Normal Vibrations and Thermodynamic Properties of Chromium and Molybdenum Hexacarbonyls

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Hawkins, Mattraw, Sabol and Carpenter¹⁾ have observed successfully infrared spectra of chromium and molybdenum hexacarbonyls in gaseous state and have made an attempt to obtain Raman spectra of molybdenum hexacarbonyl. Recently, Danti and Cotton²⁾ have reported Raman spectra of those and tungsten hexacarbonyls using chloroform as solvent. The molecular structure by electron diffraction has been reported by Brockway, Evens and Lister³⁾, and by X-ray diffraction by Rudorf and Fofmann⁴⁾, and it has been clear for the molecule to have O_h-symmetry. The assignments of the observed frequencies have been made by these investigators and the thermodynamic properties have been calculated by Hawkins, Mattraw, Sabor and Carpenter¹⁾.

Out of thirteen fundamental vibrations resulting from the O_h-symmetry of the $M(XY)_6$ type of molecule only four fundamental vibrations are infrared active, and the lowest frequency of them, which has considerably great contribution to thermodynamic properties is out of the region of the observation by a usual spectrometer. In connection with the other metal carbonyls previously reported⁵⁾ and now proceeding*, the present paper** deals with a normal coordinate analysis for chromium and molybdenum hexacarbonyls to establish the more reliable assignments of vibrational frequencies and to compute the potential constants which may afford some information concerning the nature of the metal-carbonyl and carbonyl bonds in those compounds. The thermodynamic properties based on these assignments were calculated.

Normal Coordinate Treatment

The method of group theory shows that, as explained by Hawkins, Mattraw, Sabol and Carpenter¹⁾, thirty-three normal modes of vibration of the octahedral $M(XY)_6$ type molecule are reduced to two of a_{1g}, two of e_g, one of f_{1g}, four of f_{1u}, two of f_{2g} and two of f_{2u}, and a_{1g}, e_g and f_{2g} species are active in Raman and f_{1u} species in infrared. The f_{1g} and f_{2u} species are inactive in both.

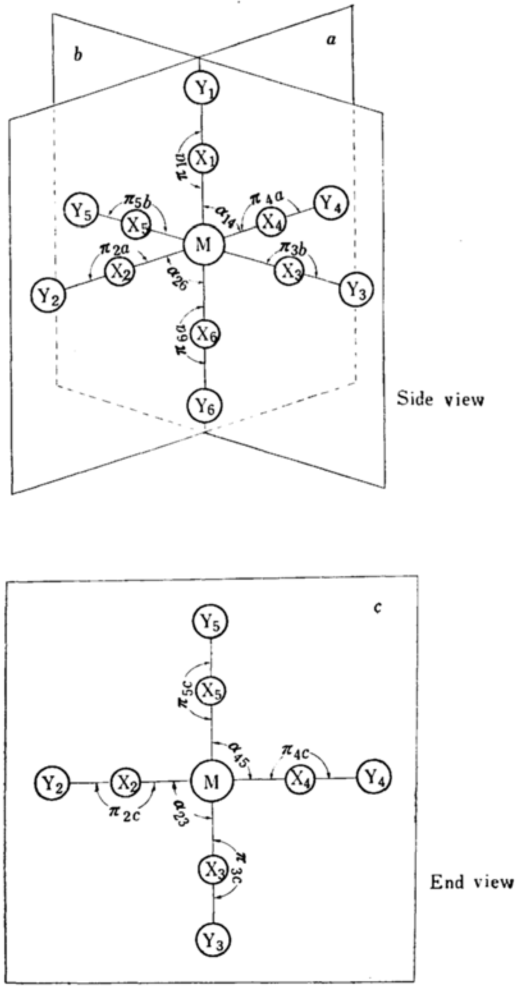

Fig. 1. Internal coordinates of $M(XY)_6$ molecule.

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1) N. J. Hawkins, H. C. Mattraw, W. W. Sabol and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).

2) A. Danti and F. A. Cotton, ibid., **28**, 736 (1958).

3) L. O. Brockway, R. V. G. Evens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

4) W. Rudorf and U. Fofmann, *Z. physik Chem.*, **B28**, 351 (1935).

5) H. Murata and K. Kawai, *J. Chem. Phys.*, **26**, 1355 (1957); K. Kawai and H. Murata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 496 (1957).

* A normal coordinate treatment of iron pentacarbonyl is being carried out in our laboratory. A part of the study has already been reported by H. Murata and K. Kawai, *J. Chem. Phys.*, **28**, 516 (1958).

** A part of this work has been reported by H. Murata and K. Kawai, *J. Chem. Phys.*, **27**, 605 (1957).

The general secular equation may be obtained by means of the Wilson's method[6]. The internal coordinates of $M(XY)_6$ molecule of this type are as follows:

$$d(\mathrm{M}-\mathrm{X}_i)=x_i \qquad d(\mathrm{X}_i-\mathrm{Y}_i)=y_i$$
$$\angle(\mathrm{M}-\mathrm{X}_i-\mathrm{Y}_i)_{\text{lying in } j\text{th plane}}=\pi_{ij}$$
$$\angle(\mathrm{X}_i-\mathrm{M}-\mathrm{X}_j)=\alpha_{ij}$$

Fig. 1 illustrates the above internal coordinates.

The symmetry coordinates were set up from these internal coordinates as follows:

For a_{1g} species:

$$R_1=1/\sqrt{6}\,(\Delta y_1+\Delta y_2+\Delta y_3+\Delta y_4+\Delta y_5+\Delta y_6)$$
$$R_2=1/\sqrt{6}\,(\Delta x_1+\Delta x_2+\Delta x_3+\Delta x_4+\Delta x_5+\Delta x_6)$$

For e_g species:

$$R_{3a}=1/\sqrt{12}(2\Delta y_1-\Delta y_2-\Delta y_3-\Delta y_4-\Delta y_5+2\Delta y_6)$$
$$R_{4a}=1/\sqrt{12}(2\Delta x_1-\Delta x_2-\Delta x_3-\Delta x_4-\Delta x_5+2\Delta x_6)$$

For f_{1g} species:

$$R_{5a}=1/2(\Delta\pi_{1a}-\Delta\pi_{2a}+\Delta\pi_{4a}-\Delta\pi_{6a})$$

For f_{1u} species:

$$R_{6a}=1/2(\Delta y_1+\Delta y_2-\Delta y_4-\Delta y_6)$$
$$R_{7a}=1/\sqrt{8}\,(\Delta\pi_{1a}+\Delta\pi_{2a}+\Delta\pi_{3b}-\Delta\pi_{3c}+\Delta\pi_{4a}+\Delta\pi_{5b}+\Delta\pi_{5c}+\Delta\pi_{6a})$$
$$R_{8a}=1/2(\Delta x_1+\Delta x_2-\Delta x_4-\Delta x_6)$$
$$R_{9a}=1/4(2\Delta\alpha_{12}+\Delta\alpha_{13}+\Delta\alpha_{15}+\Delta\alpha_{23}+\Delta\alpha_{25}-\Delta\alpha_{34}-\Delta\alpha_{36}-\Delta\alpha_{45}-\Delta\alpha_{56}-2\Delta\alpha_{46})$$

For f_{2g} species:

$$R_{10a}=1/2(\Delta\pi_{1a}+\Delta\pi_{2a}-\Delta\pi_{4a}-\Delta\pi_{6a})$$
$$R_{11a}=1/2(\Delta\alpha_{12}-\Delta\alpha_{14}-\Delta\alpha_{26}+\Delta\alpha_{46})$$

For f_{2ua} species:

$$R_{12a}=1/\sqrt{8}\,(\Delta\pi_{1a}+\Delta\pi_{2a}-\Delta\pi_{3b}+\Delta\pi_{3c}+\Delta\pi_{4a}-\Delta\pi_{5b}-\Delta\pi_{5c}+\Delta\pi_{6a})$$
$$R_{13a}=1/4\,(2\Delta\alpha_{12}-\Delta\alpha_{13}-\Delta\alpha_{15}-\Delta\alpha_{23}-\Delta\alpha_{25}+\Delta\alpha_{34}+\Delta\alpha_{36}+\Delta\alpha_{45}+\Delta\alpha_{56}-2\Delta\alpha_{46})$$

Using the table of Decius[7] and for the M−X−Y bending the method by Ferigle and Meister[8] **G** matrices were evaluated. In therms of the abbreviations ρ and τ for reciprocal of the bond lengths x and y, respectively, and μ_M, μ_X and μ_Y for the reciprocals of the atomic masses, the following **G** matrix elements were obtained***:

For a_{1g} species:

$$\boldsymbol{G}_{11}=\mu_X+\mu_Y,\quad \boldsymbol{G}_{12}=-\mu_X,\quad \boldsymbol{G}_{22}=\mu_X$$

For e_g species:

$$\boldsymbol{G}_{33}=\boldsymbol{G}_{11}(a_{1g}),\quad \boldsymbol{G}_{34}=\boldsymbol{G}_{12}(a_{1g}),$$
$$\boldsymbol{G}_{44}=\boldsymbol{G}_{22}(a_{1g})$$

For f_{1g} species:

$$\boldsymbol{G}_{55}=(\rho+\tau)^2\mu_X+\tau^2\mu_Y$$

For f_{1u} species:

$$\boldsymbol{G}_{66}=\boldsymbol{G}_{11}(a_{1g}),\quad \boldsymbol{G}_{67}=\boldsymbol{G}_{69}=0,$$
$$\boldsymbol{G}_{68}=\boldsymbol{G}_{12}(a_{1g}),$$
$$\boldsymbol{G}_{77}=4\rho^2\mu_M+(\rho+\tau)^2\mu_X+\tau^2\mu_Y,$$
$$\boldsymbol{G}_{78}=\sqrt{8}\,\rho\mu_M,$$
$$\boldsymbol{G}_{79}=-\sqrt{2}\{4\rho^2\mu_M+(\rho^2+\rho\tau)\mu_X\},$$
$$\boldsymbol{G}_{88}=2\mu_M+\mu_X,\quad \boldsymbol{G}_{89}=-4\rho\mu_M,$$
$$\boldsymbol{G}_{99}=2\rho^2(4\mu_M+\mu_X)$$

For f_{2g} species:

$$\boldsymbol{G}_{1010}=\boldsymbol{G}_{55}(f_{1g}),$$
$$\boldsymbol{G}_{1011}=-2(\rho^2+\rho\tau)\mu_X,\quad \boldsymbol{G}_{1111}=4\rho^2\mu_X$$

For f_{2u} species:

$$\boldsymbol{G}_{1212}=\boldsymbol{G}_{55}(f_{1g}),$$
$$\boldsymbol{G}_{1213}=-\sqrt{2}\,(\rho^2+\rho\tau)\mu_X,$$
$$\boldsymbol{G}_{1313}=2\rho^2\mu_x$$

Following the method of Shimanouchi[9], the Urey-Bradley type quadratic potential energy function for octahedral $M(XY)_6$ molecule may be written as:

$$\begin{aligned}2V=&\sum_{i=1}^{6}\{K(\mathrm{M}-\mathrm{X})+2[F(\mathrm{X}\cdots\mathrm{X})\\&+F'(\mathrm{X}\cdots\mathrm{X})]\}(\Delta x_i)^2\\&+\sum_{i=1}^{6}K(\mathrm{X}-\mathrm{Y})(\Delta y_i)^2\\&+\sum_{i<j=1}^{6}\{H(\mathrm{X}-\mathrm{M}-\mathrm{X})+1/2[F(\mathrm{X}\cdots\mathrm{X})\\&-F'(\mathrm{X}\cdots\mathrm{X})]\}(x_0\Delta\alpha_{ij})^2\\&+\sum_{i=1}^{6}\sum_{l=a}^{c}H(\mathrm{M}-\mathrm{X}-\mathrm{Y})(\sqrt{x_0y_0}\Delta\pi_{il})^2\\&+2\sum_{i<j=1}^{6}1/2[F(\mathrm{X}\cdots\mathrm{X})\end{aligned}$$

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6) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939), **9**, 76 (1941).

7) J. C. Decius, ibid., **16**, 1025 (1948).

8) S. M. Ferigle and A. G. Meister, ibid., **19**, 982 (1951).

*** There is one misprint in the **G** matrix elements presented by H. Murata and K. Kawai, *J. Chem. Phys.*, **26**, 605 (1957), *viz* $\boldsymbol{G}_{24}$ in f_{1u} species which corresponds to $\boldsymbol{G}_{79}$ of this paper.

9) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

$$-F'(\mathrm{X}\cdots\mathrm{X})]\,(\varDelta x_i)(\varDelta x_j)$$

$$+2\sum_{i<j=1}^{6}1/2\,[F(\mathrm{X}\cdots\mathrm{X})$$

$$+F'(\mathrm{Y}\cdots\mathrm{X})]\,(\varDelta x_i)(x_0\varDelta\alpha_{ij})$$

$$+2\sum_{i\neq j\neq k=1}^{6}1/(2x_0^2)\,\kappa\,(x_0\varDelta\alpha_{ij})(x_0\varDelta\alpha_{ik})$$

where x_0 and y_0 are the equilibrium $\mathrm{M-X}$ and $\mathrm{X-Y}$ bond distances respectively; K, H, F and F' are the potential constants and κ the intra-molecular tension whose definition and physical meaning were expressed by Shimanouchi[9].

The intra-molecular tension for the octahedral MX_6 type molecule can easily be derived from the following relation obtained for the octahedral geometrical structure

$$\sum(\varDelta\alpha_{ij})+1/2\sum(\varDelta\alpha_{ij})(\varDelta\alpha_{ik})=0$$

where the first summation extends for all of the twelve angles and the second for all the forty-eight sets of adjacent angles.

The potential energy matrix elements evaluated from the above potential function are as follows:

For a_{1g} species:

$$\boldsymbol{F}_{11}=K(\mathrm{X-Y}),\quad \boldsymbol{F}_{12}=0,$$

$$\boldsymbol{F}_{22}=K(\mathrm{M-X})+4F(\mathrm{X}\cdots\mathrm{X})$$

For e_g species:

$$\boldsymbol{F}_{33}=\boldsymbol{F}_{11}(\mathrm{a_{1g}}),\quad \boldsymbol{F}_{34}=0,$$

$$\boldsymbol{F}_{44}=K(\mathrm{M-X})+0.7F(\mathrm{X}\cdots\mathrm{X})$$

For f_{1g} species:

$$\boldsymbol{F}_{55}=x_0y_0H(\mathrm{M-X-Y})$$

For f_{1u} species:

$$\boldsymbol{F}_{66}=\boldsymbol{F}_{11}(\mathrm{a_{1g}}),\quad \boldsymbol{F}_{77}=\boldsymbol{F}_{55}(\mathrm{f_{1g}}),$$

$$\boldsymbol{F}_{88}=K(\mathrm{M-X})+1.8F(\mathrm{X}\cdots\mathrm{X}),$$

$$\boldsymbol{F}_{89}=0.9x_0F(\mathrm{X}\cdots\mathrm{X}),$$

$$\boldsymbol{F}_{99}=x_0^2\,[H(\mathrm{X-M-X})+0.55F(\mathrm{X}\cdots\mathrm{X})]+\kappa,$$

$$\boldsymbol{F}_{67}=\boldsymbol{F}_{68}=\boldsymbol{F}_{69}=\boldsymbol{F}_{78}=\boldsymbol{F}_{79}=0$$

For f_{2g} species:

$$\boldsymbol{F}_{1010}=\boldsymbol{F}_{55}(\mathrm{f_{1g}}),\quad \boldsymbol{F}_{1011}=0,$$

$$\boldsymbol{F}_{1111}=x_0^2\,[H(\mathrm{X-M-X})+0.55F(\mathrm{X}\cdots\mathrm{X})]$$

For f_{2u} species:

$$\boldsymbol{F}_{1212}=\boldsymbol{F}_{55}(\mathrm{f_{1g}}),\quad \boldsymbol{F}_{1213}=0,$$

$$\boldsymbol{F}_{1313}=x_0^2\,[H(\mathrm{X-M-X})+0.55F(\mathrm{X}\cdots\mathrm{X})]-\kappa$$

In the above elements it was assumed experimentally that $F'=-1/10F$, and consequently six potential constants are used here.

TABLE I. MOLECULAR CONSTANTS FOR $Cr(CO)_6$ AND $Mo(CO)_6$[a]

Bond	$Cr(CO)_6$	$Mo(CO)_6$
M[b]—C	1.92 Å	2.08 Å
C—O	1.16 Å	1.15 Å

Symmetry number……24 for all fundamentals

a From Ref. 3.

b M denotes Cr or Mo.

TABLE II. POTENTIAL CONSTANTS FOR $Cr(CO)_6$ AND $Mo(CO)_6$ (mdyn./Å)

Type	$Cr(CO)_6$	$Mo(CO)_6$
K(C—O)	16.2	16.02
K(M—C)	1.83	1.77
H(M—C—O)	0.41	0.34
H(C—M—C)	0.03	0.02
F(C···C)	0.15	0.12
$\kappa(MC_6)$	0.02 Å²	0.02 Å²

TABLE III. COMPARISON OF OBSERVED AND CALCULATED FUNDAMENTALS FOR $Cr(CO)_6$ AND $Mo(CO)_6$

Assignment			$Cr(CO)_6$		$Mo(CO)_6$	
Type	Fundamental	Description	Calc.	Obs.	Calc.	Obs.
a_{1g}:	σ_1	ν(C—O)	2042	2108	2037	2131
	σ_2	ν(M—C)	374	393	361	379
e_g:	σ_3	ν(C—O)	2031	2019	2029	2022
	σ_4	ν(M—C)	336	373	329	334
f_{1g}:	σ_5	δ(M—C—O)	564	539	524	477
f_{1u}:	σ_6	ν(C—O)	1992[c]	2000	1992[c]	2000
	σ_7	δ(M—C—O)	636	661	560	595
	σ_8	ν(M—C)	475	436	422	368
	σ_9	δ(C—M—C)	113	102	95	80
f_{2g}:	σ_{10}	δ(M—C—O)	608	598[b]	560	557[b]
	σ_{11}	δ(C—M—C)	111	90	101	80
f_{2u}:	σ_{12}	δ(M—C—O)	586	570[b]	541	517[b]
	σ_{13}	δ(C—M—C)	81	80	72	70

a Obtained from the values of the **L** matrix elements.

b Inferred from combination or overtone bands.

c Obtained by the method of high-frequency separation.

To evaluate numerically the above elements, the bond lengths listed in Table I and the atomic masses on a physical scale were used.

Discussion

A comparison of the normal frequencies calculated from the set of potential constants in Table II with those observed by Hawkins, Mattraw, Sabol and Carpenter[1] are summarized in Table III. The numbering of the frequencies is the same as that used by Hawkins et al.[1]

The agreement between the calculated and the observed frequencies is satisfactory except for the M—C—O bending vibrations. The present results from the Urey-Bradley type potential function in which all the M—C—O bending interaction constants are not included indicated that 213 and 310 cm^{-1} bands assigned to σ_{10} and σ_{12} respectively by Hawkins, Matraw, Sabol and Carpenter[1] and 137.1 cm^{-1} band to σ_{10} by Danti and Cotton[2] for chromium hexacarbonyl and 230 and 327 cm^{-1} bands by the former[1] and 135.7 cm^{-1} band by the latter[2] for molybdenum hexacarbonyl are too small for M—C—O bending vibrational frequencies. Based on this point of view, all of the observed bands by Hawkins, Matraw, Sabol and Carpenter[1] except for only three strong bands which may be designated as fundamentals, were reassigned as shown in Table IV for chromium hexacarbonyl and Table V for molybdenum hexacarbonyl.

TABLE IV. INFRARED BANDS OF GASEOUS $Cr(CO)_6$

Frequency (cm^{-1})	Intensity	Assignment	Calc. (cm^{-1})
4098	m	$\sigma_1+\sigma_6$	4108
4000	m	$\sigma_3+\sigma_6$	4019
2688	w	$\sigma_3+\sigma_7$	2680
2554	w	$\sigma_1+\sigma_8$, $\sigma_5+\sigma_6$	2544, 2539
2466	m	$\sigma_3+\sigma_8$	2455
2393	s	$\sigma_2+\sigma_6$	2393
2336	sh	q	
2212	w	$\sigma_1+\sigma_9$	2210
2174	w	q	
2121	s	$\sigma_3+\sigma_9$	2121
2090	s	$\sigma_6+\sigma_{11}$, $\sigma_3+\sigma_{13}$	2090, 2099
2033	sh	q	
2000	vs	σ_6	
1970	sh	q	
1912	m	$\sigma_3-\sigma_9$, $\sigma_6-\sigma_{11}$	1917, 1910
1631	w	$\sigma_6-\sigma_4$	1627
1196	s	$\sigma_5+\sigma_7$	1200
1055	sh	$\sigma_2+\sigma_7$	1054
1032	s	$\sigma_4+\sigma_7$, $\sigma_8+\sigma_{10}$	1034, 1034
963	m	$\sigma_5+\sigma_8$	975
875	s	q	
811	s	$\sigma_4+\sigma_8$	809
755	m	$\sigma_7+\sigma_{11}$	751
673	sh	$\sigma_{10}+\sigma_{13}$	678
661	vs	σ_7	
635	s (sh)	$\sigma_5+\sigma_9$	641
595	sh	q	
522	mb	$\sigma_8+\sigma_{11}$, $\sigma_{10}-\sigma_{13}$	526, 518
513	mb	$\sigma_{10}-\sigma_{13}$, $\sigma_2+\sigma_9$	518, 495
477	mb	$\sigma_4+\sigma_9$, $\sigma_{12}-\sigma_{11}$	475, 480
465	wb	q	
449	wb	$\sigma_4+\sigma_{13}$	453
436	s	σ_8	

vs Very strong; s Strong; m Medium; w Weak; b Broad; sh Shoulder; q More than binary combination or questionable band.

TABLE V. INFRARED BANDS OF GASEOUS $Mo(CO)_6$

Frequency (cm^{-1})	Intensity	Assignment	Calc. (cm^{-1})
4150	m	$\sigma_1+\sigma_6$	4131
4050	m	$\sigma_3+\sigma_6$	4022
2600	w	$\sigma_3+\sigma_7$	2617
2480	w	$\sigma_1+\sigma_8$, $\sigma_5+\sigma_6$	2499, 2477
2380	s	$\sigma_3+\sigma_8$, $\sigma_2+\sigma_6$	2390, 2379
2330	w	$\sigma_4+\sigma_6$	2334
2210	m	$\sigma_1+\sigma_9$	2211
2115	s	$\sigma_3+\sigma_9$	2102
2085	s	$\sigma_6+\sigma_{11}$, $\sigma_3+\sigma_{13}$	2080, 2092
2000	vs	σ_6	
1985	sh	q	
1955	m(sh)	$\sigma_3-\sigma_{13}$	1952
1925	m(sh)	$\sigma_6-\sigma_{11}$	1920
1650	w	$\sigma_3-\sigma_8$	1654
1615	w	$\sigma_6-\sigma_2$	1621
1070	s	$\sigma_5+\rho_7$, $\sigma_{10}+\sigma_{12}$	1072, 1074
980	s	$\sigma_2+\sigma_7$	974
927	s	$\sigma_4+\sigma_7$, $\sigma_8+\sigma_{10}$	929, 925
905	w	q	
845	s	$\sigma_5+\sigma_8$, $\sigma_4+\sigma_{12}$	845, 851
740	m	$\sigma_2+\sigma_8$	747
705	m	$\sigma_4+\sigma_8$	702
670	m	$\sigma_7+\sigma_{11}$	675
661	w	q	
595	vs	σ_7	
563	s	$\sigma_5+\sigma_9$	557
386	s	σ_8	

vs Very strong; s Strong; m Medium; w Weak; b Broad; sh Shoulder; q More than binary combination or questionable band.

In order to obtain better agreement with the observed frequencies of a_{1g} and e_g species some other sets of values of diagonal terms in F matrix were used, but as long as proper values with physical meaning were used the calculated values were not close to the observed ones. This, therefore, may suggest that the

TABLE VI. L MATRICES FOR $Cr(CO)_6$

		Q_1	Q_2	Q_3	Q_4	Q_7	Q_8	Q_9	Q_{10}	Q_{11}	Q_{12}	Q_{13}
a_{1g}:	R_1	0.381	0.017									
	R_2	−0.226	0.187									
e_g:	R_3			0.380	0.012							
	R_4			−0.224	0.169							
f_{1u}:	R_7					0.453	−0.113	0.028				
	R_8					0.120	0.242	−0.007				
	R_9					−0.258	−0.029	0.128				
f_{2g}:	R_{10}								0.452	0.034		
	R_{11}								−0.274	0.123		
f_{2u}:	R_{12}										0.453	0.017
	R_{13}										−0·191	0.094

TABLE VII. L MATRICES FOR $Mo(CO)_6$

		Q_1	Q_2	Q_3	Q_4	Q_7	Q_8	Q_9	Q_{10}	Q_{11}	Q_{12}	Q_{13}
a_{1g}:	R_1	0.382	0.015									
	R_2	−0.225	0.180									
e_g:	R_3			0.382	0.012							
	R_4			−0.224	0.182							
f_{1u}:	R_7					0.451	−0.044	−0.021				
	R_8					0.054	0.229	0.008				
	R_9					−0.021	−0.034	0.110				
f_{2g}:	R_{10}								0.445	0.031		
	R_{11}								−0.251	0.118		
f_{2u}:	R_{12}										0.446	0.016
	R_{13}										−0.175	0.090

TABLE VIII. HEAT CONTENT, FREE ENERGY, AND HEAT CAPACITY OF $Cr(CO)_6$ AND $Mo(CO)_6$ FOR THE IDEAL GASEOUS STATE AT 1 ATOMOS PRESSURE (cal. deg^{-1} mol^{-1})

	$Cr(CO)_6$				$MO(CO)_6$			
T(°K)	$(H^0-E_0^0)/T$	$-(F^0-E_0^0)/T$	S^0	C_p^0	$(H^0-E_0^0)/T$	$-(F-E_0^0)/T$	S^0	C_p^0
273.15	28.99	78.68	107.67	45.01	30.77	82.65	113.42	48.24
298.15	30.48	81.16	111.64	46.94	32.28	85.43	117.71	49.08
300	30.58	81.35	111.93	47.06	32.38	85.65	118.00	49.20
400	35.52	90.76	126.28	52.65	37.25	95.63	132.88	54.17
600	42.48	106.49	148.97	59.20	43.95	112.12	156.07	60.00
800	47.24	119.34	166.58	63.26	48.49	125.45	173.94	63.74
1000	50.73	130.36	181.09	65.98	51.78	136.77	188.55	66.28

interaction terms between X−Y and M−X or X—Y stretching internal coordinates in the Urey-Bradley type potential function are not negligibly small.

Though, as explained above, there are contained a few quetionable points and the limits of error are uncertain, we may be allowed to conclude that the assignments in Table III and the potential constants in Table II are reasonable.

As the carbon-oxygen stretching potential constant K(C−O), that of nickel carbonyl⁽⁵⁾, 16.02 mdyn./Å, was employed. For this selection the metal-carbon stretching potential constants K(M−X) were obtained to be 1.83 and 1.77 mdyn./Å for chromium and molybdenum hexacarbonyls respectively. These metal-carbon stretching potential constants are a little smaller than that of nickel carbonyl⁽⁵⁾, 2.12 mdyn./Å, and this fact is in agreement with the study by Giacometti⁽¹⁰⁾ who suggested that the shortening of chromium-carbon bond is smaller than that of nickel-carbon bond in the metal carbonyls. The values of the metal-carbon stretching potential constant, although many authors⁽¹⁰,¹¹⁾ have discussed the evidence of partial double bond caracter in such coordination compounds of various symmetry as these metal carbonyls, are nearly equal to those of Si—C and Cr—Cl bonds of tetramethylsilane⁽¹²⁾ and chromyl

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10) G. Giacometti, ibid., 23, 2068 (1955).

11) See e. g., L. Pauling, "The Nature of the Chemical Bond", Cornell University Press. Ithaca. New York (1939), p, 251.

12) K. Shimizu and H. Murata, private communication.

chloride[13] (2.72 and 2.56 mdyn./Å respectively), which are considered as single bonds.

The **L** matrices, whose components give the transformation from normal to symmetry coordinates, were calculated and listed in Table VI for chromium hexacarbonyl and Table VII for molybdenum hexacarbonyl.

Thermodynamic Properties

The heat content, free energy, entropy and heat capacity at constant pressure were calculated for seven temperatures from 273.15 to 1000°K in the rigid rotator-harmonic oscillator approximation using the probable values of the observed wave numbers listed in Table III. The molecular constants used in these computation and the symmetry number are given in Table I, while Table VIII lists the thermodynamic properties.

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[13] H. Stammreich, K. Kawai and Y. Tavares, *Spectrochim. Acta*, **1959**, 438.