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Spectroscopic Studies on Metal Carbonyls

I. Treatment of Octahedral $W(XY)_6$ Molecules with Application to Chromium and Molybdenum Hexacarbonyls

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A set of symmetry coordinates and the corresponding G matrix elements are given for the octahedral $W(XY)_6$ molecular model. Computed force constants and L matrix elements are reported for the hexacarbonyls of chromium and molybdenum.

The molecular vibrations of metal carbonyls ought to be considered with special interest since the development of non-linear shrinkage effects.[1] As a matter of fact the octahedral $W(XY)_6$ molecular model, to which the metal hexacarbonyls are ascribed, provides an excellent example of shrinkage effects obtainable from harmonic-vibration analysis. This paper deals with the mentioned analysis, including the numerical results for chromium and molybdenum hexacarbonyls. The shrinkage effects calculated from the present data are to be published elsewhere. It is also planned to give an account of the Coriolis coupling of rotation-vibration of the presently considered molecules.

SYMMETRY COORDINATES

The octahedral $W(XY)_6$ molecular model belongs to the symmetry group O_h. Fig. 1 shows the numbering of atoms and the orientation of cartesian coordinates. The presently adopted symmetry coordinates are identical with those of Pistorius and Haarhoff[2] except for the linear bending coordinates, which only differ by a constant factor. In fact our coordinates Nos. 5, 8, 10, and 12 become equal to those of the mentioned work[2] when the latter are multiplied by $2^{\frac{1}{2}}$. Since the force constants refer to a chosen symmetry coordinate system, it seems essentially important to specify clearly the presently applied set. Pistorius and Haarhoff[2] have given the expressions in terms of the valence coordinates. In the following we give the symmetry coordinates in terms of the cartesian displacements.

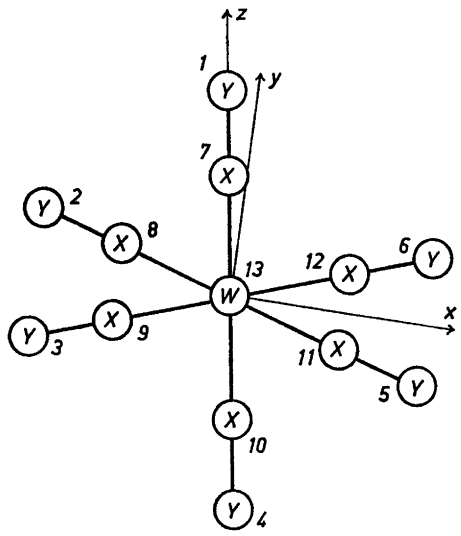

Fig. 1. Numbering of atoms, and orientation of cartesian coordinate axes for the octahedral $W(XY)_6$ molecule model.

Species A_{1g}

$$S_1 = 12^{-\frac{1}{2}}(-x_2 + y_2 - x_3 - y_3 + x_5 - y_5 + x_6 + y_6 + x_8 - y_8 + x_9 + y_9 - x_{11} + y_{11} - x_{12} - y_{12}) + 6^{-\frac{1}{2}}(z_1 - z_4 - z_7 + z_{10})$$

$$S_2 = 12^{-\frac{1}{2}}(-x_8 + y_8 - x_9 - y_9 + x_{11} - y_{11} + x_{12} + y_{12}) + 6^{-\frac{1}{2}}(z_7 - z_{10})$$

Species E_g

$$S_{3a} = 6^{-\frac{1}{2}}(-x_2 + y_2 + \tfrac{1}{2}x_3 + \tfrac{1}{2}y_3 + x_5 - y_5 - \tfrac{1}{2}x_6 - \tfrac{1}{2}y_6 + x_8 - y_8 - \tfrac{1}{2}x_9 - \tfrac{1}{2}y_9 - x_{11} + y_{11} + \tfrac{1}{2}x_{12} + \tfrac{1}{2}y_{12}) + 12^{-\frac{1}{2}}(-z_1 + z_4 + z_7 - z_{10})$$

$$S_{4a} = 6^{-\frac{1}{2}}(-x_8 + y_8 + \tfrac{1}{2}x_9 + \tfrac{1}{2}y_9 + x_{11} - y_{11} - \tfrac{1}{2}x_{12} - \tfrac{1}{2}y_{12}) + 12^{-\frac{1}{2}}(-z_7 + z_{10})$$

$$S_{3b} = 8^{-\frac{1}{2}}(x_3 + y_3 - x_6 - y_6 - x_9 - y_9 + x_{12} + y_{12}) + \tfrac{1}{2}(z_1 - z_4 - z_7 + z_{10})$$

$$S_{4b} = 8^{-\frac{1}{2}}(x_9 + y_9 - x_{12} - y_{12}) + \tfrac{1}{2}(z_7 - z_{10})$$

Species F_{1g}

$$S_{5a} = \tfrac{1}{2}(R/D)^{\frac{1}{2}}(x_1 + y_1 - x_4 - y_4) + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(z_3 - z_6) + \tfrac{1}{2}\gamma(-x_7 - y_7 + x_{10} + y_{10}) + 2^{-\frac{1}{2}}\gamma(-z_9 + z_{12})$$

$$S_{5b} = \tfrac{1}{2}(R/D)^{\frac{1}{2}}(-x_1 + y_1 + x_4 - y_4) + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(-z_2 + z_5) + \tfrac{1}{2}\gamma(x_7 - y_7 - x_{10} + y_{10}) + 2^{-\frac{1}{2}}\gamma(z_8 - z_{11})$$

$$S_{5c} = \tfrac{1}{2}(R/D)^{\frac{1}{2}}(-x_2 - y_2 + x_3 - y_3 + x_5 + y_5 - x_6 + y_6) + \tfrac{1}{2}\gamma(x_8 + y_8 - x_9 + y_9 - x_{11} - y_{11} + x_{12} - y_{12})$$

Species F_{1u}

$$S_{6a} = 2^{-\frac{1}{2}}(z_1 + z_4 - z_7 - z_{10})$$

$$S_{7a} = 2^{-\frac{1}{2}}(z_7 + z_{10} - 2z_{13})$$

$$S_{8a} = 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(-z_2 - z_3 - z_5 - z_6) + 2^{-\frac{1}{2}}\gamma(z_8 + z_9 + z_{11} + z_{12}) - 8^{\frac{1}{2}}(D/R)^{\frac{1}{2}}z_{13}$$

$$S_{9a} = 2^{-\frac{1}{2}}(z_8 + z_9 + z_{11} + z_{12} - 4z_{13})$$

$S_{6b} = \frac{1}{2}(-x_3 - y_3 - x_6 - y_6 + x_9 + y_9 + x_{12} + y_{12})$
$S_{7b} = \frac{1}{2}(-x_9 - y_9 - x_{12} - y_{12} + 2x_{13} + 2y_{13})$
$S_{8b} = \frac{1}{2}(R/D)^{\frac{1}{2}}(x_1 + y_1 + x_2 + y_2 + x_4 + y_4 + x_5 + y_5) + \frac{1}{2}\gamma(-x_7 - y_7 - x_8 - y_8 - x_{10} - y_{10} - x_{11} - y_{11}) + 2(D/R)^{\frac{1}{2}}(x_{13} + y_{13})$
$S_{9b} = \frac{1}{2}(-x_7 - y_7 - x_8 - y_8 - x_{10} - y_{10} - x_{11} - y_{11} + 4x_{13} + 4y_{13})$
$S_{6c} = \frac{1}{2}(-x_2 + y_2 - x_5 + y_5 + x_8 - y_8 + x_{11} - y_{11})$
$S_{7c} = \frac{1}{2}(-x_8 + y_8 - x_{11} + y_{11} + 2x_{13} - 2y_{13})$
$S_{8c} = \frac{1}{2}(R/D)^{\frac{1}{2}}(x_1 - y_1 + x_3 - y_3 + x_4 - y_4 + x_6 - y_6) + \frac{1}{2}\gamma(-x_7 + y_7 - x_9 + y_9 - x_{10} + y_{10} - x_{12} + y_{12}) + 2(D/R)^{\frac{1}{2}}(x_{13} - y_{13})$
$S_{9c} = \frac{1}{2}(-x_7 + y_7 - x_9 + y_9 - x_{10} + y_{10} - x_{12} + y_{12} + 4x_{13} - 4y_{13})$

Species F_{2g}

$S_{10a} = \frac{1}{2}(R/D)^{\frac{1}{2}}(x_1 + y_1 - x_4 - y_4) + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(-z_3 + z_6) + \frac{1}{2}\gamma(-x_7 - y_7 + x_{10} + y_{10}) + 2^{-\frac{1}{2}}\gamma(z_9 - z_{12})$
$S_{11a} = 2^{-\frac{1}{2}}(-x_7 - y_7 + x_{10} + y_{10}) + z_9 - z_{12}$
$S_{10b} = \frac{1}{2}(R/D)^{\frac{1}{2}}(x_1 - y_1 - x_4 + y_4) + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(-z_2 + z_5) + \frac{1}{2}\gamma(-x_7 + y_7 + x_{10} - y_{10}) + 2^{-\frac{1}{2}}\gamma(z_8 - z_{11})$
$S_{11b} = 2^{-\frac{1}{2}}(-x_7 + y_7 + x_{10} - y_{10}) + z_8 - z_{11}$
$S_{10c} = \frac{1}{2}(R/D)^{\frac{1}{2}}(-x_2 - y_2 - x_3 + y_3 + x_5 + y_5 + x_6 - y_6) + \frac{1}{2}\gamma(x_8 + y_8 + x_9 - y_9 - x_{11} - y_{11} - x_{12} + y_{12})$
$S_{11c} = 2^{-\frac{1}{2}}(x_8 + y_8 + x_9 - y_9 - x_{11} - y_{11} - x_{12} + y_{12})$

Species F_{2u}

$S_{12a} = \frac{1}{2}(R/D)^{\frac{1}{2}}(-x_1 + y_1 + x_3 - y_3 - x_4 + y_4 + x_6 - y_6) + \frac{1}{2}\gamma(x_7 - y_7 - x_9 + y_9 + x_{10} - y_{10} - x_{12} + y_{12})$
$S_{13a} = \frac{1}{2}(x_7 - y_7 - x_9 + y_9 + x_{10} - y_{10} - x_{12} + y_{12})$
$S_{12b} = 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}(z_2 - z_3 + z_5 - z_6) + 2^{-\frac{1}{2}}\gamma(-z_8 + z_9 - z_{11} + z_{12})$
$S_{13b} = 2^{-\frac{1}{2}}(-z_8 + z_9 - z_{11} + z_{12})$
$S_{12c} = \frac{1}{2}(R/D)^{\frac{1}{2}}(x_1 + y_1 - x_2 - y_2 + x_4 + y_4 - x_5 - y_5) + \frac{1}{2}\gamma(-x_7 - y_7 + x_8 + y_8 - x_{10} - y_{10} + x_{11} + y_{11})$
$S_{13c} = \frac{1}{2}(-x_7 - y_7 + x_8 + y_8 - x_{10} - y_{10} + x_{11} + y_{11})$

For the applied notation, see below.

G MATRIX

The Wilson *G* matrix based on the presently chosen symmetry coordinates is given in the following, where a sufficient number of elements is specified. (Notice that $G_{ij} = G_{ji}$, and all off-diagonal elements between coordinates of different species vanish.)

Notation

μ_W, μ_X and μ_Y are the inverse masses of the central atom (W), inner octahedron atoms (X), and the outer atoms (Y), respectively.

R = W-X equilibrium distance
D = X-Y equilibrium distance
$\gamma = (R + D)\ (RD)^{-\frac{1}{2}}$

Species A_{1g} *and* E_g (identical blocks)

$G_{11} = G_{33} = \mu_X + \mu_Y,\ G_{12} = G_{34} = -\mu_X,\ G_{22} = G_{44} = \mu_X$

Species F_{1g}

$G_{55} = 2\gamma^2\ \mu_X + 2(R/D)\mu_Y$

Species F_{1u}

$G_{66} = \mu_X + \mu_Y,\ G_{67} = -\mu_X,\ G_{68} = G_{69} = 0$
$G_{77} = 2\mu_W + \mu_X,\ G_{78} = 4(D/R)^{\frac{1}{2}}\mu_W,\ G_{79} = 4\mu_W$
$G_{88} = 8(D/R)\mu_W + 2\gamma^2\ \mu_X + 2(R/D)\ \mu_Y,\ G_{89} = 8(R/D)^{\frac{1}{2}}\mu_W + 2\gamma\mu_X$
$G_{99} = 8\mu_W + 2\mu_X$

Species F_{2g}

$G_{10\ 10} = 2\gamma^2\mu_X + 2(D/R)\mu_Y,\ G_{10\ 11} = 8^{\frac{1}{2}}\gamma\mu_X,\ G_{11\ 11} = 4\mu_X$

Species F_{2u}

$G_{12\ 12} = 2\gamma^2\mu_X + 2(D/R)\mu_Y,\ G_{12\ 13} = 2\gamma\mu_X,\ G_{13\ 13} = 2\mu_X$

Table 1. Force constants (mdyne/Å).

Symbol*	$Cr(CO)_6$	$Mo(CO)_6$
F_{11}	17.04	17.50
F_{22}	2.68	2.48
F_{33}	15.65	15.87
F_{44}	2.41	1.91
F_{55}	0.187	0.141
F_{66}	15.54	15.66
F_{77}	1.74	1.45
F_{79}	0.132	0.297
F_{88}	0.193	0.155
F_{99}	0.115	0.139
$F_{10\ 10}$	0.210	0.178
$F_{11\ 11}$	0.069	0.051
$F_{12\ 12}$	0.193	0.155
$F_{13\ 13}$	0.108	0.078

* Values assumed equal to zero are not included.

Table 2. L matrix elements ($Amu^{-1/2}$) and vibrational frequencies (cm^{-1})*.

	$Cr(CO)_6$		$Mo(CO)_6$	
	2108	393	2131	379
S_1	0.381	0.0167	0.382	0.0151
S_2	−0.226	0.179	−0.225	0.180
	$Cr(CO)_6$		$Mo(CO)_6$	
	2019	373	2022	334
S_3	0.381	0.0164	0.382	0.0129
S_4	−0.226	0.179	−0.224	0.182
	$Cr(CO)_6$		$Mo(CO)_6$	
	539		477	
S_5	0.957		0.976	
$Cr(CO)_6$	2000	661	436	102
S_6	0.381	0.0139	−0.0141	−0.000662
S_7	−0.232	0.154	−0.209	−0.0276
S_8	−0.0182	0.914	0.413	−0.0496
S_9	−0.0184	0.518	0.00292	0.228
$Mo(CO)_6$	2000	595	368	80
S_6	0.382	0.0121	−0.0103	−0.000395
S_7	−0.227	0.115	−0.192	−0.0507
S_8	−0.0176	0.909	0.414	−0.0366
S_9	−0.0137	0.453	0.0147	0.211
	$Cr(CO)_6$		$Mo(CO)_6$	
	598	90	557	80
S_{10}	0.956	−0.0451	0.975	−0.0398
S_{11}	0.520	0.250	0.515	0.260
	$Cr(CO)_6$		$Mo(CO)_6$	
	570	80	517	70
S_{12}	0.957	−0.0385	0.975	−0.0349
S_{13}	0.367	0.179	0.353	0.186

* Frequencies taken from Kawai and Murata.[3]

FORCE CONSTANTS

In order to calculate a set of force constants from the vibrational frequencies [3] alone, a number of assumptions must be made. Presently the following approximations were adopted:

(i) All off-diagonal elements except F_{79} were put equal to zero.
(ii) $F_{88} = F_{12\ 12}$.

These approximations conform with the Urey-Bradley treatment of Kawai and Murata.[3] The force constants can now be found by the GF matrix method of Wilson.[4] For the F_{1u} species the force constants were determined by an

iterations method, starting with the Kawai and Murata values, which had to be transformed to consist with our definitions.

The computed force constants are given in Table 1.

L MATRIX ($S = LQ$)

The normal-coordinate transformation matrices L were determined by the familiar secular-equation method.[4] In contrast to Kawai and Murata[3] we did not find it necessary to perform the approximation of separating high and low frequencies.

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