\frac{1}{2}\, 3^{\frac{1}{2}}(\gamma\mu_X + \varkappa\mu_Y),\; C_{4a}{}^{x}{}_{10b} = \frac{1}{2}\, 3^{\frac{1}{2}}\gamma\mu_X$

$C_{3a}{}^{x}{}_{11b} = -C_{4a}{}^{x}{}_{11b} = -\frac{1}{2}\, 6^{\frac{1}{2}}\mu_X$

(iv) $F_{1g} \times F_{1g}$

$C_{5a}{}^{x}{}_{5c} = 2^{-\frac{1}{2}}(\gamma^2\mu_X + \varkappa^2\mu_Y)$

(v) $F_{1g} \times F_{2g}$

$C_{5a}{}^{x}{}_{10c} = -2^{-\frac{1}{2}}(\gamma^2\mu_X + \varkappa^2\mu_Y),\; C_{5a}{}^{x}{}_{11c} = -\gamma\mu_X$

(vi) $F_{1u} \times F_{1u}$ (symmetric block)

	$6b$	$7b$	$8b$	$9b$
$6a$	0	0	$-2^{-\frac{1}{2}}(\gamma\mu_X + \varkappa\mu_Y)$	$-2^{-\frac{1}{2}}\mu_X$
$7a$		$2^{\frac{1}{2}}\mu_W$	$2^{-\frac{1}{2}}(4\varkappa^{-1}\mu_W + \gamma\mu_X)$	$2^{-\frac{1}{2}}(4\mu_W + \mu_X)$
$8a$			$2^{-\frac{1}{2}}(8\varkappa^{-2} + \gamma^2\mu_X + \varkappa^2\mu_Y)$	$2^{-\frac{1}{2}}(8\varkappa^{-1}\mu_W + \gamma\mu_X)$
$9a$				$2^{-\frac{1}{2}}(8\mu_W + \mu_X)$

(vii) $F_{1u} \times F_{2u}$

$C_{6a}{}^{x}{}_{12a} = -2^{-\frac{1}{2}}(\gamma\mu_X + \varkappa\mu_Y),\; C_{8a}{}^{x}{}_{12a} = -2^{-\frac{1}{2}}(\gamma^2\mu_X + \varkappa^2\mu_Y)$

$C_{7a}{}^{x}{}_{12a} = -C_{9a}{}^{x}{}_{12a} = -C_{8a}{}^{x}{}_{13a} = 2^{-\frac{1}{2}}\gamma\mu_X$

$C_{6a}{}^{x}{}_{13a} = -C_{7a}{}^{x}{}_{13a} = C_{9a}{}^{x}{}_{13a} = -2^{-\frac{1}{2}}\mu_X$

(viii) $F_{2g} \times F_{2g}$

$C_{10a}{}^{x}{}_{10c} = 2^{-\frac{1}{2}}(\gamma^2\mu_X + \varkappa^2\mu_Y),\; C_{11a}{}^{x}{}_{11c} = 2^{\frac{1}{2}}\mu_X$

$C_{11a}{}^{x}{}_{10c} = C_{10a}{}^{x}{}_{11c} = \gamma\mu_X$

(ix) $F_{2u} \times F_{2u}$

$C_{12a}{}^{x}{}_{12b} = 2^{-\frac{1}{2}}(\gamma^2\mu_X + \varkappa^2\mu_Y),\; C_{13a}{}^{x}{}_{13b} = 2^{-\frac{1}{2}}\mu_X$

$C_{13a}{}^{x}{}_{12b} = C_{12a}{}^{x}{}_{13b} = 2^{-\frac{1}{2}}\gamma\mu_X$

CORIOLIS COUPLING COEFFICIENTS

The values of ζ^{α} have been computed for chromium and molybdenum hexacarbonyl, using the data previously reported.[1] The types (iv), (viii), and (ix) are of the trivial kind, while all the other ζ^{α} values appear to be force-constant dependent. For the numerical results, see Table 2.

RELATIONS BETWEEN CORIOLIS COUPLING COEFFICIENTS

The above explained relations between values of $\zeta_{ij}{}^{\alpha}$ refer to changes of degenerate coordinates, only. It should be noted that a number of other relations

Table 2. Coriolis coupling coefficients (ζ) for chromium and molybdenum hexacarbonyl.

Type	Values of $\zeta^x[i\ j]$		$Cr(CO)_6$	$Mo(CO)_6$
(i) $A_{1g} \times F_{1g}$	[1 5*a*]		−0.569	−0.569
	[2 5*a*]		0.100	0.095
(ii) $E_g \times F_{1g}$	[3*a* 5*a*]		0.402	0.402
	[4*a* 5*a*]		−0.071	−0.070
(iii) $E_g \times F_{2g}$	[3*a* 10*b*]		−0.597	−0.599
	[4*a* 10*b*]	[3*a* 11*b*]	0.135	0.129
	[4*a* 11*b*]		0.597	0.599
(iv) $F_{1g} \times F_{1g}$	[5*a* 5*c*]		0.354*	0.354*
(v) $F_{1g} \times F_{2g}$	[5*a* 10*c*]		−0.353	−0.353
	[5*a* 11*c*]		0.017	0.014
(vi) $F_{1u} \times F_{1u}$	[6*a* 6*b*]		0.007	0.011
	[7*a* 6*b*]	[6*a* 7*b*]	−0.390	−0.411
	[8*a* 6*b*]	[6*a* 8*b*]	−0.283	−0.266
	[9*a* 6*b*]	[6*a* 9*b*]	0.142	0.117
	[7*a* 7*b*]		0.482	0.456
	[8*a* 7*b*]	[7*a* 8*b*]	−0.109	−0.112
	[9*a* 7*b*]	[7*a* 9*b*]	0.155	0.146
	[8*a* 8*b*]		0.284	0.332
	[9*a* 8*b*]	[8*a* 9*b*]	−0.422	−0.417
	[9*a* 9*b*]		−0.066	−0.092
(vii) $F_{1u} \times F_{2u}$	[6*a* 12*a*]		−0.485	−0.484
	[7*a* 12*a*]		−0.258	−0.275
	[8*a* 12*a*]		−0.271	−0.253
	[9*a* 12*a*]		−0.018	−0.033
	[6*a* 13*a*]		0.113	0.108
	[7*a* 13*a*]		0.114	0.114
	[8*a* 13*a*]		−0.276	−0.262
	[9*a* 13*a*]		−0.522	−0.531
(viii) $F_{2g} \times F_{2g}$	[10*a* 10*c*]	[11*a* 11*c*]	0.354*	0.354*
	[11*a* 10*c*]	[10*a* 11*c*]	0(exact)	0(exact)
(ix) $F_{2u} \times F_{2u}$	[12*a* 12*b*]	[13*a* 13*b*]	0.354*	0.354*
	[13*a* 12*b*]	[12*a* 13*b*]	0(exact)	0(exact)

* Exactly $8^{-\frac{1}{2}}$.

exist between the here considered ζ-values, among which one finds the ζ-sums.[2,4,5] Here we give some of the relations.

(i) $(\zeta_1{}^x{}_{5a})^2 + (\zeta_2{}^x{}_{5a})^2 = \frac{1}{3}$
(ii) $(\zeta_{3a}{}^x{}_{5a})^2 + (\zeta_{4a}{}^x{}_{5a})^2 = \frac{1}{6}$
(iii) $\zeta_{3a}{}^x{}_{10b} + \zeta_{4a}{}^x{}_{11b} = 0,\ \zeta_{4a}{}^x{}_{10b} = \zeta_{3a}{}^x{}_{11b}$

$$\begin{vmatrix} \zeta_{3a}{}^x{}_{10b} & \zeta_{3a}{}^x{}_{11b} \\ \zeta_{4a}{}^x{}_{10b} & \zeta_{4a}{}^x{}_{11b} \end{vmatrix} = -\frac{3}{8}$$

(iv) $\zeta_{5a}{}^x{}_{5c} = 8^{-\frac{1}{2}}$ (force-constant independent)
(v) $(\zeta_{5a}{}^x{}_{10c})^2 + (\zeta_{5a}{}^x{}_{11c})^2 = \frac{1}{8}$
(vi) $\zeta_{6a}{}^x{}_{6b} + \zeta_{7a}{}^x{}_{7b} + \zeta_{8a}{}^x{}_{8b} + \zeta_{9a}{}^x{}_{9b} = 2^{-\frac{1}{2}}$

and additional relations, connecting off-diagonal elements.
(vii) Sum of the eight squared ζ's is $\frac{3}{4}$. Also additional relations exist.
(viii) and (ix) Force-constant independent:

$$\zeta_{10a}{}^x{}_{10c} = \zeta_{11a}{}^x{}_{11c} = \zeta_{12a}{}^x{}_{12b} = \zeta_{13a}{}^x{}_{13b} = 8^{-\frac{1}{2}}$$
$$\zeta_{10a}{}^x{}_{11c} = \zeta_{11a}{}^x{}_{10c} = \zeta_{12a}{}^x{}_{13b} = \zeta_{13a}{}^x{}_{12b} = 0$$

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