

ently available<sup>16</sup> sign data for transition metal complexes, it is very likely that the signs are negative in the *cis* mixed-ligand complexes and positive in the *trans* (Tables I and II). In the theory of Pople and Santry<sup>17</sup> the signs of coupling constants are dependent upon the inverse of the energy difference  $(\epsilon_j - \epsilon_i)^{-1}$  and the product of coefficients of the s atomic orbitals of the coupling sites in the molecular orbitals  $\Psi_i$  (occupied) and  $\Psi_j$  (unoccupied). A tentative suggestion as to what molecular orbitals  $\Psi_i$  and  $\Psi_j$  might be responsible for the signs of  ${}^2J_{PP}$  recorded here for our complexes is given elsewhere.<sup>4</sup>

In the present absence of a detailed molecular orbital treatment for transition metal complexes, the trends in the magnitudes of  ${}^2J_{PP}$  can best be understood in terms of the s-orbital character of the bond connecting the coupling nuclei and their effective nuclear charges, both of which are parameters in the valence-bond treatment of the Fermi contact term.<sup>18</sup> This term, which is generally conceded to be the dominant coupling effect,<sup>4,12,18-23</sup> is expected to increase as the

electronegativity of the organic substituents on the phosphorus ligands is augmented. Such a trend is clearly seen in the experimentally observed rise in the absolute magnitude of  ${}^2J_{PP}$  in the order  $M[P(N(CH_3)_2)_3]_2 < M[P(N(CH_3)_2)_3][P(OCH_2)_3CR] < M[P(OCH_2)_3CR]_2$  where M is the metal carbonyl moiety in the *cis*-molybdenum, *trans*-molybdenum, or *trans*-iron complexes (Tables I and II). The similar order for the remaining series  $M[P(OCH_3)_3] < M[P(OCH_3)_3][P(OCH_2)_3CR] < M[P(OCH_2)_3CR]_2$  is reasonable only if  $P(OCH_2)_3CR$  is effectively more electronegative than  $P(OCH_3)_3$ . Displacement studies on the  $BH_3$  adducts of these phosphites confirm this point inasmuch as the bicyclic phosphite is indeed the poorer Lewis base.<sup>4,15</sup>

The larger values of  ${}^2J_{PP}$  in the *trans*- than in the *cis*-molybdenum complexes may be attributable to the fact that the  $\sigma$ -bonding electrons of *trans*-phosphorus nuclei share the same  $p_\sigma$ -metal molecular orbital whereas those *cis* do not. Although larger *trans* than *cis* couplings are generally observed,<sup>4,23</sup> it should be pointed out that chromium complexes appear to be anomalous in that the opposite observation has been made<sup>4,23</sup> with all of the ligands studied.

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## Force Constants of the Hexacarbonyls of Chromium, Molybdenum, and Tungsten from the Vibrational Spectra of Isotopic Species

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The vibrational spectra of  $M(^{12}C^{16}O)_6$ ,  $M(^{13}C^{16}O)_6$ , and  $M(^{12}C^{18}O)_6$ , with  $M = Cr, Mo, \text{ or } W$ , have been observed. Infrared spectra are reported for the vapors and solutions (in  $CCl_4$  for Cr and Mo and in  $CS_2$  for W); Raman spectra are reported for the solutions and solids. From the results most of the fundamental vibrations have been assigned. Force constants, with standard deviations, have been calculated for a general quadratic valence force field. A set of stretch-stretch interaction constants is presented which can be transferred, with discretion, to other metal carbonyls. Mean amplitudes of vibration and shrinkage effects are calculated. It is shown that the CO, C'O' force constants are best explained by a dipole-dipole interaction.

### Introduction

The bonding in metal carbonyls has held the attention of numerous research chemists in recent years. Some very important clues to the nature of the bonding lie in the values of the force constants describing the bond strengths, the directional forces, and the interactions among the bonds and bond angles. Unfortunately, for metal carbonyls, as with most polyatomic molecules, there is not enough information in the vibrational spectrum of the normal molecular species to

define the general quadratic potential constants. Therefore, in the past, one has resorted to various more or less arbitrary approximations<sup>1,2</sup> concerning some of the force constants in order to calculate values for the other force constants. Some chemists<sup>3-5</sup> have taken

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the approach that since the CO stretching frequencies are much higher than the other vibrational frequencies, meaningful force constants for the carbonyl groups can be obtained by neglecting all other frequencies and all force constants except those for CO stretching and CO,C'O' interactions. It has been shown<sup>6,7</sup> that this "CO-factored force field" may, in some cases, give reasonable relative CO stretching force constants for comparing bond strengths among metal carbonyls but that the CO,C'O' interaction constants calculated in this manner have no significance.

It is important to determine a complete quadratic force field for characteristic metal carbonyls for several reasons. First, the force constants, including interaction constants, are of fundamental interest for a discussion of the bonding. Second, it is important to compare the true quadratic force constants with the results of the various approximate treatments as an evaluation of these approximations. Also, if one can determine good values for some of the interaction constants, it is reasonable to transfer these to other molecules for which the bonding is similar but for which there is not sufficient information for calculation of a complete quadratic force field.

Since the force constants of an isolated molecule are invariant to isotopic substitution, the vibrational spectra of isotopic species give additional data for their calculation. A recent study<sup>8</sup> of the vibrational spectra of Ni(<sup>12</sup>C<sup>18</sup>O)<sub>4</sub>, Ni(<sup>13</sup>C<sup>16</sup>O)<sub>4</sub>, and Ni(<sup>12</sup>C<sup>18</sup>O)<sub>4</sub> led to estimates of the true quadratic valence force constants for nickel carbonyl. Since this molecule contains tetrahedral metal-carbon bonding, its interaction constants cannot be considered appropriate for transfer to other metal carbonyls where the linear MCO groups are at 180, 90, or 120°. A determination of the force constants of Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and W(CO)<sub>6</sub> has the advantage that 180 and 90° M-CO bonds are involved and thus the MC,C'O' and CO,C'O' interactions should be transferable to the many other compounds having 180 and 90° M-CO bond systems. Furthermore a study of these three molecules should give better estimates of the interaction constants than were obtained<sup>8</sup> for Ni(CO)<sub>4</sub> since we expect consistency for similar bonding within the three compounds. For three isotopic species of octahedral hexacarbonyls there are more vibrational frequencies than there are general quadratic force constants, so one can hope to calculate the force constants without making arbitrary approximations. Therefore, we have made a comprehensive study of the vibrational spectra of the molecules M(<sup>12</sup>C<sup>16</sup>O)<sub>6</sub>, M(<sup>13</sup>C<sup>16</sup>O)<sub>6</sub>, and M(<sup>12</sup>C<sup>18</sup>O)<sub>6</sub> where M = Cr, Mo, or W.

### Experimental Section

**Synthesis of Enriched Group VIb Metal Carbonyls.**—The enriched carbonyls of chromium, molybdenum, and tungsten were prepared by standard high-pressure methods using the ap-

propriate carbon monoxide gas <sup>12</sup>C<sup>18</sup>O (99% <sup>18</sup>O) and <sup>13</sup>C<sup>16</sup>O (93% <sup>13</sup>C). The volume of the reaction vessels (10–25 ml) and the quantity of the ingredients were scaled down to yield 1–2 g of product. Molybdenum and tungsten hexacarbonyls were conveniently obtained by the reaction of molybdenum pentachloride and tungsten hexachloride, respectively, with zinc in the presence of carbon monoxide (200 atm) and ethyl ether.<sup>9</sup> Chromium hexacarbonyl was prepared by the reductive carbonylation of chromic chloride with triethylaluminum in the presence of carbon monoxide and ether.<sup>10</sup> The yields were about 60%. Purification of the carbonyls was effected by steam distillation and vacuum sublimation. The methods were tested first with normal carbon monoxide.

Carbon monoxide, enriched to 93% carbon-13, was purchased from Mound Laboratory (Monsanto Research Corp., Miamisburg, Ohio). The oxygen-18-enriched carbon monoxide was prepared from enriched nitric oxide (99.7% nitrogen-15 and oxygen-18) produced at this laboratory. The nitric oxide was allowed to react with charcoal in two steps. First, carbon dioxide was formed at 500° and separated from nitrogen and unreacted nitric oxide by condensation at –145°. Then the oxygen-18 carbon dioxide was converted completely to carbon monoxide by further reaction with charcoal at 1000°. A gas circulation system was used. The enriched carbon monoxide was stored in charcoal.

**Observation of Spectra.**—The Raman spectra were obtained for the solids and solutions on a Cary 81 with a Spectra-Physics 125 He-Ne laser source. For Cr(CO)<sub>6</sub> and Mo(CO)<sub>6</sub>, saturated CCl<sub>4</sub> solutions were used. For W(CO)<sub>6</sub>, a saturated CS<sub>2</sub> solution was used because a CCl<sub>4</sub> solution decomposes too rapidly. The solid-state Raman spectra were obtained from the powders.

The infrared spectra were observed for the vapors and solutions on a Perkin-Elmer 521 spectrometer (250–4000 cm<sup>-1</sup>) and a Cary Model 14 spectrometer (4000–4200 cm<sup>-1</sup>). Path lengths ranging from 10 cm to 10 m were used for the vapor-phase spectra. The infrared spectra of the fundamentals  $\nu_6$ ,  $\nu_7$ , and  $\nu_8$  were also studied with a Perkin-Elmer E-13 spectrometer in order to take advantage of the higher resolution. The low-frequency infrared-active fundamental  $\nu_9$  was observed for 10-m paths of Cr(<sup>12</sup>C<sup>16</sup>O)<sub>6</sub>, Mo(<sup>12</sup>C<sup>16</sup>O)<sub>6</sub>, and Mo(<sup>13</sup>C<sup>16</sup>O)<sub>6</sub> in the vapor phase with a Beckman IR-11 spectrometer.

### Results

**Observed Spectra.**—The vapor-phase infrared spectra of Cr(CO)<sub>6</sub><sup>11</sup> and Mo(CO)<sub>6</sub><sup>11,12</sup> have been illustrated before. The spectrum of W(CO)<sub>6</sub> is similar and therefore has not been shown. The PQR structure of the CO stretching fundamentals has not previously been illustrated at grating resolution; in Figure 1 this band is displayed for Cr(CO)<sub>6</sub>. It is similar for Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub>. The spectra of M(<sup>13</sup>C<sup>16</sup>O)<sub>6</sub> and M(<sup>12</sup>C<sup>18</sup>O)<sub>6</sub> are similar to those of the normal species except for the expected frequency shifts.

The contour of the low-frequency fundamental  $\nu_9$  is used for estimation of the Coriolis coupling constant  $\zeta_9$ . The spectrum of  $\nu_9$  for Mo(CO)<sub>6</sub> is shown in Figure 2; though it is quite weak, the PQR structure is obvious and reproducible. For Cr(CO)<sub>6</sub> this band was shown previously;<sup>13</sup> the band for  $\nu_9$  for W(CO)<sub>6</sub> was not observed because of its low vapor pressure.

The observed absorption frequencies and their

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TABLE I  
 INFRARED VAPOR ABSORPTION BANDS<sup>a</sup> OF THE HEXACARBONYLS

Assignment	Approx rel intens	Cr( <sup>k</sup> C <sup>l</sup> O) <sub>6</sub>			Mo( <sup>k</sup> C <sup>l</sup> O) <sub>6</sub>			W( <sup>k</sup> C <sup>l</sup> O) <sub>6</sub>		
		<i>k,l</i>			<i>k,l</i>			<i>k,l</i>		
		12,16	13,16	12,18	12,16	13,16	12,18	12,16	13,16	12,18
$\nu_1 + \nu_6$	m <sup>b</sup>	4110.5	4017.7	4016.5	(4116.3)	4024.8	4023.4	4113.9	4019.6	4020.6
$\nu_3 + \nu_6$	m	4007.5	3917.4	3915.3	4010.4	3921.3	3917.9	3999.8	3909.8	3907.9
$\nu_1 + \nu_7$	vw	2783.5	2720.8	2734.5						
$\nu_3 + \nu_7$	vw	2692.8	2633.9	2645	2622	2561	2574			
$\nu_1 + \nu_8$	vw	2555.1	2500.6	2499	2488.5	2433.9	2434.0	2496.0	2441	2440
$\nu_3 + \nu_8$	mw	2465.3	2412.1	2409.4	} 2392.9	} 2340.5	} 2330 sh <sup>d</sup>	2396 sh	<i>c</i>	<i>c</i>
$\nu_2 + \nu_6$	w	<i>c</i>	<i>c</i>	<i>c</i>				2424 sh	<i>c</i>	<i>c</i>
$\nu_4 + \nu_6$	mw	2391.4	2340.0	2329.6				2408	2360	2343.4
$\nu_1 + \nu_9$	w, Q	2213.4	2164.7	2162.7	2203.6	2154.2	2153.8	2203.6	2153.4	2154.1
	w-mw, Q			2081.6		2084.5	2087.1		2085.3	2088.0
$\nu_3 + \nu_9$	mw, Q	2123.3	2080.4	2073.4	2108.8	2062.6	2059.7	2102.0	2055.2	2052.5
$\nu_3 + \nu_{13}$	ms				} 2083.2	} 2037.9	2037.4			
$\nu_6 + \nu_{11}$	ms	2089.0	2043.1	2038.1			2030.4	2079.1	2033.4	2029.4
	vvw	2052								
$\nu_1 - \nu_9$	vw, Q	2018.5			2043.7			2041.0		
	vw, Q				2019.8			2014		
	w, Q		2015.9			2017.7			2016.4	
M(C <sup>18</sup> O) <sub>5</sub> CO	ms, Q			2003.0			2002.9			2000.5
M( <sup>13</sup> CO) <sub>5</sub> CO	ms, Q		2002.8			2004.3			1999.0	
	vw		~1969 sh	~1968 sh		~1973 sh	~1971 sh		~1968 sh	~1973 sh
$\nu_6$	vs, Q	2000.4	1956.1	1953.4	2003.0	1959.1	1955.2	1997.6	1953.5	1950.6
M(CO) <sub>5</sub> - <sup>13</sup> CO	s, Q	1967.2		1919.8	1970.1		1921.7	1964.9		1917.2
	m, Q		1920.4			1922.7			1917.5	
$\nu_3 - \nu_9$	vw	1928.9	~1883 sh	1886.6	1945.5	1899.9	1903.3			
$\nu_6 - \nu_{11}$	w	1911.1	1867.4	1868.2	1923.4	1879.8	1879.8	1915.1	1871	1870
$\nu_3 - \nu_2$	vw	1621.6	1582.0	1586.1	1611.4	1572	1575.8			
$\nu_1 + \nu_{10}$	w	1200.2	1168.6	1196.5	1073.0	1041.4	1066.9	1068.6	1035.5	1063.7
$\nu_{10} + \nu_{12}$	w	1049 sh	1027 sh	1041 sh	985.5	953.6	979.2	1003.5	971.8	998.7
$\nu_3 + \nu_7$	m	1032.2	1007.7	1025.1	937.2	912.3	929.9	948.2	920.0	940.0
$\nu_3 + \nu_{10}$	vw	975.7	949	963.1						
	vw				907	880	895			
$\nu_3 + \nu_{12}$	m	875.0	849.3	867.4	848.8	824.1	841.1	882.9	856.9	874.0
$\nu_4 + \nu_8$	w				746.3	736.4	725.2			
$\nu_2 + \nu_8$	w	819 b <sup>d</sup>	809.2 b	797.7 b						
$\nu_3 + \nu_8$	vw		787 sh		708.4	697	697.0			
$\nu_1 + \nu_{11}$	vw	755.7	742.9	748.9	671	655.0	664			
$\nu_7$	vs	668.1	654.8	665.8	595.6	580.0	592.7	586.6	568.8	583.3
	mw		626.6							
$\nu_9 + \nu_{10}$	m	637.9	611.0	628.7	563.7	547.8	556.3	565.5	550.4	565.0
$\nu_{11} + \nu_{12}$	vw	599.5	584.0	594						
$\nu_{10} + \nu_{13}$	vw				539 sh	526 sh	533 sh			
	vw							~470	463.5	
$\nu_8 + \nu_{11}$	mw	527.2	520.2	513.2	441.1	436.9	427.9	454	449	441.5
$\nu_2 + \nu_9$	w	478.0	471.0	461.3	473.6	~470 b	458.0	506	500	
	vw				430.7					
$\nu_5 + \nu_9$	vw	459 sh	450.4	~445 sh	422 sh	414				
$\nu_5 + \nu_{13}$	vw							423	411.4	} 406 vb
$\nu_{10} - \nu_9$	vw				399.3	382 sh	397.9	402.3	388.3	
$\nu_8$	s	440.5	433.5	429.7	367.2	362.3	359.7	374.4	368.4	364.5
$\nu_9$	m, Q	97.8			81.6	81.0				

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> The intensity symbols are: s, strong; m, medium; w, weak; v, very. Bands labeled Q had PQR structure and the position of the Q-branch maximum is given; the other bands were symmetrical and featureless. <sup>c</sup> These bands were obscured by  $\nu_4 + \nu_6$  and by CO<sub>2</sub>. <sup>d</sup> sh stands for "shoulder," on the side of another band; b means broad.

assignments are given in Table I for the vapor phase. The intensities are qualitative; more quantitative intensity estimates are given in ref 2 for the normal species.

For the solutions, only the fundamentals  $\nu_6$ ,  $\nu_7$ , and  $\nu_8$  were measured. The values obtained are given along with the Raman frequencies for the solutions in Tables V-VII which summarize the fundamentals. The Raman peaks observed for the solids are recorded in

Tables II-IV. The infrared spectra of the solids are not reported as the CO stretching fundamental is extremely broad at room temperature and split into two components at low temperature making it rather useless for accurate force constant calculation. The Raman spectra of the gases were not observed.

In Tables V-VII the harmonic frequencies,  $\omega_i$ , are given for the CO stretching frequencies  $\nu_1$ ,  $\nu_3$ , and  $\nu_6$ . The anharmonic corrections were determined pre-

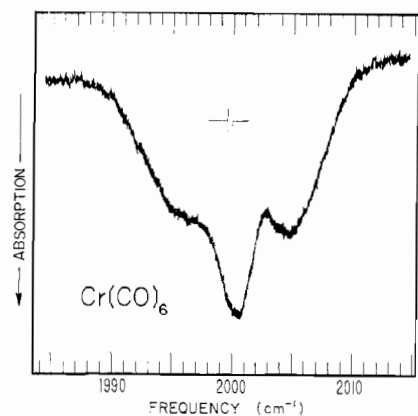


Figure 1.—The fundamental  $\nu_6$  for  $\text{Cr}^{(12}\text{C}^{16}\text{O})_6$  vapor; resolution  $0.4 \text{ cm}^{-1}$ .

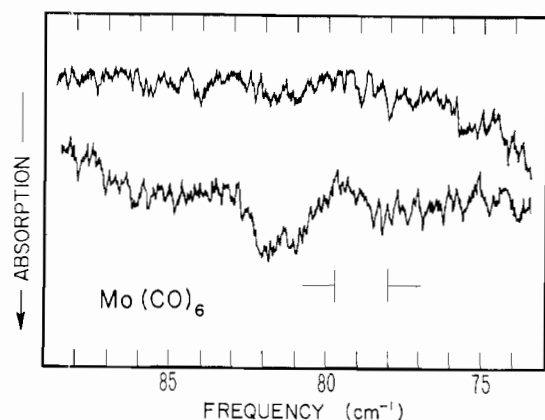


Figure 2.—The fundamental  $\nu_6$  for  $\text{Mo}(\text{CO})_6$  vapor; resolution about  $1.6 \text{ cm}^{-1}$ . The upper curve is the background.

Assign- ment <sup>a</sup>	$\text{Cr}^{(12}\text{C}^{16}\text{O})_6$		$\text{Cr}^{(12}\text{C}^{18}\text{O})_6$		$\text{Cr}^{(13}\text{C}^{16}\text{O})_6$	
	$\nu^b$	$I^c$	$\nu$	$I$	$\nu$	$I$
$\nu_9$	104.0	37	103.3	31	99.3	38
$\nu_{11}$	114.2	100	113.8	100	108.4	100
$\nu_2$	388.0	79	381.8	71	375.1	66
$\nu_4$	397.7	3	392.4	5	384.7	5
$\nu_{10}$	533.1	0.8	514.0	1.4	532.2	1.1
	560	0.05	551	0.2	...	
$2\nu_6$	735.4	0.15	714.4	0.2	726.9	0.2
	1964.5	0.4	1921.8	0.7	1917.6	0.3
	2001.8	1	1956.9	1.9	1957.0	3.4
$\nu_3$	2006.1	13	1960.7	23	1961.4	24
	2016.7	0.4	1970.2	0.9	1970.0	0.8
	2022.9	1.6	1977.4	2.4	1977.9	4
	2031.7	0.1	...	...	1984.5	0.2
	2105.3	0.1	...	...	...	
$\nu_1$	2109.9	1	2061.2	2.3	2063.6	1.5
			2073.7	0.6		

<sup>a</sup> Frequencies are in  $\text{cm}^{-1}$ . <sup>b</sup>  $I$  gives the relative intensity at the band maximum based on 100 for the strongest peak using the Cary 81 with an He-Ne laser.

viously<sup>14</sup> for the normal species in solution. In that work<sup>14</sup> it was found that  $3\nu_6$  of  $\text{W}(\text{CO})_6$  was split, indicating an anharmonic constant  $G_{66} \approx 4.0 \text{ cm}^{-1}$  for internal angular momentum coupling. Though such a

Assign- ment <sup>a</sup>	$\text{Mo}^{(12}\text{C}^{16}\text{O})_6$		$\text{Mo}^{(12}\text{C}^{18}\text{O})_6$		$\text{Mo}^{(13}\text{C}^{16}\text{O})_6$	
	$\nu^b$	$I^c$	$\nu$	$I$	$\nu$	$I$
$\nu_9$	91.9	15	91	40	89	17
$\nu_{11}$	103.7	100	103.0	100	98.8	100
$\nu_6$	347	0.04			343	0.08
$\nu_8$	~365	w, b	~362	0.5		
$\nu_4$	392.2	1.8	385.0	1.7	379.6	4.5
$\nu_2$	406.8	23	400.1	21	392.5	19
$\nu_{10}$	476.5	0.7	462.0	2.4	475.1	1
$\nu_{12}$	508.5	0.04			507.6	0.1
$\nu_7$	594.5	0.2			591.5	0.1
$\nu_9 + \nu_{12}$	603	0.1			599	0.08
$2\nu_6$	692	0.3	674	0.2	683	0.2
$2\nu_8$	730.5	0.3	727	0.3	721	0.2
$2\nu_4$						
$\nu_2 + \nu_8$	777	0.06				
$\nu_6 + \nu_{10}$	823	0.06				
$\nu_7 + \nu_8$	958	0.09				
$2\nu_{12}$	1022	0.07				
$2\nu_7$	1189	0.04				
	1942	0.1				
	1965.1	1	1923.5	0.6	1917.8	1
	2001.7	0.2			1956.5	3
$\nu_3$	2005.2	13	1960.0	23	1959.9	42
	2015.7	0.5			1969.0	0.6
	2022.4	2	1977.0	2.7	1976.9	6
	2030.7	0.2				
	2109.5	0.3				
$\nu_1$	2113.6	4	2064.0	1.4	2067.4	12
			2077.0	1.3		
			2087.3	0.2		

<sup>a</sup> Several weak peaks were observed for  $\text{Mo}^{(12}\text{C}^{16}\text{O})_6$  at 460, 523, 531, 541, and 559  $\text{cm}^{-1}$  and for  $\text{Mo}^{(12}\text{C}^{18}\text{O})_6$  at 432 and 458  $\text{cm}^{-1}$ . These are unassigned. <sup>b</sup> Frequencies are in  $\text{cm}^{-1}$ . <sup>c</sup>  $I$  gives the relative intensity of the band maximum based on 100 for the strongest peak using the Cary 81 with an He-Ne laser.

Assign- ment	$\text{W}^{(12}\text{C}^{18}\text{O})_6$		$\text{W}^{(12}\text{C}^{16}\text{O})_6$		$\text{W}^{(13}\text{C}^{18}\text{O})_6$	
	$\nu^a$	$I^b$	$\nu$	$I$	$\nu$	$I$
$\nu_9$	91	23	90.6	25	86	13
$\nu_{11}$	107.6	100	106.9	100	102.1	100
$\nu_6$					364	0.1
$\nu_4$	418.3	6	413.1	3	403.3	2.6
$\nu_2$	433.8	50	429.1	23	418.7	21
$\nu_{10}$	485.0	2	467.9	1.2	481.6	1.6
$\nu_{12}$	524	0.2	506	0.05	522	0.2
$\nu_7$	588	0.1	568	0.03	584	0.1
$2\nu_5$	730.5	0.2	708.7	0.2	726.5	0.3
$2\nu_6$	745	0.2	733	0.2		
	1957.0	1.7	1915.1	0.4	1910.5	0.8
	1994.6	6			1950	1
$\nu_3$	1998.4	51	1952.9	8.8	1953.4	18
	2012.7	17			1965.1	0.7
	2017.4	9	1971.7	0.9	1972.5	3.4
	2110.9	0.6			2065.1	0.1
$\nu_1$	2115.3	4.6	2065.7	2	2070.4	2
			2078.0	0.5		
			2088	0.07		

<sup>a</sup> Frequencies are in  $\text{cm}^{-1}$ . <sup>b</sup>  $I$  gives the relative intensity at the band maximum based on 100 for the strongest peak, using the Cary 81 with an He-Ne laser.

splitting was not obvious for  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  we have, for consistency, assumed  $G_{66} \approx 5.0$  for these molecules. The larger value was chosen because the anharmonic constants are somewhat larger for  $\text{Mo}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  than for  $\text{W}(\text{CO})_6$ . The anharmonic corrections for the  $^{13}\text{C}$  and  $^{18}\text{O}$  isotopic species were

TABLE V  
 FUNDAMENTAL FREQUENCIES OF  $\text{Cr}(\text{C}^{18}\text{O})_6$  IN  $\text{CM}^{-1}$ 

Assignment	Solid			CCl <sub>4</sub> solution			Vapor <sup>a</sup>			
	12,16	13,16	12,18	12,16	13,16	12,18	12,16	13,16	12,18	
A <sub>1g</sub>	$\nu_1$	2109.9 ± 0.2 <sup>b</sup>	2061.2 ± 0.2	2063.6 ± 0.2	2112.4 ± 0.3	2063.6 ± 0.5	2066.2 ± 0.3	2118.7	2070.3	2072.1
	$\omega_1$	2130.4 <sup>c</sup>	2080.7	2083.1	2132.9	2083.1	2085.7	2139.2	2089.8	2091.6
	$\nu_2$	388.0 ± 0.2	381.8 ± 0.2	375.1 ± 0.2	381.2 ± 0.4	375.4 ± 0.4	367.8 ± 0.4	379.2	373.8	366.9
E <sub>g</sub>	$\nu_3$	2006.1 ± 0.4	1960.7 ± 0.4	1961.4 ± 0.4	2018.4 ± 0.4	1972.3 ± 0.3	1972.8 ± 0.3	2026.7	1980.7	1981.4
	$\omega_3$	2024.6	1978.3	1979.0	2036.9	1989.9	1990.4	2045.2	1998.3	1999.0
	$\nu_4$	397.7 ± 0.5	392.4 ± 0.5	384.7 ± 0.5	394 ± 3	...	381.3 ± 3	390.6	384.2	376.6
F <sub>1g</sub>	$\nu_5$	367.7 <sup>d</sup>	357.2 <sup>d</sup>	363.5 <sup>d</sup>				364.1	352.9	359.3
F <sub>1u</sub>	$\nu_6$				1984.4 ± 0.2	1940.3 ± 0.2	1937.6 ± 0.2	2000.4 ± 0.1	1956.1 ± 0.1	1953.4 ± 0.1
	$\omega_6$				2027.2	1981.7	1978.9	2043.7	1997.5	1994.7
	$\nu_7$				664.6 ± 0.3	651.5 ± 0.3	662.1 ± 0.3	668.1 ± 0.3	654.8 ± 0.3	665.8 ± 0.3
F <sub>2g</sub>	$\nu_8$				443.8 ± 0.5	436.0 ± 0.5	434.0 ± 0.5	440.5 ± 0.5	433.5 ± 0.5	429.7 ± 0.5
	$\nu_9$	104.0 ± 0.5	103.3 ± 0.5	99.3 ± 0.5	103 ± 1 <sup>e</sup>			97.2 ± 0.5		93.6 ± 0.5
	$\nu_{10}$	533.1 ± 0.2	514.0 ± 0.5	532.2 ± 0.5				532.1	513.8	530.7
F <sub>2u</sub>	$\nu_{11}$	114.2 ± 0.8	113.8 ± 0.5	108.4 ± 0.5	100.8 ± 0.5	100.0 ± 0.6	95.1 ± 0.5	89.7	88.4	84.8
	$\nu_{12}$							510.9	496.4	508.1
	$\nu_{13}$							67.9		63.3

<sup>a</sup> Only the F<sub>1u</sub> frequencies were observed directly for the vapor. The others (A<sub>1g</sub>, E<sub>g</sub>, F<sub>1g</sub>, F<sub>2g</sub>, and F<sub>2u</sub> for the vapor) were estimated from observed combination bands as described in the text. <sup>b</sup> The ± limits are estimated observational errors. <sup>c</sup> The  $\omega_i$  are harmonic CO stretching frequencies, estimated by applying anharmonic corrections as described in the text. <sup>d</sup> Estimated from 2 $\nu_5$ . <sup>e</sup> See ref 14.

 TABLE VI  
 FUNDAMENTAL FREQUENCIES OF  $\text{Mo}(\text{C}^{18}\text{O})_6$  IN  $\text{CM}^{-1}$ 

Assignment	Solid			CCl <sub>4</sub> solution			Vapor <sup>a</sup>			
	12,16	13,16	12,18	12,16	13,16	12,18	12,16	13,16	12,18	
A <sub>1g</sub>	$\nu_1$	2113.6 ± 0.3 <sup>b</sup>	2064.0 ± 0.3	2067.4 ± 0.3	2116.7 ± 0.2	2067.2 ± 0.2	2070.7 ± 0.1	2120.7	2072.7	2074.9
	$\omega_1$	2137.1 <sup>c</sup>	2086.4	2089.9	2140.2	2089.6	2093.2	2144.2	2095.1	2097.4
	$\nu_2$	406.8 ± 0.3	400.1 ± 0.3	392.5 ± 0.3	402.2 ± 0.3	396.1 ± 0.5	385.6 ± 0.7	391.2	386.8	379.2
E <sub>g</sub>	$\nu_3$	2005.2 ± 0.3	1960.0 ± 0.3	1959.9 ± 0.3	2018.8 ± 0.2	1972.9 ± 0.2	1973.1 ± 0.2	2024.8	1978.7	1979.1
	$\omega_3$	2023.7	1977.6	1977.5	2037.3	1990.5	1990.7	2043.3	1996.3	1996.7
	$\nu_4$	392.2 ± 0.3	385.0 ± 0.6	379.6 ± 0.6	392 ± 1	386 ± 2	375.5 ± 1	381		
F <sub>1g</sub>	$\nu_5$	346.0 <sup>d</sup>	337.0 <sup>d</sup>	341.5 <sup>d</sup>				341.6	332.3	337.2
F <sub>1u</sub>	$\nu_6$				1986.1 ± 0.2	1942.7 ± 0.2	1938.6 ± 0.2	2003.0 ± 0.1	1959.1 ± 0.1	1955.2 ± 0.1
	$\omega_6$				2026.2	1981.1	1976.8	2043.1	1997.5	1993.4
	$\nu_7$				592.8 ± 0.4	576.8 ± 0.4	589.5 ± 0.4	595.6 ± 0.4	580.0 ± 0.4	592.7 ± 0.4
F <sub>2g</sub>	$\nu_8$				367.0 ± 0.5	362.0 ± 0.5	359.3 ± 0.5	367.2 ± 0.5	362.3 ± 0.5	359.7 ± 0.5
	$\nu_9$	91.8 ± 0.5	91.5 ± 1.0	89.0 ± 0.5	91 ± 1 <sup>e</sup>			81.6 ± 0.5	81.3 ± 0.5	78.2 ± 0.5
	$\nu_{10}$	476.5 ± 0.5	462.0 ± 0.5	475.1 ± 0.5				477.4	461.4	474.2
F <sub>2u</sub>	$\nu_{11}$	103.7 ± 0.5	103.0 ± 0.5	98.8 ± 0.5	91 ± 1	89.5 ± 1	84 ± 1	79.2	79.0	75.2
	$\nu_{12}$	508.5 ± 1		507.6 ± 1				507.2	491.8	503.9
	$\nu_{13}$							60		

<sup>a</sup> Only the F<sub>1u</sub> frequencies were observed directly for the vapor. The others (A<sub>1g</sub>, E<sub>g</sub>, F<sub>1g</sub>, F<sub>2g</sub>, and F<sub>2u</sub> for the vapor) were estimated from observed combination bands as described in the text. <sup>b</sup> The ± limits are estimated observational errors. <sup>c</sup> The  $\omega_i$  are harmonic CO stretching frequencies, estimated by applying anharmonic corrections as described in the text. <sup>d</sup> Estimated from 2 $\nu_5$ . <sup>e</sup> See ref 14.

 TABLE VII  
 FUNDAMENTAL FREQUENCIES OF  $\text{W}(\text{C}^{18}\text{O})_6$  IN  $\text{CM}^{-1}$ 

Assignment	Solid			CS <sub>2</sub> solution			Vapor <sup>a</sup>			
	12,16	13,16	12,18	12,16	13,16	12,18	12,16	13,16	12,18	
A <sub>1g</sub>	$\nu_1$	2115.3 ± 0.2 <sup>b</sup>	2065.7 ± 0.3	2070.4 ± 0.3	2116.6 ± 0.3	2066.6 ± 0.3	2070.9 ± 0.3	2126.2	2076.0	2080.0
	$\omega_1$	2142.3 <sup>c</sup>	2091.6	2096.3	2143.6	2092.5	2096.8	2153.2	2101.9	2105.9
	$\nu_2$	433.8 ± 0.3	429.1 ± 0.2	418.7 ± 0.5	427.1 ± 0.3	421.2 ± 0.4	412.0 ± 0.5	426		
E <sub>g</sub>	$\nu_3$	1998.4 ± 0.2	1952.9 ± 0.3	1953.4 ± 0.2	2009.8 ± 0.3	1963.6 ± 0.3	1963.9 ± 0.3	2021.1	1974.8	1975.8
	$\omega_3$	2014.9	1968.9	1969.2	2026.3	1979.6	1979.8	2037.6	1990.8	1991.7
	$\nu_4$	418.3 ± 0.3	413.1 ± 0.6	403.3 ± 0.6	412 ± 2			410		
F <sub>1g</sub>	$\nu_5$	365.3 <sup>d</sup>	351.4 <sup>d</sup>	363.3 <sup>d</sup>				361.6	351.2	356.7
F <sub>1u</sub>	$\nu_6$				1976.6 ± 0.2	1933.1 ± 0.2	1929.9 ± 0.2	1997.6 ± 0.1	1953.5 ± 0.1	1950.6 ± 0.1
	$\omega_6$				2016.6	1971.4	1968.1	2037.6	1991.8	1988.8
	$\nu_7$				583.1 ± 0.2	564.9 ± 0.2	579.9 ± 0.2	586.6 ± 0.2	568.8 ± 0.2	583.3 ± 0.2
F <sub>2g</sub>	$\nu_8$				374.4 ± 0.4	369.2 ± 0.4	365.0 ± 0.4	374.4 ± 0.2	368.4 ± 0.2	364.5 ± 0.2
	$\nu_9$	90.7 ± 0.5	90.6 ± 0.3	86.1 ± 0.3	92.0 ± 1 <sup>e</sup>			82.0 ± 0.5		
	$\nu_{10}$	485.0 ± 0.3	467.9 ± 0.3	481.6 ± 0.3				482.0	466.7	480.4
F <sub>2u</sub>	$\nu_{11}$	107.6 ± 0.5	106.9 ± 0.5	102.1 ± 0.5	92.0 ± 1			81.4	80.2	70.2
	$\nu_{12}$	524	506	522				521.3	505.7	517.3
	$\nu_{13}$							61.4		

<sup>a</sup> Only the F<sub>1u</sub> frequencies were observed directly for the vapor. The others (A<sub>1g</sub>, E<sub>g</sub>, F<sub>1g</sub>, F<sub>2g</sub>, and F<sub>2u</sub> for the vapor) were estimated from observed combination bands as described in the text. <sup>b</sup> The ± limits are estimated observational errors. <sup>c</sup> The  $\omega_i$  are harmonic CO stretching frequencies, estimated by applying anharmonic corrections as described in text. <sup>d</sup> Estimated from 2 $\nu_5$ . <sup>e</sup> See ref 14.

calculated from the expression<sup>15</sup>  $X_{kl}^{(i)} = X_{kl}^{(j)} \omega_k^{(i)} \omega_l^{(i)} / \omega_k^{(j)} \omega_l^{(j)}$ .

**Frequency Assignments.**—For the most part the

frequency assignments are straightforward and follow from ref 14. A number of the entries in Tables V–VII were not observed but were determined from combination bands. For consistency among the different isotopic species and among the three different molecules

(15) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 220.

the same combination bands were used, where possible, for determination of a given frequency.

For the solids,  $\nu_5$  was taken as half of  $2\nu_5$ . For the vapor a number of combinations was used:  $\nu_1$  was estimated from  $\nu_1 + \nu_6$  and the anharmonicity constant  $X_{16}$ ;<sup>14</sup> similarly,  $\nu_3$  was estimated from  $\nu_3 + \nu_6$  and  $X_{36}$ ;  $\nu_2$  was estimated from  $\nu_6 - \nu_2$  except for  $\text{W}(\text{CO})_6$  for which  $\nu_6 - \nu_2$  is not observed and  $\nu_2 + \nu_6$  is used instead;  $\nu_4$  was estimated from  $\nu_4 + \nu_6$  for  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  but for  $\text{Mo}(\text{CO})_6$  it was estimated as  $\nu_4^{\text{gas}} = \nu_4^{\text{soln}} + \nu_2^{\text{gas}} - \nu_2^{\text{soln}}$ ;  $\nu_5$  was estimated from  $\nu_5 + \nu_7$ ;  $\nu_{10}$  was estimated from  $\nu_7 + \nu_{10}$ ;  $\nu_{11}$  was estimated from  $\nu_6 - \nu_{11}$  for  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  and from  $\nu_6 + \nu_{11}$  for  $\text{Mo}(\text{CO})_6$ ;  $\nu_{12}$  was estimated from  $\nu_5 + \nu_{12}$ . The assignment of  $\nu_{13}$  is somewhat doubtful. The combination assigned as  $\nu_5 + \nu_{13}$  for  $\text{W}(\text{CO})_6$  has no other simple explanation and leads to the values given in Table VII. For  $\text{Mo}(\text{CO})_6$ ,  $\nu_5 + \nu_{13}$  is evidently mixed in with  $\nu_{10} - \nu_9$ , and for  $\text{Cr}(\text{CO})_6$   $\nu_5 + \nu_{13}$  is obscured by  $\nu_8$ . The "shoulders" assigned as  $\nu_{10} + \nu_{13}$  for  $\text{Mo}(\text{CO})_6$  give a crude estimate of  $\nu_{13}$ . For  $\text{Cr}(\text{CO})_6$   $\nu_{10} + \nu_{13}$  is probably mixed with  $\nu_{11} + \nu_{12}$  so an estimate of  $68 \text{ cm}^{-1}$  is made for  $\nu_{13}$  of the normal species by comparison with  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ .

**Coriolis Coupling Constants.**—Other data which are useful for force constant calculation are the Coriolis coupling constants,  $\zeta_i$ , for the  $F_{1u}$  vibrations. These can be estimated<sup>16</sup> from the separation of P and R branches in the fundamental bands of the vapor. The values so determined are given for the normal species in Table VIII.

	$\text{Cr}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$
$\zeta_6$	$-0.11 \pm 0.06$	$-0.07 \pm 0.06$
$\zeta_9$	$-0.02 \pm 0.06$	$0.02 \pm 0.06$

### Calculation of Force Constants

The force constants were calculated using the least-squares program of Schachtschneider.<sup>17</sup> For the CO stretches the harmonic frequencies,  $\omega_i$ , were used. For other vibrational frequencies the observed  $\nu_i$  were used. Examination of the many combination bands observed shows that the anharmonic corrections,  $X_{kl}$ , are quite small (less than  $3 \text{ cm}^{-1}$  in most cases<sup>18</sup>) if  $k$  and  $l$  are not both CO stretches.

The potential function used is a general quadratic valence force field. The symmetry  $F$  matrix has been given before.<sup>19</sup> However, because of a change in nomenclature, and for convenience, we repeat the  $F$  matrix in Table IX. See Figure 3 for the definition of

(16) W. F. Edgell and R. E. Moynihan, *J. Chem. Phys.*, **27**, 155 (1957).

(17) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).

(18) The only apparent exception to this is the combination  $\nu_9 + \nu_{10}$ . For normal  $\text{Cr}(\text{CO})_6$  vapor this combination is  $8.6 \text{ cm}^{-1}$  higher than the sum of  $(\nu_9)_0$  and  $(\nu_{10})_0$ . Thus, from this one would say  $X_{9,10} \approx +8.6 \text{ cm}^{-1}$ . There may be interaction with  $\nu_7$  and with  $\nu_{11} + \nu_{12}$  or perhaps some ternary combination.

(19) L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962).

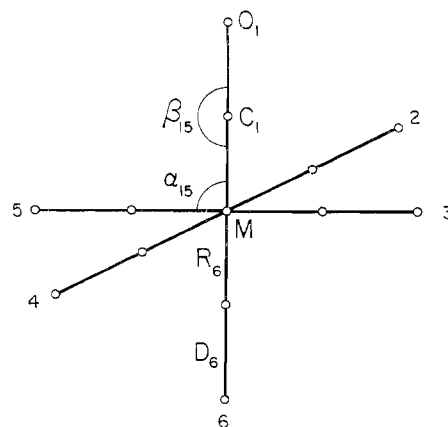


Figure 3.—Internal coordinates of  $[\text{M}(\text{CO})_6]$ .

valence force constants. The M-C and C-O bond distances used were  $1.916$  and  $1.171 \text{ \AA}$  for  $\text{Cr}(\text{CO})_6$ ,<sup>20</sup>  $2.063$  and  $1.145 \text{ \AA}$  for  $\text{Mo}(\text{CO})_6$ ,<sup>21</sup> and  $2.059$  and  $1.148 \text{ \AA}$  for  $\text{W}(\text{CO})_6$ .<sup>21</sup>

**$A_{1g}$  and  $E_g$  Symmetry Force Constants.**—The  $A_{1g}$  and  $E_g$  frequencies of Tables V–VII were used for a least-squares determination of the force constants. The harmonic  $\omega_i$  were used for the CO stretch. In the least-squares program,  $\sum[(\nu_i^2)_{\text{obsd}} - (\nu_i^2)_{\text{calcd}}]^2$  is minimized. Therefore, where error estimates ( $\epsilon_i$ ) are given in the frequency tables, the individual frequencies were weighted as  $(\epsilon_i \nu_i)^{-2}$ . Where no error estimates are given, each  $\nu_i$  is weighted as  $(\nu_i)^{-2}$ , which assumes equal probable errors for each  $\nu_i$ . The calculated symmetry force constants are given in Table X.

**$F_{1g}$ ,  $F_{2g}$ , and  $F_{2u}$  Symmetry Force Constants.**—The vibrations in these symmetry representations involve only bending. Except for  $F_{2g}$  in the solid they are determined from combination bands so the results are subject to somewhat greater uncertainty. The least-squares weighting factors were determined as for the  $A_{1g}$  and  $E_g$  frequencies. The calculated force constants are given in Table XI.

The differences of observed frequencies from those calculated with the force constants of Tables X and XI are given in Table XII. These deviations are somewhat greater than expected, leading to rather large standard deviations for some of the force constants. The experimental values for  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  should be quite accurate for the solids and solutions. The deviations listed in Table XII for  $\nu_2$  and  $\nu_3$  of solid  $\text{Cr}(\text{CO})_6$  and  $\nu_2$  for  $\text{Mo}(\text{CO})_6$  solution and  $\text{W}(\text{CO})_6$  solid are well outside the observational error. The reasons for these discrepancies are not understood at present, though for the solid they could arise from lattice effects. For the gas phase the frequencies were determined rather indirectly; therefore, the observed discrepancies are not surprising. For the solids and solutions the frequency  $\nu_4$  is less certain than  $\nu_2$  because it is much weaker and in some cases seriously over-

(20) A. Whitaker and J. W. Jeffery, *Acta Cryst.*, **23**, 977 (1967).

(21) S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, **20**, 2711 (1966)

TABLE IX  
 SYMMETRY  $F$  MATRIX<sup>a-c</sup> FOR OCTAHEDRAL  $M(\text{CO})_6$ 

$A_{1g}$	$F_{11} = F_{\text{CO}} + 4F_{\text{CO,CO}'} + F_{\text{CO,CO}''}$
	$F_{22} = F_{\text{MC}} + 4F_{\text{MC,MC}'} + F_{\text{MC,MC}''}$
	$F_{12} = F_{\text{MC,CO}} + 4F_{\text{MC,CO}'} + F_{\text{MC,CO}''}$
$E_g$	$F_{33} = F_{\text{CO}} - 2F_{\text{CO,CO}'} + F_{\text{CO,CO}''}$
	$F_{44} = F_{\text{MC}} - 2F_{\text{MC,MC}'} + F_{\text{MC,MC}''}$
	$F_{34} = F_{\text{MC,CO}} - 2F_{\text{MC,CO}'} + F_{\text{MC,CO}''}$
$F_{1g}$	$F_{55} = F_{\beta} - F_{\beta\beta'} - 2F_{\beta\beta''}$
$F_{1u}$	$F_{66} = F_{\text{CO}} - F_{\text{CO,CO}'}'$
	$F_{77} = F_{\text{MC}} - F_{\text{MC,MC}'}'$
	$F_{88} = F_{\beta} + F_{\beta\beta'} + 2F_{\beta\beta''}$
	$F_{99} = (F_{\alpha} - F_{\alpha\alpha'}) + 2(F_{\alpha\alpha''} - F_{\alpha\alpha'''})$
	$F_{67} = F_{\text{MC,CO}} - F_{\text{MC,CO}'}'$
	$F_{68} = 2\sqrt{2}F_{\text{CO},\beta}'$
	$F_{69} = 2(F_{\text{CO},\alpha}' - F_{\text{CO},\alpha}'')$
	$F_{78} = 2\sqrt{2}F_{\text{MC},\beta}'$
	$F_{79} = 2(F_{\text{MC},\alpha}' - F_{\text{MC},\alpha}'')$
	$F_{89} = \sqrt{2}(F_{\alpha\beta}' + F_{\alpha\beta}'' + 2F_{\alpha\beta}''')$
$F_{2k}$	$F_{10,10} = F_{\beta} - F_{\beta\beta'} + 2F_{\beta\beta''}$
	$F_{11,11} = (F_{\alpha} - F_{\alpha\alpha'}) + 2(F_{\alpha\alpha''} - F_{\alpha\alpha'''})$
	$F_{10,11} = 2(F_{\alpha\beta}' - F_{\alpha\beta}'')$
$F_{2u}$	$F_{12,12} = F_{\beta} + F_{\beta\beta'} - 2F_{\beta\beta''}$
	$F_{13,13} = (F_{\alpha} - F_{\alpha\alpha'}) - 2(F_{\alpha\alpha''} - F_{\alpha\alpha'''})$
	$F_{12,13} = \sqrt{2}(F_{\alpha\beta}' + F_{\alpha\beta}'' - 2F_{\alpha\beta}''')$

<sup>a</sup> This differs from the matrix of ref 18 in two respects. The interaction constant  $F_{\beta\beta}''''$  is omitted as it can be shown to be zero. The second expressions given in ref 18 for  $F_{99}$ ,  $F_{11,11}$ ,  $F_{13,13}$ ,  $F_{69}$ , and  $F_{79}$  are not valid as B. L. Crawford, Jr., and J. Overend, *J. Mol. Spectry.*, **12**, 307 (1964), have shown that the "redundant force constants" are indeterminate and not necessarily equal to zero as stated by R. Gold, J. M. Dowling, and A. G. Meister, *ibid.*, **2**, 9 (1958). <sup>b</sup> The valence force constants are defined as follows by reference to Figure 3:  $F_{\text{CO}}$  and  $F_{\text{MC}}$  are the primary stretching force constants;  $F_{\beta}$  and  $F_{\alpha}$  are the MCO and CMC bending constants, respectively;  $F_{k,l}^c$  indicates *cis* stretch-stretch interaction (bonds at  $90^\circ$ );  $F_{k,l}^t$  indicates *trans* stretch-stretch interaction (bonds at  $180^\circ$ );  $F_{\text{MC,CO}}$  indicates interaction of MC and CO involving the same carbon;  $F_{\beta\beta}' = \beta_{12}$  with  $\beta_{22}$ ;  $F_{\beta\beta}'' = \beta_{12}$  with  $\beta_{21}$ ;  $F_{\beta\beta}'''$  with  $\beta_{12}$  with  $\beta_{22}$ ;  $F_{\alpha\alpha}' = F_{\alpha\alpha}'' - f_{\alpha}$ ;  $f_{\alpha}$  is the coefficient of the linear term  $\Sigma\alpha_{ij}$  in potential energy to allow for  $\alpha$  redundancy;  $F_{\alpha\alpha}' = \alpha_{12}$  with  $\alpha_{13}$ ;  $F_{\alpha\alpha}'' = \alpha_{12}$  with  $\alpha_{46}$ ;  $F_{\alpha\alpha}''' = \alpha_{12}$  with  $\alpha_{36}$ ;  $F_{\alpha\alpha}'''' = \alpha_{12}$  with  $\alpha_{14}$ ;  $F_{79}' = r_1$  with  $\beta_{21}$  ( $r = \text{MC or CO}$ );  $F_{79}'' = r_1$  with  $\alpha_{12}$ ;  $F_{79}''' = r_1$  with  $\alpha_{26}$ ;  $F_{\alpha\beta}' = \alpha_{12}$  with  $\beta_{12}$ ;  $F_{\alpha\beta}'' = \alpha_{12}$  with  $\beta_{22}$ ;  $F_{\alpha\beta}''' = \alpha_{12}$  with  $\beta_{32}$ . <sup>c</sup> Symmetry coordinates:  $S_1^{A_{1g}} = (\sqrt{6})^{-1}(D_1 + D_2 + D_3 + D_4 + D_5 + D_6)$ ;  $S_2^{A_{1g}} = (\sqrt{6})^{-1}(R_1 + R_2 + R_3 + R_4 + R_5 + R_6)$ ;  $S_3^{E_g} = (\sqrt{12})^{-1}(2D_1 + 2D_6 - D_2 - D_3 - D_4 - D_5)$ ;  $S_4^{E_g} = 1/2(D_2 + D_4 - D_3 - D_5)$ ;  $S_5^{E_g} = (\sqrt{12})^{-1}(2R_1 + 2R_6 - R_2 - R_3 - R_4 - R_5)$ ;  $S_6^{F_{1g}} = 1/2(\beta_{22} - \beta_{32} - \beta_{43} + \beta_{52})$ ;  $S_7^{F_{1u}} = (\sqrt{2})^{-1}(D_1 - D_6)$ ;  $S_8^{F_{1u}} = (\sqrt{2})^{-1}(R_1 - R_6)$ ;  $S_9^{F_{1u}} = 1/2(\beta_{21} + \beta_{31} + \beta_{41} + \beta_{51})$ ;  $S_{10}^{F_{2g}} = (\sqrt{8})^{-1}(\alpha_{12} + \alpha_{13} + \alpha_{14} + \alpha_{15} - \alpha_{26} - \alpha_{36} - \alpha_{46} - \alpha_{56})$ ;  $S_{11}^{F_{2g}} = 1/2(\beta_{23} + \beta_{32} - \beta_{43} - \beta_{52})$ ;  $S_{12}^{F_{2g}} = 1/2(\alpha_{23} + \alpha_{45} - \alpha_{25} - \alpha_{34})$ ;  $S_{13}^{F_{2u}} = 1/2(\beta_{12} + \beta_{41} - \beta_{31} - \beta_{51})$ ;  $S_{14}^{F_{2u}} = (\sqrt{8})^{-1}(\alpha_{12} + \alpha_{14} + \alpha_{36} + \alpha_{56} - \alpha_{26} - \alpha_{46} - \alpha_{13} - \alpha_{15})$ .  $D_i = \Delta C_i O_i$ ;  $R_i = \Delta \text{MC}_i$ ;  $\beta_{ij} = \angle \text{MC}_i O_i$  bending in  $ij$  plane;  $\alpha_{ij}$  = change in  $C_i \text{MC}_j$  angle. For the triply degenerate sets only one symmetry coordinate is given. This is oriented along one of the fourfold axes. The other two are readily obtained by orienting along the other two fourfold axes.

lapped by  $\nu_2$ . The agreement for  $\nu_5$  through  $\nu_{13}$  is satisfactory considering that most of these values were determined from combination bands.

**$F_{1u}$  Force Constants.**—As expected, this symmetry block caused the most trouble as there are 10 force constants to be calculated from 12 frequencies. Furthermore the isotope shift for the CMC bending frequencies

TABLE X

A <sub>1g</sub> AND E <sub>g</sub> SYMMETRY FORCE CONSTANTS FOR M(CO) <sub>6</sub>				
Molecule	F <sub>ij</sub>	Solid	Solution	Vapor
Cr(CO) <sub>6</sub>	A <sub>1g</sub> F <sub>11</sub>	17.90 <sup>a</sup> ± 0.13 <sup>b</sup>	17.80 ± 0.07	18.11 ± 0.16
	F <sub>22</sub>	2.56 ± 0.02	2.48 ± 0.01	2.44 ± 0.02
	F <sub>12</sub>	0.37 ± 0.11	0.22 ± 0.05	0.38 ± 0.13
	E <sub>g</sub> F <sub>33</sub>	16.62 ± 0.15	16.78 ± 0.02	16.84 ± 0.07
	F <sub>44</sub>	2.65 ± 0.01	2.60 ± 0.01	2.55 ± 0.01
	F <sub>34</sub>	0.81 ± 0.13	0.77 ± 0.02	0.69 ± 0.05
Mo(CO) <sub>6</sub>	A <sub>1g</sub> F <sub>11</sub>	17.86 ± 0.06	17.83 ± 0.07	18.13 ± 0.31
	F <sub>22</sub>	2.82 ± 0.01	2.77 ± 0.01	2.61 ± 0.04
	F <sub>12</sub>	0.32 ± 0.05	0.22 ± 0.05	0.38 ± 0.25
	E <sub>g</sub> F <sub>33</sub>	16.69 ± 0.12	16.83 ± 0.07	16.84 ± 0.04
	F <sub>44</sub>	2.58 ± 0.01	2.55 ± 0.01	2.42 ± 0.01
	F <sub>34</sub>	0.87 ± 0.10	0.79 ± 0.06	0.68 ± 0.04
W(CO) <sub>6</sub>	A <sub>1g</sub> F <sub>11</sub>	17.77 ± 0.26	17.87 ± 0.10	18.10 ± 0.03
	F <sub>22</sub>	3.26 ± 0.04	3.14 ± 0.02	3.10 ± 0.01
	F <sub>12</sub>	0.28 ± 0.21	0.32 ± 0.08	0.36 ± 0.02
	E <sub>g</sub> F <sub>33</sub>	16.54 ± 0.12	16.75 ± 0.00	16.78 ± 0.10
	F <sub>44</sub>	2.92 ± 0.01	2.83 ± 0.00	2.81 ± 0.01
	F <sub>34</sub>	0.96 ± 0.10	0.96 ± 0.00	0.82 ± 0.08

<sup>a</sup> Units are millidynes per ångström. <sup>b</sup> Error limits are least-squares standard deviations.

is not very sensitive to the force constant solution. Thus, we are essentially limited to determination of 10 force constants from 10 frequencies even if all 12 are known.<sup>22</sup> It was not possible to converge on a solution by allowing all force constants to vary because the frequencies are rather insensitive to some of the  $F_{1u}$  force constants. However, for  $W(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  it was possible to achieve a solution by holding the force constant  $F_{69} = 2(F_{\text{CO},\alpha}' - F_{\text{CO},\alpha}'')$  at a fixed value. For  $W(\text{CO})_6$  vapor such a procedure leads to reasonable force constants; however, for  $W(\text{CO})_6$  solution and for  $\text{Mo}(\text{CO})_6$  large values (0.7–1.6 mdyn/radian) are calculated for  $F_{68} = 2\sqrt{2}F_{\text{CO},\beta}'$  with very large standard deviations.

An idea of reasonable ranges for  $F_{68}$  and  $F_{69}$  can be obtained by looking at the other force constants. A large number of solutions have been investigated for all three molecules and the quantity  $(F_{\text{MC},\alpha}' - F_{\text{MC},\alpha}'')$  is found to lie in the range 0 to  $-0.45$  mdyn/radian. However, as will be shown later, the high negative values (close to  $-0.45$ ) are not acceptable and we take  $(F_{\text{MC},\alpha}' - F_{\text{MC},\alpha}'')$  to be  $-0.15 \pm 0.05$  mdyn/radian. The  $\text{CO},\alpha$  interaction should be less than the  $\text{MC},\alpha$  interaction because such an interaction goes through the MC bond. However, to be safe we have allowed the constant  $(F_{\text{CO},\alpha}' - F_{\text{CO},\alpha}'')$  to vary in the range  $-0.25$  to  $+0.25$  mdyn/radian. We expect  $F_{\text{CO},\beta}'$  to be considerably less than  $(F_{\text{CO},\alpha}' - F_{\text{CO},\alpha}'')$  because it represents interaction of a CO bond with a  $\beta$  angle separated from the CO bond by two MC bonds. Therefore, we have allowed  $F_{\text{CO},\beta}'$  to vary in the range  $-0.07$  to  $+0.07$  mdyn/radian. Varying the  $\text{CO},\alpha$  and  $\text{CO},\beta$  interaction constants in these ranges does not have a major effect on the other calculated force constants because the corresponding  $G$  matrix elements

(22) One might argue that since the product rule fixes two frequencies from the other ten, we only have ten independent data to determine the ten force constants. However, in performing the least-squares calculation one does not consider this dependency and, in reality, twelve frequencies give us twelve independent data. As long as we have sufficient data to calculate the force constants (in this case four frequencies from one molecule and three frequencies from each of the other two) we can theoretically calculate all of the constants and any additional frequencies can be treated as independent data.

TABLE XI  
 $F_{1g}$ ,  $F_{2g}$ , AND  $F_{2u}$  FORCE CONSTANTS FOR  $M(\text{CO})_6$ 

Molecule	$F_{ij}$	$F_{ij}$		Vapor	
		Solid	Solution <sup>c</sup>		
$\text{Cr}(\text{CO})_6$	$F_{1g}$	$F_{35}$	$0.383 \pm 0.001^b$	$0.375 \pm 0.001$	
	$F_{2g}$	$F_{10,10}$	$0.34 \pm 0.03^b$	$(0.31 \pm 0.03)$	$0.39 \pm 0.10$
		$F_{11,11}$	$0.91 \pm 0.08$	$(0.83 \pm 0.08)$	$0.54 \pm 0.16$
		$F_{10,11}$	$-0.09 \pm 0.01$	$(-0.14 \pm 0.01)$	$-0.17 \pm 0.02$
	$F_{2u}$	$F_{12,12}$			$0.59 \pm 0.13$
		$F_{13,13}$			$0.35 \pm 0.12$
$F_{12,13}$				$-0.11 \pm 0.12$	
$\text{Mo}(\text{CO})_6$	$F_{1g}$	$F_{35}$	$0.355 \pm 0.002$	$0.346 \pm 0.001$	
	$F_{2g}$	$F_{10,10}$	$0.46 \pm 0.08$	$(0.43 \pm 0.13)$	$0.44 \pm 0.02$
		$F_{11,11}$	$0.52 \pm 0.09$	$(0.44 \pm 0.17)$	$0.34 \pm 0.02$
		$F_{10,11}$	$-0.05 \pm 0.05$	$(-0.09 \pm 0.07)$	$-0.11 \pm 0.01$
	$F_{2u}$	$F_{12,12}$			$0.55 \pm 0.10$
		$F_{13,13}$			$0.39 \pm 0.13$
$F_{12,13}$				$-0.19 \pm 0.09$	
$\text{W}(\text{CO})_6$	$F_{1g}$	$F_{35}$	$0.395 \pm 0.004$	$0.385 \pm 0.001$	
	$F_{2g}$	$F_{10,10}$	$0.47 \pm 0.01$	$(0.43 \pm 0.02)$	$0.41 \pm 0.11$
		$F_{11,11}$	$0.54 \pm 0.01$	$(0.45 \pm 0.03)$	$0.39 \pm 0.14$
		$F_{10,11}$	$-0.04 \pm 0.01$	$(-0.10 \pm 0.01)$	$-0.13 \pm 0.05$
	$F_{2u}$	$F_{12,12}$			$0.64 \pm 0.10$
		$F_{13,13}$			$0.33 \pm 0.10$
$F_{12,13}$				$-0.14 \pm 0.10$	

<sup>a</sup> The units are  $\text{mdyn } \text{\AA} \text{ radian}^{-2}$  for all  $F_{ij}$  in this table. <sup>b</sup> The error limits are chosen to span the range of calculated values for  $F_{35}$ . For the other  $F_{ij}$  values the error limits are least-squares standard deviations. <sup>c</sup> The solution values for  $F_{2g}$  were calculated assuming  $\nu_{10}$  for solution is the same as  $\nu_{10}$  for the solid. The similarity of  $\nu_{10}$  observed for vapor and solid indicates that this is not a bad assumption.

 TABLE XII  
 DEVIATIONS IN FREQUENCIES,  $\nu_{\text{obsd}} - \nu_{\text{calcd}}$ , FOR  $M(^k\text{C}^l\text{O})_6$  IN  $\text{CM}^{-1}$ 

	$k,l$	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$	$\Delta\nu_5$	$\Delta\nu_{10}$	$\Delta\nu_{11}$	$\Delta\nu_{12}$	$\Delta\nu_{13}$	
$\text{Cr}(\text{CO})_6$	Solid	12,16	-0.2	-0.4	-0.8	-0.3	-0.4	-0.5	-0.1		
		13,16	0.1	-0.2	0.2	0.5	0.2	0.3	-0.2		
		12,18	0.2	0.6	0.5	0.3	0.1	0.2	0.4		
	Soln	12,16	-0.2	-0.2	-0.1	-0.6		-0.5	0.3		
		13,16	0.3	0.2	0.0	...		0.3	-0.3		
		12,18	0.1	0.1	0.0	0.6		0.2	0.1		
	Vapor	12,16	-0.4	-0.7	-0.3	0.0	0.0	-0.7	-0.3	-1.4	0.7
		13,16	0.2	0.1	0.2	0.1	-0.1	0.2	-0.9	0.9	[66.8] <sup>a</sup>
		12,18	0.2	0.5	0.1	-0.2	0.0	0.5	1.3	0.5	-0.7
$\text{Mo}(\text{CO})_6$	Solid	12,16	0.0	-0.1	-0.3	-0.1	-0.5	-1.2	-0.1		
		13,16	-0.1	-0.2	0.1	-0.7	0.8	0.8	-0.2		
		12,18	0.0	0.3	0.2	1.1	-0.4	0.5	0.3		
	Soln	12,16	0.0	0.2	-0.1	1.1		-1.2	0.0		
		13,16	0.1	0.5	0.1	1.7		0.8			
		12,18	0.0	-1.9	0.0	-1.6		0.5			
	Vapor	12,16	-0.8	-1.3	-0.1	0.0	-0.3	-0.2	0.2	-0.8	0.0
		13,16	0.5	0.7	0.1		0.6	0.1	0.0	0.5	[59.6] <sup>a</sup>
		12,18	0.4	0.7	0.1		-0.2	0.1	-0.2	0.4	[57.1] <sup>a</sup>
$\text{W}(\text{CO})_6$	Solid	12,16	-0.3	-1.0	-0.2	-0.3	-1.2	0.2	0.1		
		13,16	0.3	1.2	0.4	1.5	-1.1	-0.1	-0.1		
		12,18	0.0	-0.2	0.1	-0.5	1.7	-0.1	0.1		
	Soln	12,16	0.0	-0.4	0.0	0.0		0.2	0.0		
		13,16	0.0	0.5	0.0			-0.1			
		12,18	0.0	0.0	0.0			-0.1			
	Vapor	12,16	0.1	0.0	-0.3	0.0	-0.1	-1.0	-0.3	-0.8	0.0
		13,16	0.0		0.2		0.3	0.4	-1.1	0.5	[61.0] <sup>a</sup>
		12,18	0.0		0.1		-0.2	0.7	1.6	0.3	[58.5] <sup>a</sup>

<sup>a</sup> Calculated frequencies; not observed.

are zero. Therefore, we consider that the constraint of  $F_{68} (=2\sqrt{2}F_{\text{MC},\beta'})$  to  $0 \pm 0.2$  and  $F_{69} [=2(F_{\text{CO},\alpha'} - F_{\text{CO},\alpha''})]$  to  $0 \pm 0.5$  is a reasonable assumption with generous limits and does not seriously affect the other calculated force constants.

In Table XIII we give the force constants calculated from the frequencies of Tables V-VII, using the har-

monic  $\omega_6$  and fixing  $F_{68}$  and  $F_{69}$  in the ranges  $0 \pm 0.2$  and  $0 \pm 0.5$   $\text{mdyn/radian}$ , respectively. The results for  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  are reasonably consistent; that is, except for the primary stretching force constants, the calculated constants are about the same for solution and gas and for  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , within the standard deviations. However, for  $\text{Cr}(\text{CO})_6$  the results are



TABLE XIII  
 PRELIMINARY SOLUTIONS FOR  $F_{1u}$  SYMMETRY FORCE CONSTANTS<sup>a</sup> OF  $M(\text{CO})_6$ 

	$\text{Cr}(\text{CO})_6$		$\text{Mo}(\text{CO})_6$		$\text{W}(\text{CO})_6$	
	Soln	Gas	Soln	Gas	Soln	Gas
$F_{66}$	$16.86 \pm 0.13^b$	$17.02 \pm 0.11$	$17.13 \pm 0.06$	$17.35 \pm 0.05$	$16.91 \pm 0.05$	$17.23 \pm 0.05$
$F_{77}$	$1.28 \pm 0.27$	$0.96 \pm 0.27$	$1.35 \pm 0.13$	$1.31 \pm 0.15$	$1.73 \pm 0.10$	$1.86 \pm 0.12$
$F_{88}$	$0.72 \pm 0.17$	$0.88 \pm 0.18$	$0.55 \pm 0.07$	$0.51 \pm 0.06$	$0.52 \pm 0.05$	$0.46 \pm 0.06$
$F_{99}$	$1.1 \pm 0.4$	$1.6 \pm 0.6$	$0.82 \pm 0.20$	$0.94 \pm 0.20$	$1.00 \pm 0.13$	$0.92 \pm 0.16$
$F_{67}$	$0.59 \pm 0.17$	$0.42 \pm 0.15$	$0.87 \pm 0.09$	$0.81 \pm 0.08$	$0.93 \pm 0.07$	$0.94 \pm 0.09$
$F_{68}$	$[0 \pm 0.2]^c$		$[0 \pm 0.2]^c$		$[0 \pm 0.2]^c$	
$F_{69}$	$[0 \pm 0.5]^c$		$[0 \pm 0.5]^c$		$[0 \pm 0.5]^c$	
$F_{78}$	$-0.31 \pm 0.10$	$-0.33 \pm 0.10$	$-0.10 \pm 0.08$	$-0.15 \pm 0.07$	$-0.11 \pm 0.11$	$0.04 \pm 0.18$
$F_{79}$	$-0.67 \pm 0.22$	$-0.88 \pm 0.12$	$-0.35 \pm 0.22$	$-0.50 \pm 0.21$	$-0.26 \pm 0.26$	$-0.08 \pm 0.43$
$F_{89}$	$0.03 \pm 0.22$	$0.31 \pm 0.27$	$-0.23 \pm 0.08$	$-0.23 \pm 0.10$	$-0.29 \pm 0.05$	$-0.36 \pm 0.04$

<sup>a</sup> Units are  $\text{mdyn}/\text{\AA}$  for  $F_{66}$ ,  $F_{77}$ , and  $F_{67}$ ;  $\text{mdyn}/\text{radian}$  for  $F_{68}$ ,  $F_{69}$ ,  $F_{78}$ , and  $F_{79}$ ;  $\text{mdyn}/\text{\AA}^2$  for  $F_{88}$ ,  $F_{99}$ , and  $F_{89}$ . <sup>b</sup> The limits of error given are the standard deviations plus the variation in calculated  $F_{ij}$  arising from the indicated ranges for  $F_{68}$  and  $F_{69}$  for all three molecules. <sup>c</sup> These values were held fixed in the indicated range.

considerably different, especially for the gas. Notably,  $F_{77}$  is unexpectedly small,  $F_{99}$  is quite large,  $F_{79}$  is a much larger negative value than for  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , and  $F_{89}$  is positive while it is negative for the other two molecules. Therefore, we must conclude that either the  $\text{Cr}(\text{CO})_6$  molecule contains quite different interatomic forces from the other two or there is a systematic error in some of the observed frequencies. The latter situation may arise for  $\nu_8$  of  $\text{Cr}(\text{CO})_6$  which overlaps the combination  $\nu_5 + \nu_9$ ; the proximity of these two bands, which is different for the three isotopic molecules of  $\text{Cr}(\text{CO})_6$ , may give rise to Fermi resonance resulting in significant displacement of the band center.

We have some additional information from the observed Coriolis coupling constants,  $\zeta_9$ , for  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  (see Table VIII). For normal  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  the Coriolis constants were calculated for a number of different force constant solutions, with various force constants held fixed over ranges of values. Just as for  $\text{Ni}(\text{CO})_4$ ,<sup>8</sup> it was found that  $\zeta_9$  is nearly a linear function of  $F_{\text{MC},\alpha}$ , as shown in Figure 4. No such dependence was found in the other force constants. From the limits given for the observed  $\zeta_9$  we can bracket the values of  $F_{79}$ . Using Figure 4 we find  $F_{79}[\text{Cr}(\text{CO})_6] = -0.165 \pm 0.14$  and  $F_{79}[\text{Mo}(\text{CO})_6] = -0.335 \pm 0.12$   $\text{mdyn}/\text{radian}$ . Note that the value of  $F_{79}$  calculated for  $\text{Mo}(\text{CO})_6$  from  $\zeta_9$  agrees reasonably well with the values in Table XIII. However, for  $\text{Cr}(\text{CO})_6$  the agreement is extremely poor. Though there is some doubt<sup>23</sup> about the accuracy obtained in using  $\zeta$  values for force constant calculations, the discrepancy noted here is far greater than can be expected. We conclude that the vibrational frequencies,  $\nu_8$ , of  $\text{Cr}(\text{CO})_6$  are significantly affected by Fermi interaction with  $\nu_5 + \nu_9$ , or some other perturbations, so that the "observed" isotope shifts are not reliable for force constant calculations.

For consistency we now take the following approach. The interaction constant,  $F_{79}$ , represents interaction of a metal-carbon stretch with an included carbon-metal-carbon bend. Though we do not as yet understand this interaction there appears to be no reason for it to be

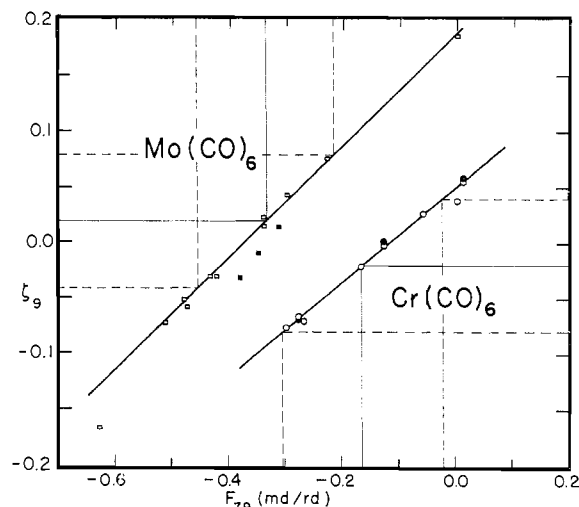


Figure 4.—Dependence of  $\zeta_9$  on  $F_{79}$  for  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$ . Points obtained from the use of vapor-phase frequencies are represented by open symbols; from solution frequencies, by solid symbols. Experimental values of  $\zeta_9$  and their estimated ranges are also shown.

greatly different for the three molecules. Therefore, we shall make the hypothesis that  $F_{79}$  is the same for all three molecules. After a suitable value has been chosen, we can test this hypothesis using Hamilton's criteria.<sup>24a</sup> In order to estimate  $F_{79}$  we have taken a weighted mean<sup>24b</sup> of the values calculated for  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , gas and solution, and the values calculated from  $\zeta_9$  for  $\text{Mo}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$ . The weights used are  $1/\sigma_i^2$  where  $\sigma_i$  is the standard deviation for  $F_{79}$  of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  from Table XIII and the estimated uncertainty of  $F_{79}$  determined from  $\zeta_9$  for  $\text{Mo}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$ . The value arrived at is  $F_{79} = -0.29 \pm 0.08$ . Admittedly the weighting scheme is somewhat arbitrary in treating the estimated uncertainties from the  $\zeta$ 's as equivalent to the standard deviations of Table XIII. However, if we vary the weights from zero to infinity for  $F_{79}$  from the  $\zeta$ 's, for this case fortunately the mean varies only from  $-0.35$  to  $-0.26$ . Therefore, we feel justified in assigning the

(24) (a) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965); (b) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, p 42.

TABLE XIV  
 "BEST ESTIMATES" OF  $F_{ij}$  FORCE CONSTANTS<sup>a</sup> OF THE HEXACARBONYLS

	Cr(CO) <sub>6</sub>		Mo(CO) <sub>6</sub>		W(CO) <sub>6</sub>	
	Soln	Gas	Soln	Gas	Soln	Gas
$F_{66}$	16.96 ± 0.14 <sup>b</sup>	17.22 ± 0.11	17.14 ± 0.06	17.39 ± 0.06	16.91 ± 0.06	17.21 ± 0.04
$F_{77}$	1.63 ± 0.14	1.64 ± 0.16	1.38 ± 0.10	1.43 ± 0.12	1.71 ± 0.07	1.80 ± 0.07
$F_{88}$	0.56 ± 0.16	0.55 ± 0.22	0.55 ± 0.07	0.48 ± 0.09	0.52 ± 0.05	0.47 ± 0.07
$F_{99}$	0.83 $\left\{ \begin{array}{l} + 0.35 \\ - 0.25 \end{array} \right.$	0.79 $\left\{ \begin{array}{l} + 0.46 \\ - 0.28 \end{array} \right.$	0.79 $\left\{ \begin{array}{l} + 0.21 \\ - 0.13 \end{array} \right.$	0.83 $\left\{ \begin{array}{l} + 0.25 \\ - 0.16 \end{array} \right.$	0.99 $\left\{ \begin{array}{l} + 0.14 \\ - 0.10 \end{array} \right.$	0.93 $\left\{ \begin{array}{l} + 0.14 \\ - 0.09 \end{array} \right.$
$F_{67}$	0.79 ± 0.15	0.78 ± 0.13	0.89 ± 0.08	0.88 ± 0.07	0.92 ± 0.06	0.91 ± 0.06
$F_{68}$	[0 ± 0.2] <sup>c</sup>		[0 ± 0.2] <sup>c</sup>		[0 ± 0.2] <sup>c</sup>	
$F_{69}$	[0 ± 0.5] <sup>c</sup>		[0 ± 0.5] <sup>c</sup>		[0 ± 0.5] <sup>c</sup>	
$F_{78}$	-0.20 ± 0.09	-0.18 ± 0.09	-0.09 ± 0.07	-0.07 ± 0.08	-0.12 ± 0.07	-0.04 ± 0.06
$F_{79}$	[-0.3 ± 0.1] <sup>c</sup>		[-0.3 ± 0.1] <sup>c</sup>		[-0.3 ± 0.1] <sup>c</sup>	
$F_{89}$	-0.20 ± 0.09	-0.21 ± 0.12	-0.24 ± 0.07	-0.30 ± 0.07	-0.29 ± 0.05	-0.34 ± 0.04
$\zeta_6^d$	(-0.11 ± 0.06) <sup>e</sup>	0.00	(-0.07 ± 0.06) <sup>e</sup>	0.00		0.00
$\zeta_7$		0.77		0.67		0.62
$\zeta_8$		0.30		0.28		0.18
$\zeta_9$	(-0.02 ± 0.06) <sup>e</sup>	-0.07	(0.02 ± 0.06) <sup>e</sup>	0.05		0.20
$\Delta\nu_6$	0.3	0.2	0.1	0.1	0.1	0.1
$\Delta\nu_7$	-0.2	0	0	-0.1	0	0.1
$\Delta\nu_8$	0.4	0	-0.2	-0.4	-0.1	0.1
$\Delta\nu_9$	0	-0.3	0	-0.1	0	0
$\Delta\omega_6$	-0.2	-0.1	-0.1	-0.1	-0.1	0
$\Delta\nu_7$	0.2	0	0	0.1	0	0
$\Delta\nu_8$	0.5	0.9	0	0.3	-0.1	-0.1
$\Delta\nu_9$	[102.4] <sup>g</sup>	[97.0] <sup>g</sup>	[90.6] <sup>g</sup>	0	[91.7] <sup>g</sup>	[81.8] <sup>g</sup>
$\Delta\omega_6$	-0.1	-0.1	-0.1	-0.1	0	0
$\Delta\nu_7$	0	0	0	0	0	0
$\Delta\nu_8$	-1.0	-2.7	0.1	0.1	0.2	0
$\Delta\nu_9$	[98.6] <sup>g</sup>	0.3	[87.1] <sup>g</sup>	0.1	[87.9] <sup>g</sup>	[78.4] <sup>g</sup>

<sup>a</sup> Units are mdyne/Å for  $F_{66}$ ,  $F_{77}$ , and  $F_{87}$ ; mdyne/radian for  $F_{68}$ ,  $F_{69}$ ,  $F_{78}$ , and  $F_{79}$ ; mdyne Å/radian<sup>2</sup> for  $F_{88}$ ,  $F_{99}$ , and  $F_{89}$ . <sup>b</sup> The limits of error given are the standard deviations plus the variation in calculated  $F_{ij}$  arising from the indicated ranges for  $F_{68}$ ,  $F_{69}$ , and  $F_{79}$ . <sup>c</sup> These values were held in the indicated range for reasons discussed in the text. <sup>d</sup> The  $\zeta$  values given were calculated for the normal species in the gas phase using the estimated mean force constants. The  $\zeta$ 's for the isotopic species are almost the same, differing from the corresponding values for the normal species by at most 0.018 and usually much less. <sup>e</sup> These are observed  $\zeta$  values as estimated<sup>16</sup> from the band contours for the normal species in the gas phase. <sup>f</sup> The numbers listed for  $\Delta\nu_i$  are  $\nu_{\text{obsd}} - \nu_{\text{calcd}}$  in  $\text{cm}^{-1}$  where  $\nu_{\text{calcd}}$  is the value calculated from the listed  $F_{ij}$ . <sup>g</sup> Calculated frequencies; not observed.

value  $F_{79} = -0.30 \pm 0.10$  for all three molecules. When this is done, we arrive at the solutions of Table XIV.

Before proceeding further there are several points to note concerning the results of Tables XIII and XIV. A comparison of the sums of the squares of the residuals  $[\sum_i (\lambda_i^{\text{obsd}} - \lambda_i^{\text{calcd}})^2]$  shows that for  $\text{W}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$ , solution and vapor, the hypothesis that  $F_{79} = -0.30$  can be rejected<sup>24</sup> only at the 0.40 level, meaning that if the hypothesis is rejected there is more than a 40% chance of error. One would ordinarily accept the hypothesis at this level<sup>24</sup> and thus it is appropriate to fix  $F_{79}$  at  $-0.3$  mdyne/radian for  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ . For  $\text{Cr}(\text{CO})_6$  solution and vapor the rejection levels are 0.2 and 0.09, respectively. This implies that for  $\text{Cr}(\text{CO})_6$  gas the vibrational frequencies are not in agreement with the hypothesis that  $F_{79} = -0.3$ . As seen from Table XIV the deviation for  $\nu_8$  of  $\text{Cr}(\text{C}^{18}\text{O})_6$  is  $2.7 \text{ cm}^{-1}$  which is well outside experimental error. We conclude that this frequency is probably lowered significantly by Fermi resonance with  $\nu_8 + \nu_9$  and that our best approach is to fix  $F_{79}$  at  $-0.3$  mdyne/radian to agree with the other molecules and with  $\zeta_9$  for  $\text{Cr}(\text{CO})_6$ . In accord with this conclusion is the result that the other interaction constants,  $F_{67}$ ,  $F_{78}$ , and  $F_{89}$ , are now essentially the same for all three molecules

within the standard deviations. Such consistency is expected for such similar molecules.

**Characterization of Normal Vibrations.**—It is of interest to characterize the normal vibrations as arising from displacements of particular internal coordinates. For this purpose we report the usual potential energy distribution,  $V_{kl,\nu_i} = L_{k,\nu_i} F_{kl} L_{l,\nu_i}$ . The results are given in Table XV. Of particular note is the strong mixture of MCO bending and CMC bending in the frequencies around  $100 \text{ cm}^{-1}$  and around  $550\text{--}650 \text{ cm}^{-1}$ . Thus, in spite of the rather large frequency separation,  $\nu_7$  and  $\nu_9$  are strong mixtures of MCO bending and CMC bending with a significant amount of MC stretch as well. The same situation pertains to  $\nu_{10}$  and  $\nu_{11}$  and to a lesser extent to  $\nu_{12}$  and  $\nu_{13}$ . Thus, we are oversimplifying the description considerably to talk about MCO bending vibrations as distinct from CMC bending vibrations.

In order to obtain a better picture of these results we have prepared Figure 5 which displays the Cartesian displacement coordinates on a relative scale for the vibrations of  $\text{Mo}(\text{CO})_6$  vapor. This is designed to show only the relative motion of the various atoms for a given normal vibration. Of particular interest are the vibrations  $\nu_7$ ,  $\nu_{10}$ , and  $\nu_{12}$  (in the  $450\text{--}650\text{-cm}^{-1}$  range). Note that they involve considerable distortion of the

TABLE XV  
 POTENTIAL ENERGY DISTRIBUTION FOR  $M(^{12}C^{16}O)_6$  VAPOR

		Cr(CO) <sub>6</sub>				Mo(CO) <sub>6</sub>				W(CO) <sub>6</sub>			
		$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$
A <sub>1g</sub>	$V_{11}^a$	0.98	0.02			0.97	0.03			0.97	0.04		
	$V_{22}$	0.05	0.96			0.05	0.95			0.06	0.94		
	$V_{12}$	-0.02	0.02			-0.02	0.02			-0.02	0.02		
E <sub>g</sub>	$V_{33}$			1.00	0.02			1.00	0.01			1.00	0.01
	$V_{44}$			0.05	0.96			0.05	0.96			0.06	0.96
	$V_{34}$			-0.05	0.03			-0.05	0.02			-0.06	0.03
F <sub>1u</sub>	$V_{66}$	1.02	0	0	0	1.03	0	0	0.01	1.03	0	0	0
	$V_{77}$	0.03	0.16	0.64	0.46	0.03	0.07	0.82	0.29	0.04	0.04	0.90	0.16
	$V_{88}$	0	0.39	0.21	0.65	0	0.41	0.12	0.88	0	0.43	0.07	0.92
	$V_{99}$	0	0.24	0	1.09	0	0.20	0	1.32	0	0.20	0	1.29
	$V_{67}$	-0.05	0	0.01	-0.01	-0.06	0	0	-0.01	-0.06	0	0.01	-0.01
	$V_{68}$	0	0	0	0	0	0	0	0	0	0	0	0
	$V_{69}$	0	0	0	0	0	0	0	0	0	0	0	0
	$V_{78}$	0	-0.10	0.15	-0.23	0	-0.03	0.06	-0.09	0	-0.01	0.02	-0.03
	$V_{79}$	0	0.10	-0.01	-0.34	0	0.06	0	-0.34	0	0.04	-0.01	-0.21
	$V_{89}$	0	0.20	0.01	-0.62	0	0.28	0	-1.04	0	0.30	0.01	-1.12
	F <sub>2g</sub>	$V_{10,10}$	0.47	0.70			0.63	0.46			0.58	0.53	
$V_{11,11}$		0.27	0.90			0.17	0.92			0.20	0.92		
$V_{10,11}$		0.27	-0.60			0.19	-0.38			0.22	-0.44		
F <sub>2u</sub>	$V_{12,12}$			0.79	0.28			0.71	0.51			0.79	0.32
	$V_{13,13}$			0.09	0.98			0.08	1.13			0.07	1.04
	$V_{12,13}$			0.13	-0.26			0.20	-0.63			0.14	-0.36

<sup>a</sup> The subscripts identify  $V_{kl}$  with the symmetry coordinates  $k$  and  $l$  as defined in footnote  $c$  of Table IX.

 TABLE XVI  
 VALENCE STRETCHING FORCE CONSTANTS<sup>a</sup> OF  $M(CO)_6$ 

	Cr(CO) <sub>6</sub>		Mo(CO) <sub>6</sub>		W(CO) <sub>6</sub>	
	Soln	Gas	Soln	Gas	Soln	Gas
$F_{CO}$	17.04 ± 0.07	17.24 ± 0.07	17.15 ± 0.04	17.33 ± 0.06	17.02 ± 0.03	17.22 ± 0.04
$F_{MC}$	2.10 ± 0.07	2.08 ± 0.08	2.00 ± 0.05	1.96 ± 0.06	2.32 ± 0.04	2.36 ± 0.04
$F_{CO,C'O'}$	0.17 ± 0.01	0.21 ± 0.03	0.17 ± 0.02	0.22 ± 0.05	0.19 ± 0.02	0.22 ± 0.02
$F_{CO,C'O''}$	0.08 ± 0.07	0.02 ± 0.07	0.01 ± 0.04	-0.06 ± 0.06	0.11 ± 0.03	0.00 ± 0.04
$F_{MC,MC'}$	-0.020 ± 0.002	-0.019 ± 0.003	0.037 ± 0.003	0.031 ± 0.009	0.052 ± 0.003	0.049 ± 0.002
$F_{MC,MC''}$	0.47 ± 0.07	0.44 ± 0.08	0.62 ± 0.05	0.53 ± 0.06	0.61 ± 0.04	0.56 ± 0.04
$F_{MC,CO}$	0.69 ± 0.08	0.68 ± 0.07	0.74 ± 0.05	0.73 ± 0.06	0.84 ± 0.03	0.79 ± 0.04
$F_{MC,C'O'}$	-0.09 ± 0.01	-0.05 ± 0.03	-0.09 ± 0.01	-0.05 ± 0.04	-0.11 ± 0.02	-0.08 ± 0.02
$F_{MC,C'O''}$	-0.10 ± 0.08	-0.10 ± 0.07	-0.15 ± 0.05	-0.15 ± 0.06	-0.09 ± 0.03	-0.12 ± 0.04

<sup>a</sup> Units are mdyne/Å. Force constants are defined in footnote  $b$  to Table IX.

CMC angles as well as the MCO angles. In these vibrations the carbon atoms move much more than the oxygen atoms showing why the isotope shift is much greater for  $^{12}C \rightarrow ^{13}C$  than for  $^{16}O \rightarrow ^{18}O$ . For  $\nu_9$ ,  $\nu_{11}$ , and  $\nu_{13}$  again CMC and MCO angles both change, the former somewhat more. For these low-frequency vibrations the oxygen atom moves considerably more than the carbon atom. It is also apparent that the "metal-carbon" stretch,  $\nu_8$ , also involves considerable MCO bending and that  $\nu_7$  involves significant MC stretching.

**Valence Force Constants for  $M(CO)_6$ .**—The internal coordinate valence force constants are of more basic interest than the symmetry force constants. The stretching force constants can be calculated for solution and vapor, using the relations of Tables IX, X, and XIV, and are given in Table XVI. Since the  $F_{2u}$  force constants have been determined only for the vapor, the bending force constants cannot be calculated

for solution or solid. The results for the vapor are given in Table XVII.

The stretch-bend interactions are not well determined in this work. As discussed earlier in this paper,  $F_{CO,\beta'}$  and  $(F_{CO,\alpha'} - F_{CO,\alpha''})$  have been fixed at  $0 \pm 0.07$  and  $0 \pm 0.25$  mdyne/radian. The other two interactions,  $F_{MC,\beta'}$  and  $(F_{MC,\alpha'} - F_{MC,\alpha''})$  are found to be  $-0.04 \pm 0.01$  and  $-0.15 \pm 0.05$  mdyne/radian, respectively. The former value is determined from the weighted mean of the  $F_{78}$  values of Table XIV.

**Mean Amplitudes and Shrinkage Effects.**—The mean amplitudes of vibration and the shrinkage effects have been calculated for these molecules at 298°K, using the force fields of Tables X, XI, and XIV. The results are presented in Table XVIII and compared with the experimental values of Arnesen and Seip<sup>21</sup> for  $Mo(CO)_6$  and  $W(CO)_6$ , obtained by electron diffraction. The mean amplitudes agree quite well with the exception of  $u(O-C-W-C-O)$ , for which the electron diffrac-

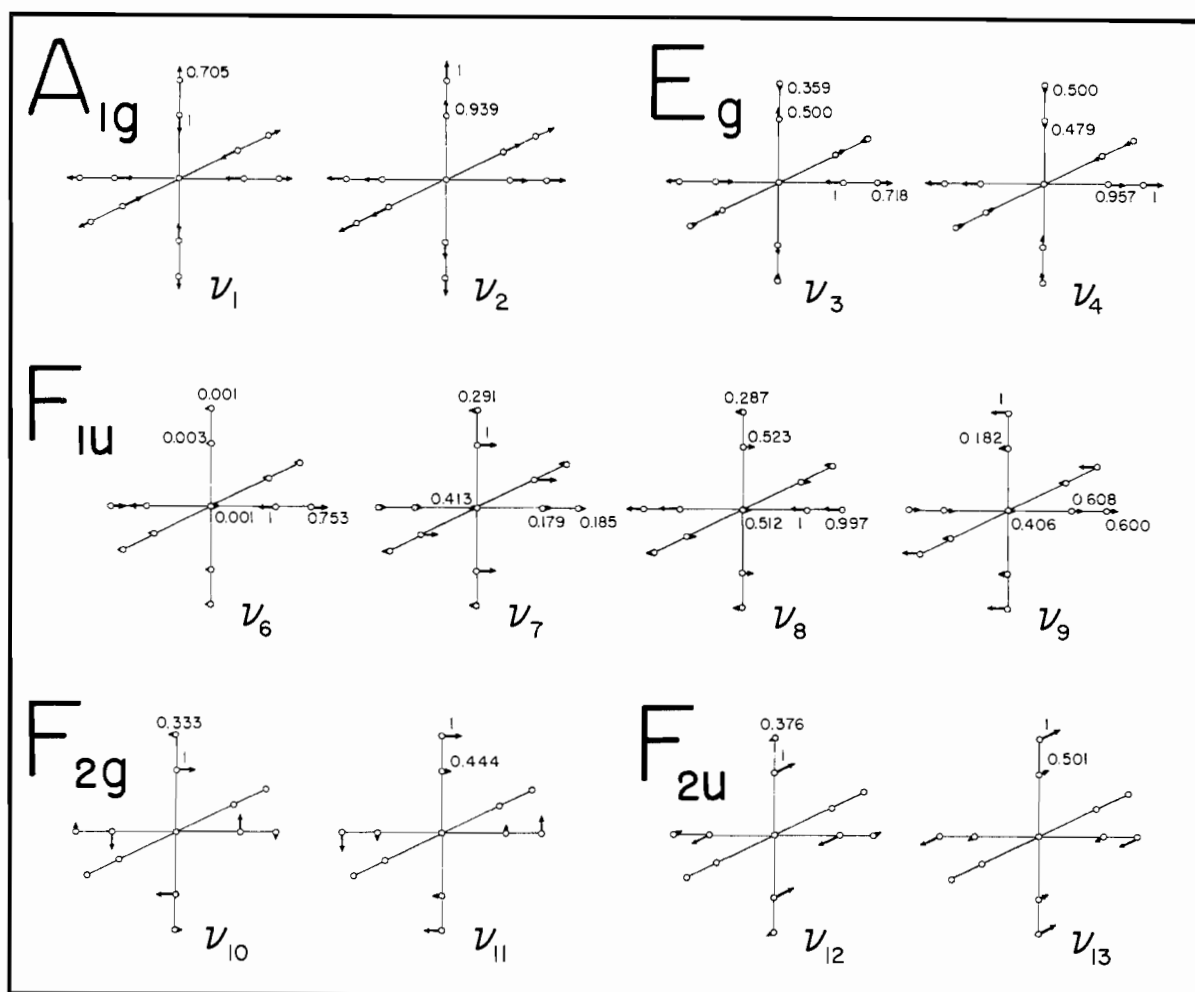


Figure 5.—Cartesian displacements for normal coordinates of  $\text{Mo}(^{12}\text{C}^{16}\text{O})_6$  vapor. Only one component of each degenerate mode is shown. The numbers indicate the relative nuclear displacements; each unnumbered vector is equivalent by symmetry to one which is numbered. For  $\nu_9$ , the lengths of several of the vectors have been exaggerated so that their direction would be obvious.

TABLE XVII  
VALENCE ANGLE BENDING FORCE CONSTANTS<sup>a</sup> OF  $\text{M}(\text{CO})_6$  VAPOR

	$\text{Cr}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$	$\text{W}(\text{CO})_6$
$F_\beta$	$0.48 \pm 0.07$	$0.45 \pm 0.03$	$0.48 \pm 0.05$
$F_{\beta\beta'}$	$0.09 \pm 0.07$	$0.06 \pm 0.03$	$0.08 \pm 0.05$
$F_{\beta\beta''}$	$0.00 \pm 0.03$	$0.02 \pm 0.01$	$0.01 \pm 0.03$
$F_{\beta\beta'''}$	$-0.01 \pm 0.06$	$-0.02 \pm 0.03$	$-0.04 \pm 0.03$
$F_\alpha$	$0.57$	$0.61$	$0.63$
$F_{\alpha\alpha''}$	$\begin{cases} +0.24 \\ -0.16 \end{cases}$	$\begin{cases} +0.14 \\ -0.10 \end{cases}$	$\begin{cases} +0.09 \\ -0.07 \end{cases}$
$F_{\alpha\alpha'}$	$0.11$	$0.13$	$0.14$
$F_{\alpha\alpha''}$	$\begin{cases} +0.12 \\ -0.08 \end{cases}$	$\begin{cases} +0.07 \\ -0.05 \end{cases}$	$\begin{cases} +0.05 \\ -0.04 \end{cases}$
$F_\alpha$	$0.56$	$0.50$	$0.51$
$F_{\alpha\alpha''}$	$\begin{cases} +0.15 \\ -0.11 \end{cases}$	$\begin{cases} +0.07 \\ -0.05 \end{cases}$	$0.51 \pm 0.08$
$F_{\alpha\beta'}$	$-0.10 \pm 0.03$	$-0.11 \pm 0.02$	$-0.12 \pm 0.02$
$F_{\alpha\beta''}$	$-0.02 \pm 0.03$	$-0.05 \pm 0.02$	$-0.05 \pm 0.02$
$F_{\alpha\beta'''}$	$-0.02 \pm 0.03$	$-0.02 \pm 0.02$	$-0.04 \pm 0.02$

<sup>a</sup> Units are  $\text{mdyn } \text{\AA}/\text{radian}^2$ . Force constants are defined in footnote *b* to Table IX. The stretch-bend interaction constants are  $F_{\text{CO},\beta'} = 0 \pm 0.07$ ,  $(F_{\text{CO},\alpha'} - F_{\text{CO},\alpha''}) = 0 \pm 0.25$ ,  $F_{\text{MC},\beta'} = -0.04 \pm 0.01$ , and  $(F_{\text{MC},\alpha'} - F_{\text{MC},\alpha''}) = -0.15 \pm 0.05$ .

tion value seems inconsistent. The calculated shrinkage effects are also reasonably close to the experimental values; the poorest agreement is for  $\delta(\text{C}\cdots\text{C}')$ , which our calculations suggest should show almost no shrinkage effect, while the electron diffraction results show an

unlikely large negative shrinkage. Previous calculations, using less complete force fields, have been reported by Brunvoll.<sup>25</sup> The mean amplitudes are not extremely sensitive to the force constants, and accordingly there is little significant difference between Brunvoll's results and ours.

## Discussion

**Primary Stretching Force Constants.**—The CO stretching force constants are quite similar for these three hexacarbonyls. The value of  $F_{\text{CO}}$  for  $\text{W}(\text{CO})_6$  appears to be smaller than that for  $\text{Mo}(\text{CO})_6$  though the difference is barely outside one standard deviation. The results for  $\text{Cr}(\text{CO})_6$  are almost identical with those for  $\text{W}(\text{CO})_6$ . For  $\text{W}(\text{CO})_6$  the metal-carbon stretching force constant is definitely larger than for the other two molecules, for which  $F_{\text{MC}}$  is about the same. The larger value of  $F_{\text{MC}}$ , along with the somewhat smaller value of  $F_{\text{CO}}$ , suggests somewhat greater metal-ligand  $\pi$  bonding for  $\text{W}(\text{CO})_6$ . However, the differences of  $F_{\text{MC}}$  among these hexacarbonyls are more striking than

TABLE XVIII  
 MEAN AMPLITUDES OF VIBRATION AND SHRINKAGE EFFECTS<sup>a</sup>

	Amplitude, $\mu$					Shrinkage, $\delta$				
	Cr(CO) <sub>6</sub> Calcd	Mo(CO) <sub>6</sub> Calcd Obsd <sup>b</sup>		W(CO) <sub>6</sub> Calcd Obsd <sup>b</sup>		Cr(CO) <sub>6</sub> Calcd	Mo(CO) <sub>6</sub> Calcd Obsd <sup>b</sup>		W(CO) <sub>6</sub> Calcd Obsd <sup>b</sup>	
C-O	0.0346	0.0346	0.034	0.0346	0.037	...	...	...	...	...
M-C	0.0577	0.0588	0.063	0.0533	0.059	...	...	...	...	...
M-C-O	0.0571	0.0578	0.056	0.0526	0.059	0.009	0.010	0.009	0.009	0.013
C-M-C	0.0694	0.0697	0.072	0.0661	0.071	0.010	0.011	0.010	0.011	0.002
C-M-C-O	0.0696	0.0699	0.073	0.0663	0.073	0.024	0.025	0.010	0.027	0.026
O-C-M-C-O	0.0696	0.0699	0.073	0.0664	0.092	0.042	0.042	0.036	0.046	0.058
C...C'	0.136	0.155	0.131	0.149	0.160	0.001	0.001	-0.037	0.008	-0.027
C...O'	0.180	0.197	0.218	0.196	0.198	0.008	0.009	0.002	0.002	-0.009
O...O'	0.262	0.271	0.294	0.280	0.286	0.017	0.020	0.012	0.018	0.033

<sup>a</sup> All units are ångströms. <sup>b</sup> Electron diffraction values of Arnesen and Seip.<sup>21</sup>

those of  $F_{CO}$  suggesting that the W-C  $\sigma$  bonding is stronger than for Mo-C and Cr-C.<sup>26</sup>

A comparison with the results on nickel carbonyl,<sup>8</sup> for which  $F_{CO}$  is definitely greater (17.85 and 17.68 mdyne/Å for vapor and solution, respectively), indicates significantly stronger metal-ligand  $\pi$  bonding<sup>27</sup> for  $M(CO)_6$  than for  $Ni(CO)_4$ . The force constant for a good CO triple bond, such as in  $CO^+$ ,<sup>27</sup> is about 19.8 mdyne/Å. The CO double-bond force constant is not well known but appears to be 12–13 mdyne/Å.<sup>28</sup> If we assume a linear relation between bond order and force constant, as done by Cotton,<sup>29</sup> we find for the vapor a CO bond order of 2.73 for  $Ni(CO)_4$  and 2.65 for  $M(CO)_6$ , the latter falling between the values of 2.5 suggested by Cotton<sup>29</sup> and 2.75 suggested by Dobson.<sup>30</sup> The significance of this figure for "bond order" is questionable as a good value for  $C=O$  is not available and the linearity of a bond order-force constant relation has not been established. Molecular orbital calculations by Schreiner and Brown<sup>31</sup> suggest a CO bond order of about 2.71. All such estimates are based on the assumption that the CO bond order equals 3 less the number of  $\pi$ -electron pairs donated by the metal to the CO antibonding  $\pi$  orbitals. It is interesting that the apparent CO bond order diminishes slightly in solution, presumably owing to minor interaction with the solvent molecules.

The similarity of  $F_{MC}$  for  $Ni(CO)_4$ ,  $Cr(CO)_6$ , and  $Mo(CO)_6$  suggests that the former molecule has stronger M-C  $\sigma$  bonding than the latter two, thus compensating for the lesser M-CO  $\pi$  bonding. The molecular orbital calculations of Schreiner and Brown<sup>31</sup> suggest that the

M-C bond is significantly stronger for  $Cr(CO)_6$  than for  $Ni(CO)_4$ ; however, this is apparently not the case.

**Stretch-Stretch Interaction Constants.**—In general the stretch-stretch interaction constants are about the same for all three molecules with the following two exceptions. The constant  $F_{MC,CO}$  is significantly greater for  $W(CO)_6$  than for  $Cr(CO)_6$  [for  $Mo(CO)_6$  the value lies between the other two]. The same trend is observed for  $F_{MC,MC'}$ , except that the value for  $Mo(CO)_6$  is indistinguishable from that for  $W(CO)_6$ . Together these trends can be correlated with greater metal-carbon  $\sigma$  bonding in the order  $Cr-C < Mo-C < W-C$ . Stronger  $\sigma$ -bond overlap may lead to greater interactions as the overlap will be more sensitive to slight changes in distance.

The other interaction constants are all rather small with perhaps the exception of  $F_{CO,C'O'}$  which is about 0.2 mdyne/Å. It seems appropriate at this time to use the mean values of the interaction constants for the last seven entries of Table XVI for normal-coordinate calculations on other metal carbonyls having linear MCO groups at 90° and/or 180° to each other when sufficient independent information is not available. The values arrived at by this procedure are given in Table XIX along with similarly calculated mean values of the bend-bend interactions of Table XVII.

 TABLE XIX  
 MEAN VALUES OF INTERACTION CONSTANTS FOR  $M(CO)_6$ 

	$\bar{x}^a$	$\sigma^b$		$\bar{x}^a$	$\sigma^b$
$F_{CO,C'O'}$	0.20	0.03	$F_{\beta\beta'}$	0.08	0.02
$F_{CO,C'O'}$	0.03	0.06	$F_{\beta\beta''}$	0.01	0.01
$F_{MC,MC'}$	0.02	0.03	$F_{\beta\beta'''}$	-0.02	0.02
$F_{MC,MC'}$	0.54	0.07	$F_{\alpha\beta'}$	-0.11	0.01
$F_{MC,CO}$	0.75	0.06	$F_{\alpha\beta''}$	-0.04	0.02
$F_{MC,C'O'}$	-0.08	0.02	$F_{\alpha\beta'''}$	-0.03	0.01
$F_{MC,C'O'}$	-0.12	0.03	$\bar{F}_{\alpha\alpha'} - F_{\alpha\alpha''}$	0.13	0.02
$F_{MC,\beta'}$	-0.04	0.01	$F_{MC,\alpha'} - F_{MC,\alpha''}$	-0.15	0.05

<sup>a</sup> Units are mdyne/Å for stretch-stretch, mdyne Å/radian<sup>2</sup> for bend-bend, and mdyne/radian for stretch-bend. <sup>b</sup> These are calculated standard deviations assuming no systemic variations and equal precision for solution and gas and for the three molecules.

The values of  $I_{MC,C'O'}$  and  $I_{MC,C'O'}$  are essentially the same and also are equal to  $F_{MC,C'O'}$  found for nickel carbonyl.<sup>8</sup> Thus it is appropriate to use the value -0.1

(26) It is of interest to compare the force constants with the thermochemical and electron impact estimates of Cr-C, Mo-C, and W-C bond energies: see F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, **81**, 800 (1959); F. A. Cotton, *Helv. Chim. Acta*, Fascilius Extraordinarius, Alfred Werner Commemoration Volume, 117 (1967); and R. E. Winters and R. W. Kiser *Inorg. Chem.*, **4**, 157 (1965). These articles report a significant increase in M-C bond energy in the order  $W-C > Mo-C > Cr-C$ . We indeed find that  $F_{WC}$  is significantly greater than  $F_{MoC}$  and  $F_{CrC}$ ; however, the latter two are about the same, and, in fact,  $F_{MoC}$  may be slightly less than  $F_{CrC}$ . Thus, the equilibrium bond strengths as estimated from vibrational frequencies are not in complete accord with the thermochemical and electron impact estimates of dissociation energy.

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TABLE XX  
CO FORCE CONSTANTS AND CO,C'O' INTERACTION CONSTANTS FOR  
M(CO)<sub>6</sub> IN SOLUTION<sup>a</sup> AND IN THE VAPOR PHASE FOR DIFFERENT APPROXIMATIONS

	General quadratic				CO-factored field <sup>c</sup>			
	Harmonic		Anharmonic <sup>b</sup>		Harmonic		Anharmonic <sup>b</sup>	
	Soln	Vapor	Soln	Vapor	Soln	Vapor	Soln	Vapor
	Cr(CO) <sub>6</sub>							
$F_{CO}$	17.04	17.24	16.52	16.74	16.95	17.16	16.45	16.64
$F_{CO,C'O'}^c$	0.17	0.21	0.15	0.21	0.27	0.27	0.26	0.26
$F_{CO,C'O'}^t$	0.08	0.02	0.28	0.22	0.35	0.28	0.54	0.48
	Mo(CO) <sub>6</sub>							
$F_{CO}$	17.15	17.33	16.65	16.82	16.96	17.15	16.46	16.66
$F_{CO,C'O'}^c$	0.17	0.22	0.16	0.20	0.29	0.29	0.27	0.27
$F_{CO,C'O'}^t$	0.01	-0.06	0.20	0.12	0.38	0.29	0.54	0.45
	W(CO) <sub>6</sub>							
$F_{CO}$	17.02	17.22	16.52	16.72	16.84	17.10	16.35	16.60
$F_{CO,C'O'}^c$	0.19	0.22	0.16	0.19	0.33	0.33	0.30	0.29
$F_{CO,C'O'}^t$	0.11	0.01	0.27	0.17	0.41	0.33	0.57	0.48

<sup>a</sup> CCl<sub>4</sub> solution for Cr(CO)<sub>6</sub> and Mo(CO)<sub>6</sub>; CS<sub>2</sub> solution for W(CO)<sub>6</sub>. <sup>b</sup> Force constants calculated in mdyne/Å using observed CO stretching frequencies uncorrected for anharmonicity. <sup>c</sup> Force constants calculated for M(<sup>12</sup>C<sup>16</sup>O)<sub>6</sub> assuming all other force constants are zero.

mdyne/Å for  $F_{MC,C'O'}$  whether the MC bond is oriented at 90, 109.5, or 180°, or probably any angle between 90 and 180°, to the linear MC'O' group.

The interaction constant  $F_{MC,MC'}$  for nickel carbonyl<sup>18</sup> is about 0.1 mdyne/Å. This is much smaller than the *trans*-MC,MC' interaction but somewhat greater than the negligible *cis*-MC,MC' interaction of M(CO)<sub>6</sub>. This is quite reasonable as the tetrahedral angle is closer to 90° than to 180°.

The CO,C'O' interactions are quite interesting. On the basis of  $\pi$ -bonding arguments it was hypothesized<sup>3,32</sup> that  $F_{CO,C'O'}^t$  should be about twice  $F_{CO,C'O'}^c$ . Indeed, this is found to be the case if one makes the calculations based on a CO-factored force field using observed frequencies uncorrected for anharmonicity. However, our results of Table XVI show that  $F_{CO,C'O'}^t$  is much smaller than  $F_{CO,C'O'}^c$ . Haas and Sheline<sup>33</sup> have made calculations of  $F_{CO,C'O'}^c$  and  $F_{CO,C'O'}^t$  based on interaction of the oscillating CO dipoles, assuming that when one CO dipole changes its length the moving charges interact electrostatically with another CO dipole. Their calculations<sup>33</sup> yielded  $F_{CO,C'O'}^c = 0.32$  mdyne/Å and suggested that  $F_{CO,C'O'}^t$  as calculated using a CO-factored force field was *about the right magnitude to be explained by such an interaction*, but that  $F_{CO,C'O'}^t$  should be about half  $F_{CO,C'O'}^c$ . They concluded that other interactions must come into play to increase  $F_{CO,C'O'}^t$ . These approximations<sup>33</sup> were rather crude; for the interactions they considered an M(CO)<sub>2</sub> molecule with MCO groups at either 90 or 180°. However, the actual M(CO)<sub>6</sub> molecule has both *cis* and *trans* groups, which interact simultaneously. Thus, stretching one CO group will affect the four *cis*-CO groups through this dipole-dipole interaction; the displacement charge in these four *cis*-CO groups will then affect the *trans*-CO group in an opposite direction.

It does not appear possible to make a quantitative estimate of the relative values of  $F_{CO,C'O'}^c$  and  $F_{CO,C'O'}^t$  based on "interaction of oscillating dipoles"; however, it is apparent that, barring other interactions,  $F_{CO,C'O'}^c$  should be the much larger of the two and  $F_{CO,C'O'}^t$  may even go to zero or a small negative number. We therefore conclude that the CO,C'O' interactions arise primarily from CO dipole-C'O' dipole interaction and that changes in  $\pi$  bonding do not enter appreciably, contrary to previous hypotheses.<sup>3,19,32</sup> The value of 0.12 for  $F_{CO,C'O'}^t$  of nickel carbonyl<sup>18</sup> agrees with this conclusion also as the dipole-dipole interaction at 109.5° should be significantly less than that at 90°.

A more meaningful discussion of the bonding can be made from a knowledge of the "interaction displacement coordinates."<sup>34</sup> However, we have decided to defer calculation of these values until we are able to estimate meaningful standard deviations for such quantities.

**Comparison with Approximate Force Fields.**—It is of interest to compare our results for the CO stretching constants and CO,C'O' interaction constants with those calculated from one or both of the following approximations: CO energy factoring and neglect of anharmonicity. The results are given in Table XX. When anharmonic CO stretching frequencies are used for a general quadratic solution (second column of Table XX), all force constants other than  $F_{CO}$ ,  $F_{CO,C'O'}^c$ , and  $F_{CO,C'O'}^t$  are very close to those calculated using the harmonic CO frequencies (column 1 of Table XX).

We see from Table XX that the inclusion of anharmonic corrections has a significant effect on  $F_{CO}$  and  $F_{CO,C'O'}^t$  but not on  $F_{CO,C'O'}^c$ . The use of the CO-factored force field leads to large errors for both  $F_{CO,C'O'}^c$  and  $F_{CO,C'O'}^t$ . The values of  $F_{CO}$  calculated with a CO-factored force field are really no more quantitative than the average of the observed CO stretching fre-

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(33) H. Haas and R. K. Sheline, *J. Chem. Phys.* **47**, 2996 (1967).

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quencies for comparison of CO bond strengths. A similar conclusion has been reached by Bower and Stiddard<sup>35</sup> from a study of substituted hexacarbonyls.

**Bending Force Constants.**—The constant  $F_\beta$ , for MCO bending, is about the same (0.47 mdyn Å/radian<sup>2</sup>) for all three hexacarbonyls. It is significantly greater than the value for nickel carbonyl (0.31). This may arise from the greater M–CO  $\pi$  bonding leading to a more rigid linear MCO group for the hexacarbonyls. The CMC bending constant,  $F_\alpha$ , is very much greater for the hexacarbonyls than for Ni(CO)<sub>4</sub> (compare 0.5–0.6 mdyn Å/radian<sup>2</sup> with 0.2–0.3). This must arise either from carbon–carbon interaction (which is, of course, greater for the smaller CMC angle) or from more rigidly directional valence orbitals for the hexacarbonyls, or both. It will be interesting to compare these results with the 90 and 120° CMC bending constants of Fe(CO)<sub>5</sub>.

At the present time the implications of the bend–bend interactions are not obvious. The values are rather small and it will be much more appropriate to relate the interaction displacement coordinates to the bond structure.

### Conclusion

The vibrational spectra of the species  $M(^{12}C^{16}O)_6$ ,  $M(^{13}C^{16}O)_6$ , and  $M(^{12}C^{18}O)_6$  have been observed and valence force constants have been calculated therefrom, using a general quadratic valence force field. Most of

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the interaction constants (see Table XIX) are appropriate for transfer to other metal carbonyls having similarly oriented MCO groups, but for which sufficient information for an independent normal-coordinate calculation is lacking. The CO, C'O' interactions are shown to be consistent with the oscillating dipole model discussed by Haas and Sheline,<sup>33</sup> without a significant contribution from changes in  $\pi$  bonding.

The results are compared with those for nickel carbonyl.<sup>8</sup> The values of the primary force constants, as well as the interaction constants, form a consistent picture. The metal–ligand  $\pi$  bonding is apparently greater for the hexacarbonyls, in agreement with molecular orbital studies.<sup>31</sup> The W–C  $\sigma$  bonding is significantly stronger than for Cr–C and Mo–C. The results lend encouragement for the establishing of order in the relations of force constants to bonding and structure for the metal carbonyls.

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## Raman Frequencies and Metal–Metal Force Constants for $M_2(CO)_{10}$ Species<sup>1</sup>

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Raman spectra are reported for  $Mn_2(CO)_{10}$ ,  $Re_2(CO)_{10}$ , and  $MnRe(CO)_{10}$ . A simple normal-coordinate analysis was applied to the low-frequency vibrations of the transition metal decacarbonyls in order to estimate metal–metal stretching force constants. The following values (in mdyn/Å) were obtained:  $f_{Mn-Mn} = 0.59$ ,  $f_{Tc-Re} = 0.72$ ,  $f_{Re-Re} = 0.82$ ,  $f_{Mn-Re} = 0.81$ . The force constants correlate satisfactorily with bond dissociation energies obtained from electron impact measurements. The present results are discussed together with previous analyses of  $Ru_3(CO)_{12}$ ,  $Os_3(CO)_{12}$ , and  $Ir_3(CO)_{12}$ . For the polynuclear carbonyls, metal–metal force constants increase with increasing atomic number within a given row or period, in accord with the expectation based on chemical stabilities, mass spectral fragmentation patterns, and internuclear distances. Metal–metal force constants calculated with neglect of the carbonyl ligands are not seriously in error and are quite satisfactory for the third transition row.

### Introduction

The transition metal carbonyls offer a rich variety of polynuclear structures for the study of metal-to-metal bonding. Much interest attaches to the simplest representatives, the dinuclear decacarbonyls,  $M_2(CO)_{10}$  ( $M = Mn, Tc, Re$ ), in which two square-pyramidal  $M(CO)_5$  groups are joined in a staggered orientation by an M–M bond<sup>2–4</sup> (Figure 1). Assignments of metal–

metal stretching frequencies in Raman spectra have been suggested for  $Re_2(CO)_{10}$ ,<sup>5–7</sup>  $Mn_2(CO)_{10}$ ,<sup>8,9</sup>  $MnRe(CO)_{10}$ ,<sup>8</sup> and  $Tc_2(CO)_{10}$ .<sup>10</sup> We present here a study of the low-frequency Raman spectra of these molecules,

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