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Contribution from the Department of Inorganic Chemistry,
The University, Newcastle upon Tyne, NE1 7RU, England

Photochemistry of the Group VI Hexacarbonyls in Low-Temperature Matrices. II.[1] Infrared Spectra and Structures of ^{13}CO-Enriched Hexacarbonyls and Pentacarbonyls of Chromium, Molybdenum, and Tungsten

ROBIN N. PERUTZ and JAMES J. TURNER*

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The infrared spectra of the ^{13}CO-enriched metal hexacarbonyls and pentacarbonyls have been studied in Ar and CH_4 matrices at 20 K. The hexacarbonyl spectra can be fitted very accurately in frequency and intensity using a CO-factored force field. The spectra of the pentacarbonyls are inconsistent with a D_{3h} structure but can be fitted accurately using a C_{4v} structure. Using intensity data, axial–radial bond angles (C_{4v} structure) between 90 and 95° are calculated. The structure and force constants are almost independent of the matrix material.

Chromium, molybdenum and tungsten pentacarbonyls have been generated by uv photolysis of the hexacarbonyls in hydrocarbon glasses[2] at 77 K and in argon matrices[1] at 20 K. In the ir spectra three bands were observed in the C–O stretching region (*e.g.*, $Cr(CO)_5$ in Ar: 2093 (vvw), 1965.6 (s), 1936.1 (m) cm^{-1}). The bands were assigned to the A_1, E, and A_1 bands, respectively, of a square-pyramidal (C_{4v}) molecule. The evidence for this structure as opposed to that for a D_{3h} structure was based on the presence of the very weak high-frequency band and on the intensity ratio of the low-frequency bands. During investigation of the uv spectra of the pentacarbonyls in different matrices,[3] it became essential to have stronger evidence that the D_{3h} structure was incorrect and to estimate bond angles for a C_{4v} structure.

In the experiments described below, the ir spectra of ^{13}CO-enriched metal pentacarbonyls were studied using the methods of analysis developed by Haas and Sheline,[4] Bor,[5] and Darling and Ogden.[6] The results prove that the C_{4v} structure for photochemically generated $M(CO)_5$ is indeed correct.

Analysis of Spectra

When a metal carbonyl is enriched to approximately 50% ^{13}CO, all possible isotopic molecules ($M(^{12}CO)_x(^{13}CO)_{n-x}$, $x = 0, 1, ..., n$) are present in a scrambled mixture whose composition is determined by the statistical weights of the different molecules. Since the vibrational symmetry is lowered by ^{13}CO substitution, the ir spectrum in the C–O stretching region consists of the sum of the superimposed spectra of all the individual molecules, each of which has a different vibrational pattern.

Darling and Ogden[6] have calculated the patterns of the isotopic spectra of metal carbonyls for those cases in which the parent molecule has no permanent dipole moment and all CO groups are equivalent (*i.e.*, $M(^{12}CO)_x(^{13}CO)_{n-x}$: $n = 2$, $D_{\infty h}$ geometry; $n = 3$, D_{3h} geometry; $n = 4$, T_d or D_{4h}; $n = 6$, O_h). In such molecules there is only one C–O stretching force constant and not more than two CO–CO interaction constants. Such calculations have been used to assign the spectra of a number of metal carbonyls and dinitrogen species.[7]

$M(CO)_5$ presents a more complex case because it must have at least two different CO stretching force constants and three interaction constants whether the molecular symmetry is D_{3h} or C_{4v}. In intensity calculations for the C_{4v} geometry we must include bond angle and bond moment data.[8] The distinction between C_{4v}, D_{3h}, or any geometry of lower symmetry rests on detailed comparison of experimental spectra and a range of possible theoretical spectra. We assume that the molecule has the simplest structure for which the experimental spectra can be matched (*i.e.*, the structure with the minimum number of force constants).

Such an assignment depends on having an estimate of the errors expected in the prediction of the isotopic spectra. There have been a number of studies of isotopically enriched carbonyls in solution but most have involved only partial enrichment.[9] $Ni(CO)_4$ and $Co(CO)_3NO$[5] have been examined with more extensive enrichment but these compounds have relatively few bands; Noack and Ruch[10] studied $Fe(CO)_5$ but did not optimize the force constants. Johnson, *et al.*,[11] have examined the spectrum of $Mn(CO)_5Br$ in chloroform during $C^{16}O$–$C^{18}O$ exchange and have refined the Cotton–Kraihanzel parameters and calculated intensity data; the spectra however were only of moderate resolution. Darling[12] has generated $C^{18}O$-substituted $Cr(CO)_6$ in Kr matrices by cocondensation of Cr atoms and CO–Kr mixtures, but the spectra are not sharp enough to merit complete analysis. We therefore decided to analyze the $M(CO)_6$ species in low-temperature matrices as a check on our calculations and to obtain an estimate of the systematic errors in the method. (Details of the methods of calculation of frequency and intensity are given in Appendix 2.)

Low-temperature matrices have the advantage that the

Table I. Observed and Calculated Wave Numbers of $Cr(CO)_6$ in CH_4 (cm^{-1})^c

		Obsd	Calcd
$Cr(^{12}CO)_6$ (0) O_h	A_{1g}	*a*	2113.1
	E_g	*a*	2017.5
	T_{1u}	1985.4	1985.6
$Cr(^{12}CO)_5(^{13}CO)$ (1) C_{4v}	A_1	2107.6	2107.3
	A_1	2009.6	2009.4
	A_1	1954.3	1954.5
	B_2	*a*	2017.5
	E	1985.4	1985.6
trans-$Cr(^{12}CO)_4(^{13}CO)_2$ (t2) D_{4h}	A_{1g}	*a*	2101.5
	A_{1g}	*a*	1983.4
	B_{1g}	*a*	2017.5
	E_u	1985.4	1985.6
	A_{2u}	1941.7	1941.3
cis-$Cr(^{12}CO)_4(^{13}CO)_2$(c2) C_{2v}	A_1	2101.3	2100.9
	A_1	2013.2	2013.0
	A_1	1957.1	1957.1
	B_2	1952.1	1951.9
	B_2	2006.8	2006.6
	B_1	1985.4	1985.6
fac-$Cr(^{12}CO)_3(^{13}CO)_3$ (f3) C_{3v}	A_1	2093.7	2093.6
	A_1	1959.4	1959.5
	E	2006.8	2006.6
	E	1952.1	1951.9
mer-$Cr(^{12}CO)_3(^{13}CO)_3$ (m3) C_{2v}	A_1	*b*	2094.4
	A_1	2011.3	2011.3
	A_1	1983.1	1983.6
	A_1	1953.7	1953.7
	B_2	1985.4	1985.6
	B_1	1941.7	1941.3
trans-$Cr(^{12}CO)_2(^{13}CO)_4$ (t4) D_{4h}	A_{1g}	*a*	2087.3
	A_{1g}	*a*	1996.9
	B_{1g}	*a*	1972.5
	E_u	1941.7	1941.3
	A_{2u}	1985.4	1985.6
cis-$Cr(^{12}CO)_2(^{13}CO)_4$ (c4) C_{2v}	A_1	2086.1	2086.1
	A_1	*b*	1983.7
	A_1	1955.2	1955.4
	B_2	1952.1	1951.9
	B_2	2006.8	2006.6
	B_1	1941.7	1941.3
$Cr(^{12}CO)(^{13}CO)_5$ (5) C_{4v}	A_1	2076.4	2077.3
	A_1	1994.0	1994.2
	A_1	*b*	1953.3
	B_2	*a*	1972.5
	E	1941.7	1941.3
$Cr(^{13}CO)_6$ (6) O_h	A_{1g}	*a*	2066.0
	E_g	*a*	1972.5
	T_{1u}	1941.7	1941.7

^{a} Ir inactive. ^{b} Not resolved. ^{c} No single observed band was used more than once in the refinement of force constants. Key: c = cis; t = trans; m = mer; f = fac.

bands are almost always very sharp (half-width of about 0.8 cm^{-1}) allowing fine structure to be resolved. However the drawbacks of matrices are (i) the molecule may adopt a structure distorted from "the ideal gas-phase structure" and (ii) there may be different sites in the matrix which perturb the vibrational potential function of identical molecules in different ways. As a result of either of these effects the spectrum may show more bands than expected. Any detailed analysis must either eliminate or account for these possibilities.

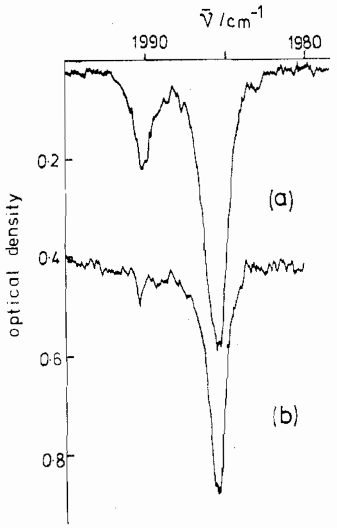


Figure 1. (a) Ir spectrum of $Cr(^{12}CO)_6$ in CH_4 matrix at 20 K before photolysis. (b) Ir spectrum of $Cr(^{12}CO)_6$ after 20-sec photolysis with unfiltered Hg lamp, followed by 10-min photolysis with an Hg lamp and λ >375 nm filter.

Fortunately it is frequently possible to eliminate such *matrix splittings* either by photochemical methods or by suitable choice of matrix material.

Results and Discussion

1. The Isotopic Spectra of Metal Hexacarbonyls ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$). The ir spectrum of $Cr(^{12}CO)_6$ in a methane matrix[13] at 20 K shows a doublet (1990, 1985 cm^{-1}; Figure 1a) in the C–O stretching region. The corresponding phenomenon in argon matrices has been discussed extensively elsewhere[1] and has been attributed to a slight distortion of the octahedral molecule which lifts the degeneracy of the T_{1u} vibration. However uv photolysis to produce $Cr(CO)_5$ + CO, followed by long-wavelength irradiation, regenerates $Cr(CO)_6$ in a form in which the splitting has almost entirely disappeared (Figure 1b). It was argued that all the molecules now have the octahedral structure.[1]

Figure 2a shows the result of repeating this process with $Cr(CO)_6$ enriched to 50% ^{13}CO in a scrambled mixture of isotopic molecules. Again almost all signs of distortion have disappeared. In this spectrum 19 out of a possible 22 bands were observed which could be assigned to undistorted $Cr(^{12}CO)_x(^{13}CO)_{6-x}$ species (x = 0–6).

Using CO-factored force constants from room-temperature solution studies[14] an approximate band pattern was calculated from which four prominent bands could be assigned to the C_{3v} *fac*-$Cr(^{12}CO)_3(^{13}CO)_3$ molecule (bands marked f3 in Figure 2a). From these frequencies three new force constants were calculated and the complete spectrum was assigned. Already at this stage the fit of the observed to the calculated frequencies is remarkably good. (The mean error measured as $(\sigma^2/n)^{1/2}$ was 0.34 cm^{-1} and the maximum error was 0.9 cm^{-1}.) The force constants were then refined to give the best fit (Table I). An estimate of the errors in the force constants obtained

Table II. Anharmonic (C-K) Metal Hexacarbonyl C-O Force Constants (mdyn Å^{-1})^a

Metal	Matrix or solvent	k	k_c	k_t	Mean error in calcd freq, cm^{-1}
Cr	CH_4 (20 K)	16.4427	0.2658	0.5235	0.31
		±0.0014	±0.0010	±0.0048	
Cr	Ar (20 K)	16.5099	0.2614	0.5205	0.34
Cr	C_6H_{12} soln^b	16.4347	0.2621	0.5147	0.36
Cr	C_6H_{12} soln^c	16.46	0.26	0.54	
Mo	CH_4 (20 K)	16.4740	0.2776	0.5261	0.36
W	CH_4 (20 K)	16.3964	0.2984	0.5421	0.33

^{a} See Figure 5 for definitions of force constants. ^{b} This work. ^{c} Reference 14.

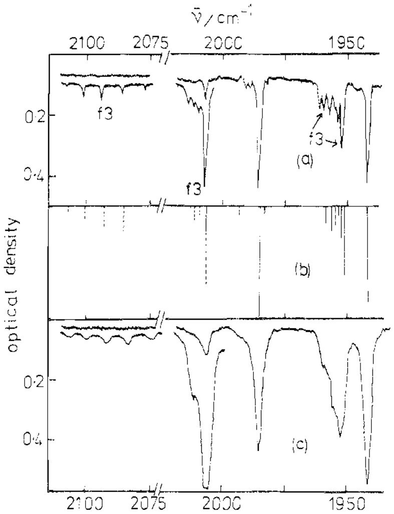


Figure 2. (a) Spectrum of ^{13}CO-enriched $Cr(CO)_6$ in CH_4 at 20 K, after deposition of four pulses; 25-sec photolysis with unfiltered Hg lamp, followed then by 8-min photolysis with an Hg lamp and λ >375 nm filter. In the superimposed spectrum the quantity of $Cr(CO)_6$ has been increased approximately 4 times. Dotted bands at ~1990 cm^{-1} are due to the small number of $Cr(CO)_6$ molecules still distorted; those at 1961 cm^{-1} are due to $Cr(CO)_5$. Bands marked f3 are those of *fac*-$Cr(^{12}CO)_3(^{13}CO)_3$. (b) Calculated spectrum for the O_h structure with $[^{13}CO]/[^{12}CO] = 1$. Force constants are as in Table II. The dotted spectrum represents a fourfold increase in the amount of $Cr(CO)_6$. (c) Spectrum of ^{13}CO-enriched $Cr(CO)_6$ in cyclohexane solution at 300 K; $[^{13}CO]/[^{12}CO] = 1.14$.

in this way was obtained by recalculating the best set of force constants for each isotopic molecule in turn for which there were sufficient data. The force constants obtained by averaging the six sets calculated in this way were almost identical with those calculated using all observed frequencies at once (Table II).

The calculated spectrum of isotopically substituted $Cr(CO)_6$ is shown in Figure 2b. Not only do the frequencies match the experimental values very well (their error is approximately equal to the experimental error) but so do the intensities, demonstrating that the model used in the calculations is valid and that the mixture was scrambled.

We have also repeated the $Cr(CO)_6$ experiment in an Ar matrix (Tables II, III). The interaction force constants show very little change, despite a general upward shift in the bands of about 4 cm^{-1} from methane. The spectrum of isotopically substituted $Cr(CO)_6$ in cyclohexane at room temperature (Figure 2c) has much broader bands than in the matrices. Nevertheless enough bands are well resolved to calculate a set of force constants which are very similar to those for the methane matrix (Table II) but slightly different from those calculated by Abel, *et al.*[14] The similarity of the solution and matrix force constants confirms that the problem of matrix splitting has indeed been overcome for $Cr(CO)_6$.

Corresponding matrix experiments have been performed using $Mo(CO)_6$ and $W(CO)_6$ in CH_4 (Tables II and III). The force constants show that the Cotton–Kraihanzel (C–K) approximation[15] $2k_{cis} = k_{trans}$ holds well for all the hexacarbonyls.

These experiments have shown that (a) a very high proportion of the possible bands for $M(^{12}CO)_{6-x}(^{13}CO)_x$ can be observed in a single-matrix experiment, (b) their frequencies can be fitted to a mean error of 0.3–0.4 cm^{-1} using the CO-factored force field, and (c) the calculated intensities agree well with the experimental intensities.

Table III. Observed Wave Numbers for Metal Hexacarbonyls $M(^{12}CO)_x(^{13}CO)_{6-x}$ (cm^{-1})

$Cr(CO)_6$, Ar matrix	Cr, C_6H_{12} soln	Mo, CH_4 matrix	W, CH_4 matrix	Assignment[d]
2110.3	2105.9	2112.2	*e*	1
2103.8	2099.5	2105.9	2107.2	c2
2096.7	2091.8	2098.6	2099.6	f3
2088.6	2084.1	2090.3	2091.2	c4
2079.5	2074.8	2081.1	2082.2	5
2017.4	*b*	2013.8	2007.3	c2
2015.8	*b*	2012.3	2006.1	m3
2014.2	2009.2[c]	2010.4	2004.4	1
2011.4	2005.8	2007.4	2001.3	c2, f3, c4
1998.2	*b*	*a*	1989.0	5
1990.4	1985.5	1987.2	1981.5	0, 1, t2, c2, m3, t4
1987.7	*b*	1984.1	1978.1	m3
1964.0	*b*	1961.1	1955.6	f3
1961.2	*b*	1958.8	1953.1	c2
1959.4	*b*	1956.8	1950.9	c4
1958.2[c]	1954.3[c]	1956.0	*b*	1
1957.6	*b*	1955.0	1949.5	t3
b	*b*	*b*	1948.9	5
1956.2	1951.8	1953.4	1947.5	c2, f3, c4
1946.1	1941.8	1944.0	1937.9	t2, m3, t4, c4, 5, 6

[a] Obscured by $Mo(CO)_5$ band. [b] Not resolved. [c] Value from spectrum without enrichment—natural abundance ^{13}CO. [d] The numbers in the assignment refer to the degree of substitution (see Table I). [e] Not observed.

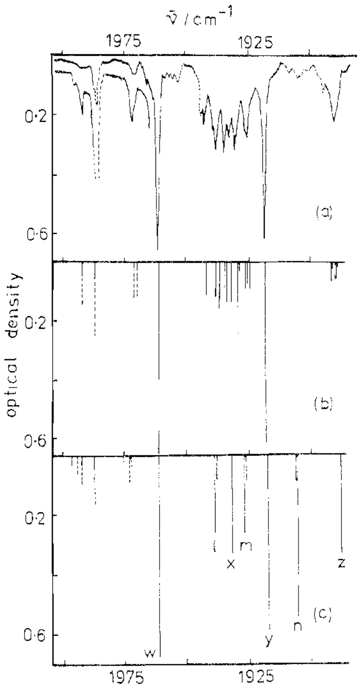


Figure 3. (a) Spectrum of ^{13}CO-enriched $Cr(CO)_5$ in CH_4 at 20 K; 20 pulses deposited, followed by 4.5-min photolysis with an unfiltered Hg lamp. In the superimposed spectrum the quantity of $Cr(CO)_5$ has been increased 4 times; $[^{12}CO]/[^{13}CO] = 1.0$. Lettering refers to text. (Region above 2000 cm^{-1} shown in Figure 4a.) (b) Calculated spectrum of $Cr(CO)_5$ for the C_{4v} structure. Force constants and bond angles are given in Tables V and VII. Arbitrary intensity units. The dotted spectrum represents a fourfold increase in the amount of $Cr(CO)_5$. (c) Calculated spectrum for the D_{3h} structure: $\cos\beta = 0$, $k_e = 15.991$, $k_a = 15.994$, $k_{ee} = 0.4635$, $k_{aa} = 0.9231$, $k_{ae} = 0.2800$.

2. Isotopic Pattern and Structure of the Pentacarbonyls $Cr(CO)_5$, $Mo(CO)_5$ and $W(CO)_5$. Figures 3a and 4a show the spectrum observed for $Cr(CO)_5$ generated by photolysis of $Cr(CO)_6$ in a methane matrix. Important features are (1) the clustering of at least six bands between 1925 and 1945 cm^{-1}, (2) the absence of any bands between 1890 and 1915 cm^{-1}, (3) the presence of two weak bands at 1992 and 1971 cm^{-1} and a shoulder on the $Cr(CO)_6$ band at 1987 cm^{-1}, and (4) the presence of at least six distinct high-frequency bands between 2055 and 2085 cm^{-1}. We compared this spectrum with theoretical spectra for D_{3h} and C_{4v} structures.

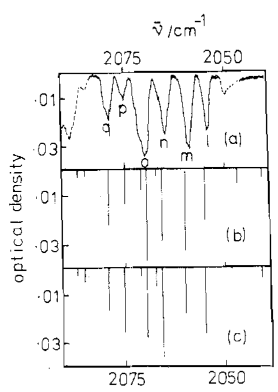


Figure 4. (a) Spectrum of ^{13}CO-enriched $Cr(CO)_5$ in CH_4 at 20 K; approximately 4 times more $Cr(CO)_5$ than in Figure 2a; $[^{12}CO]/[^{13}CO] = 0.9$. The dotted part of the spectrum is not due to $Cr(CO)_5$. (b) Calculated spectrum for C_{4v} structure–*in phase* solution. Force constants and bond angles are given in Tables V and VII. Scale 4 times that of Figure 2b. (c) Calculated spectrum for the C_{4v} structure–*out-of-phase* solution.

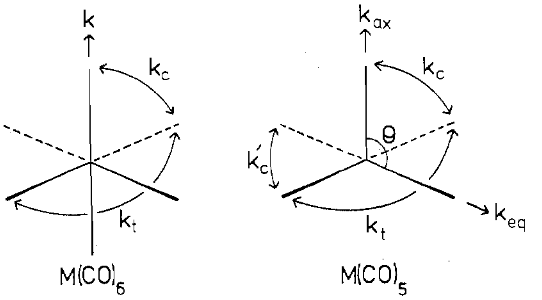


Figure 5. Force constants and angles of O_h hexacarbonyls and C_{4v} pentacarbonyls.

The D_{3h} Structure. The expected isotopic pattern for a D_{3h} structure was calculated, for a range of force constants satisfying the infrared spectrum of the parent molecule (A_1' 2088, E' 1961, A_2'' 1932 cm^{-1}). (Details will be found in Appendix 3.) In every case the spectrum in the region below 1960 cm^{-1} is very simple (Figure 3c). Essentially only three new bands (l–n in Figure 3c) are predicted in addition to those of $Cr(^{12}CO)_5$ and $Cr(^{13}CO)_5$, two to high frequency of the E' mode of $Cr(^{13}CO)_5$ and one to low frequency (at about 1905 cm^{-1}). The four prominent bands corresponding to the bands of $Cr(^{12}CO)_5$ and $Cr(^{13}CO)_5$ are marked w–z in Figure 3c. All these bands should be intense. These predictions are incompatible with the observed spectrum, in which there are *no* bands between 1890 and 1945 cm^{-1} and six intense bands between the E' modes of $Cr(^{12}CO)_5$ and $Cr(^{13}CO)_5$. There are further difficulties in matching the spectrum above 2045 cm^{-1}. However from these arguments alone, it is seen that there is no basis even for an assignment of the isotopic spectrum, and the trigonal-bipyramidal structure (D_{3h}) must be rejected.

The C_{4v} Structure. An initial set of force constants for a molecule of C_{4v} symmetry can be obtained using the C–K approximations[15] ($k_{cis(eq-ax)} = k'_{cis(eq-eq)} = {}^1/_2k_{trans}$; see Figure 5) and the three bands of the parent molecule. The calculated frequency pattern of the isotopic molecules reproduces all the features of the observed spectrum (the intensities are discussed below). The two features at 1992 and 1971 cm^{-1} can be assigned to bands derived from the infrared-inactive B_2 mode of the parent molecule. The standard deviation predicted from observed bands was 1.1 cm^{-1} but was reduced on refinement of all five force constants to 0.41 cm^{-1}. Twenty-three frequencies were fitted using five independent force constants (Table IV, Figure 3b, and Figure 4b). Errors in the force constants (Table V) were calculated by the same method as for $Cr(CO)_6$, but using pairs of molecules so that the number of observed bands always exceeded the number of force constants. The force constants show a large difference between k_{cis} and k'_{cis} but the approximation $k'_{cis(eq-eq)} = {}^1/_2k_{trans}$ holds very well both for $Cr(CO)_6$ and $Cr(CO)_5$, as predicted also by the valence-shell force field.[16] As for the hexacarbonyls, the deviations from this approximation increase in the direction Cr to Mo to W.

Table IV. Observed and Calculated Wave Numbers for $Cr(CO)_5$ in CH_4 (cm^{-1})

Molecule	Symmetry	Obsd	Calcd
$Cr(^{12}CO)_5$ (0) C_{4v}	A_1	2087.8	2086.9
	A_1	1931.8	1932.1
	B_2	*a*	1998.7
	E	1960.8	1961.6
$Cr(^{12}CO)_4(^{13}CO)$ (1a) C_{4v}	A_1	*b*	2083.4
	A_1	*b*	1892.3
	B_2	*a*	1998.7
	E	1960.8	1961.6
$Cr(^{12}CO)_4(^{13}CO)$ (1b) C_s	A'	2079.5	2079.0
	A'	1992.0	1991.8
	A'	1938.1	1938.0
	A'	1926.0	1926.0
	A''	1960.8	1961.6
$Cr(^{12}CO)_3(^{13}CO)_2$ (2a) C_s ax–eq	A'	2075.2	2075.2
	A'	1992.0	1991.8
	A'	*b*	1933.3
	A'	*b*	1891.1
	A''	1960.8	1961.6
$Cr(^{12}CO)_3(^{13}CO)_2$ (2b) C_s eq–eq	A'	2069.9	2069.6
	A'	1941.3	1941.4
	A'	1924.8	1924.7
	A''	1986.5	1986.8
	A''	1929.6	1929.4
$Cr(^{12}CO)_3(^{13}CO)_2$ (2c) C_{2v}	A_1	*b*	2071.0
	A_1	*b*	1972.9
	A_1	*b*	1928.4
	B_1	1960.8	1961.6
	B_2	1918.3	1917.9
$Cr(^{12}CO)_2(^{13}CO)_3$ C_s ax–eq (3a)	A'	2059.3	2059.7
	A'	1970.6	1970.7
	A'	1933.6	1933.8
	A'	*b*	1925.3
	A''	1918.3	1917.9
$Cr(^{12}CO)_2(^{13}CO)_3$ C_s eq–eq (3b)	A'	2064.8	2065.4
	A'	1936.8	1936.8
	A'	*b*	1890.1
	A''	1986.5	1986.8
	A''	1929.6	1929.4
$Cr(^{12}CO)_2(^{13}CO)_3C_{2v}$ (3c)	A_1	*b*	2067.0
	A_1	*b*	1971.5
	A_1	*b*	1890.5
	B_1	1918.3	1917.9
	B_2	1960.8	1961.6
$Cr(^{12}CO)(^{13}CO)_4$ C_{4v} (4a)	A_1	*b*	2046.3
	A_1	*b*	1926.5
	B_2	*a*	1954.1
	E	1918.3	1917.9
$Cr(^{12}CO)(^{13}CO)_4$ C_s (4b)	A'	2054.1	2054.9
	A'	1969.5	1969.7
	A'	1932.2	1931.8
	A'	1889.9	1889.6
	A''	1918.3	1917.9
$Cr(^{12}CO)_5$ C_{4v} (5)	A_1	*b*	2040.4
	A_1	*b*	1889.1
	B_2	*a*	1954.1
	E	1918.3	1917.9

[a] Ir inactive. [b] Not resolved.

By using the same methods we were able to observe the isotopic spectra (Table VI) of $Cr(CO)_5$ in Ar and $Mo(CO)_5$ and $W(CO)_5$ in CH_4 matrices. The force constants and the mean errors in the predicted frequencies are shown in Table V. From these results it follows that all three pentacarbonyls have the square-pyramidal (C_{4v}) structure when generated

Table V. Anharmonic (C-K) Metal Pentacarbonyl C-O Force Constants (All at 20 K in mdyn Å^{-1})[a]

Metal	Matrix	k_{ax}	k_{eq}	k_c	k'_c	k_t	Mean error in calcd freq, cm^{-1}
Cr	CH_4	15.3145	16.1369	0.3699	0.3037	0.5998	0.41
		±0.0033	±0.0009	±0.0013	±0.0014	±0.0061	
Cr	Ar	15.3948	16.2136	0.3853	0.3016	0.6005	0.41
Mo	CH_4	15.1992	16.2166	0.3812	0.3163	0.5910	0.40
W	CH_4	15.2350	16.0926	0.3963	0.3396	0.6185	0.49

[a] See Figure 5 for definitions of force constants.

Table VI. Observed Wave Numbers and Assignments for Metal Pentacarbonyls $M(^{12}CO)_x(^{13}CO)_{5-x}$ (cm^{-1})

Cr in Ar	Mo in CH_4	W in CH_4	Assignment[a]
2093.1	2093.0	2091.8	0
2084.8	2084.7	2083.5	1b
2080.9	2080.7	2078.7	2a
2075.2	2074.8	2073.5	2b
2070.2	2070.5	2068.2	3b
2064.5	2064.3	2063.0	3a
2059.8	2059.5	2057.2	4b
1996.6	1994.9	1986.4	1b, 2a
b	1990.1	1981.2	2b, 3b
1975.9	*b*	*b*	3a
1974.7	*b*	1963.9	4b
1965.6	1966.6	1957.2	0, 1a, 1b, 2a, 2c, 3c
b	1944.4	1936.6	2b
1942.9	1940.4	1933.3	1b
1941.8	1942.2	1933.3	3b
1938.4	1938.0	1929.3	2a
b	1937.1	1928.7	3a
1936.7	*b*	1927.7	4b
1936.1	1925.5	1926.0	0
1933.9	1934.5	1925.2	2b, 3b
1930.0	1922.4	1920.8	1b
b	*b*	1919.9	3a
1929.0	1920.6	1919.2	2b
1922.6	1923.9	1914.4	2c, 3a, 3c, 4a, 4b, 5
1893.4	1882.6	*b*	3b
b	*b*	1882.7	4b

[a] The numbers in the assignment refer to the degree of substitution; the lettering, to Table IV. [b] Not resolved.

Table VII. Intensities and Bond Angles of Pentacarbonyls (See Text)[a]

Metal	Matrix	R_1	R_2	θ, deg	μ'_a/μ'_r
Cr	CH_4	0.043	5.34	92.79 (102.4)	0.877 (0.749)
Cr	Ar	0.038	3.48	94.14 (105.14)	1.080 (0.916)
Mo	CH_4	0.077	3.18	90.94 (107.42)	1.163 (0.935)
W	CH_4	0.031	4.95	93.72 (102.15)	0.902 (0.787)

[a] $R_1 = I(A_1^{high})/I(A_1^{low})$; $R_2 = I(E)/I(A_1^{low})$. Values of θ and μ'_a/μ'_r are given for the in-phase solution with the out-of-phase solution in parentheses. Errors: in R_1, 50%; in R_2, 25%; in θ, 1.8°; in μ'_a/μ'_r, 0.14.

photochemically in a matrix. The results for $Cr(CO)_5$ in Ar demonstrate that this structure is not confined to a CH_4 matrix. There is no evidence for a significant C_{2v} distortion from the isotopic data, since the observed spectrum can be simulated so well using the five force constants required for a C_{4v} molecule in the high-frequency approximation.

Bond Angles and Intensity Data. For C_{4v} $M(CO)_5X$ species several authors[11,17-22] have considered the relationship between CO band intensities, geometries, coupling between modes of the same symmetry, and variation in CO dipole moment derivatives during normal vibrations. Graham, *et al.*,[1] calculated bond angles for $M(CO)_5$ species using the method of Haines and Stiddard.[19] Now that considerably more data are available, we feel justified in extending their treatment and correcting some minor errors. For reasons outlined in Appendix 4 we have used the method of Braterman, *et al.*[17] These authors have shown that a convenient way of using the two intensity ratios obtained from the spectrum of the parent molecule is to calculate the angle[23] between the axial and radial CO groups, θ, and the ratio of the gradients of the dipole moments of the two sets of CO groups (μ'_a/μ'_r) (see Figure 5). Two solutions are obtained: one when the A_1 modes are in phase and one when they are out of phase.

Measurement of intensities of infrared bands in matrices is particularly difficult. Since the concentration of $Cr(CO)_5$ is unknown, the intensities must be relative rather than absolute. Both the E and low-frequency A_1 of $Cr(CO)_5$ are often very sharp and subject to small *matrix splittings* which may affect the relative intensity significantly. The three bands of $M(CO)_5$ form an awkward set because the high-frequency A_1 is so weak and the low-frequency A_1 overlaps with tetracarbonyl bands. The matrix splitting of the low-frequency A_1 of $Cr(CO)_5$ may be eliminated in Ar and CH_4 matrices by stimulating partial recombination to $Cr(CO)_6$ by long-wavelength photolysis. However, the small side band of the E mode cannot be removed in this way. By including any matrix splittings and averaging optical density and total intensity measurements, the intensity ratios given in Table VII were obtained for the bands of the parent molecules and values of θ and μ'_a/μ'_r were calculated. These solutions were then tested against the isotopic data, using the value of the $[^{13}CO]/[^{12}CO]$ concentration ratio derived from the hexacarbonyl spectrum.

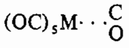
The isotopic intensity patterns predicted for the low-frequency region (1880–2000 cm^{-1}) are almost identical for both *in-* and *out-of-phase* solutions (Figure 3b) and agree well with experiment. On the other hand, the patterns predicted for the high-frequency region (2040–2095 cm^{-1}) are quite different for the two solutions (Figure 4b and 4c). For the in-phase solution bands l and n should be weaker than m and o, and p should be the weakest of l to q. For the out-of-phase solution l should be stronger than m, n stronger than o, and p of equal intensity to o.

The observed spectrum is strikingly similar to the predictions for the in-phase solution which is consequently accepted as the true solution. The same arguments may also be applied to the other pentacarbonyls. All the bond angles are calculated to be between 90 and 94°,[24] but the range of μ'_a/μ'_r is much greater (0.88–1.16). Braterman, *et al.*,[17] also found that the out-of-phase solution was incorrect, but their rejection was based on a comparison with geometrical data from X-ray and electron diffraction.

3. Generation of $Cr(CO)_5$ in CO Matrices—the Isocarbonyl Question. We have shown above that $Cr(CO)_5$ has a C_{4v} structure when generated photolytically in a CH_4 or Ar matrix. We have also examined its infrared spectrum (unenriched) in a wide range of other matrices (Ne, Kr, Xe, SF_6, CF_4, CO_2, CO).[3] In all these matrices the two characteristic bands are found in the region below 2000 cm^{-1} at about 1960 and 1930 cm^{-1} in very similar intensity ratios. It is reasonable to conclude that the structure of $Cr(CO)_5$ is always C_{4v}, although there may be slight variation in bond angle from one matrix to another (see above).

On the other hand it is possible that $Cr(CO)_5$ adopts the C_{4v} structure in all matrices because of interaction with some *pseudoligand* in the vacant coordination site. It has previously been argued[1] that the species cannot be $(OC)_5MOC$ (*i.e.*, strong M to isocarbonyl bond) because of the absence of bands attributable to the isocarbonyl group, the molecular CO produced, and the $C^{18}O$ exchange experiments.[1] Additionally, it is impossible to reconcile the sensitivity of the $Cr(CO)_5$ visible absorption band to the matrix (Ne matrix,[25] 624 nm, Ar[1] 533 nm, CH_4[26] 489 nm) with such a structure.

We can also eliminate the possibility of $(OC)_5M\cdots OC$, $(OC)_5M\cdots CO$, or



$$(OC)_5M\cdots\overset{C}{\underset{O}{}}$$

in all matrices except CO, where the CO group is very weakly attached to the C_{4v} fragment.[27] In a subsequent paper[3] we will report the effects of using mixed matrices on the ir and visible spectra of $M(CO)_5$. This evidence demonstrates that the only viable explanation of the changes in the uv-vis spectrum involves the species $(OC)_5M\cdots X$ (X = Ne, Ar, etc., occupying the sixth coordination site). The $M(CO)_5\cdots OC$ hypothesis may then be discarded in all but the CO matrices.

In the CO matrix, $Cr(CO)_5$ may be generated in low yield (1963, 1932.5 cm^{-1}), but the high-frequency A_1 band cannot be seen because it is obscured by the bands of $^{13}C^{16}O$ and $^{12}C^{18}O$ in natural abundance, nor, of course, can any increase in molecular CO band intensity due to ejection from $M(CO)_6$ be observed. In the CO matrix the visible band of photochemically generated $Cr(CO)_5$ is at 462 nm, where presumably a CO molecule must occupy the vacant coordination site in some orientation. Since in the other matrices the band is both very different from that of the CO matrix and sensitive to the particular matrix, we are able to distinguish $(OC)_5M\cdots OC$ from $(OC)_5M\cdots X$ (X = Ne, Ar, etc.). We can assert therefore that the ejected CO does not influence the geometry in any matrix except CO.[28]

The Limitations of the Force Field. We have used isotopic substitution to investigate the CO-factored force field and to prove the structure of $Cr(CO)_5$. The results demonstrate that the force field gives a much more accurate means of predicting the spectrum than had previously been realized, even when the molecules are quite complex. They also demonstrate the suitability of matrix isolation for such investigations.

As with all least-squares treatments there is no way of telling whether a true minimum has been obtained although the overdetermination of this problem should help to prevent false minima. When the force constants were deliberately offset and refined again, the same results were obtained. However, there is always a second minimum at a completely different set of force constants, but this is rejected in the C–K force field because $k_1 > k_2$ and the interaction force constants are negative. In order for the force constants to be meaningful, there should preferably be bands observed in regions corresponding to all C–O vibrations of the parent molecule, ir active or inactive.[29] This condition was fulfilled in both the metal hexacarbonyls and the metal pentacarbonyls.

It is of considerable interest to understand why such a simple force field produces such excellent predictions in a complex situation. It is by no means trivial to be able to predict all four A' bands of a C_s substituted pentacarbonyl to 0.4 cm^{-1}. Some bands may be relatively insensitive to the force constant, but others (in particular the high-frequency bands) are very sensitive. Abel, *et al.*,[14] have argued convincingly that the most serious approximation in the C–K force field is the neglect of anharmonicity. The estimate of the errors in our calculated force constants provides further evidence of the effect of anharmonicity. The trans-interaction force constant of $Cr(CO)_6$ has a much larger anharmonicity correction than k_{cis};[14] likewise the value of k_{trans} obtained here has a much larger error than k_{cis} (Table II). k_{trans} also has the largest error of the pentacarbonyl force constants (Table V).

The force constants calculated for the hexacarbonyls and pentacarbonyls indicate that some of the approximations used in simpler versions of the C–K force field are very much better held than others. It is also significant that an approximation may hold better for some compounds (*e.g.*, $Cr(CO)_5$) than for others (*e.g.*, $W(CO)_5$) with the same structure but a different central metal atom.

In Appendix 5, we discuss the effect of neglecting anharmonicity on a simple model compound, $M(CO)_2$, and by analogy on other binary metal carbonyls. Using these arguments, the empirical result that anharmonicities may be neglected in the calculations of isotopic patterns has the following implications. (a) The anharmonicities of the bands of the partially substituted molecules must approximate to a linear function of the anharmonicities of the bands of the parent molecule; (b) the magnitude of the coupling between modes of the same symmetry in an isotopic molecule must be small enough for neglect of anharmonicity to make no difference.

The results of our experiments confirm the great power of the Cotton–Kraihanzel force field in predicting isotopic spectra and its use in determining the structures of binary metal carbonyls. Indeed the predictions are often as good as those obtained from much more sophisticated force fields.[30] The lack of direct chemical meaning in the absolute values of the force constants[31] (particularly the interaction force constants) does not invalidate the use of the method for *structure* determination.

Experimental Section

All experiments were conducted on an Air Products Displex CS202 refrigerator equipped with automatic temperature controller. Temperatures were measured with a thermocouple and hydrogen vapor bulb. The detailed setup is very similar to that described previously.[1,32]

Spectra were recorded on a Grubb Parsons Spectromajor (or ocassionally a Perkin-Elmer 521). Both spectrometers could be scanned on the upper grating to 1850 cm^{-1}. Spectra were calibrated with DBr and DCl cells inserted in the beam before and after sample absorptions in each spectrum. Strong bands were reproducible to 0.2 cm^{-1} and weak ones, to 0.4 cm^{-1}; resolution was better than 0.5 cm^{-1}. All spectra were recorded with a Ge filter to remove visible light from the Nernst glower. Relative ir intensities were measured by peak height (if their half-widths were the same) and by tracing the peaks and weighing them. The two methods were consistent with each other. No corrections were made for the finite slit width but rather larger errors are quoted than strictly necessary.

The photolysis source, a Philips HPK 125W medium-pressure mercury arc, was used in conjunction with a 4-cm quartz water cell, to act as a heat filter. Long-wavelength radiation ($\lambda > 375$ Å) was produced with a Balzer Calflex C filter.

Matrix gases (BOC grade X) and metal hexacarbonyls (BDH) were used without further purification. Samples were deposited by pulsed matrix isolation[33,34] with a matrix:carbonyl ratio of 3000:1.

Samples of ^{13}CO-enriched hexacarbonyls were synthesized by gas-phase photolysis.[35] The mixture of $Cr(CO)_6$ vapor, ^{12}CO, and ^{13}CO (Prochem 90% ^{13}CO) was photolyzed for 15 hr using a high-pressure Hg arc, and the carbonyl was separated by passing the mixture slowly through a spiral trap at 77 K.

All calculations were performed on a Hewlett-Packard 2000E computer.

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Appendices

1. Isotopic Intensity Ratios for Molecules with a Permanent Dipole Moment.

Within the approximation of both mechanical and electrical harmonicity the intensity of the *kth* normal mode is

$$I_k = \frac{N\pi}{3c}\left[\left(\frac{\partial\mu_x}{\partial Q_k}\right)_0^2 + \left(\frac{\partial\mu_y}{\partial Q_k}\right)_0^2 + \left(\frac{\partial\mu_z}{\partial Q_k}\right)_0^2\right]$$

Crawford[36] has shown that

$$\sum_k I_k = \sum_{k',k''} \frac{\partial \mu}{\partial S_{k'}} \left(\frac{\partial \mu}{\partial S_{k''}} \right) G_{k'k''}$$

$$\sum \frac{I_k}{\lambda_k} = \sum_{k'k''} \frac{\partial \mu}{\partial S_{k'}} \left(\frac{\partial \mu}{\partial S_{k''}} \right) F_{k'k''}{}^{-1}$$

(summed over all vibrations of same symmetry). If the molecule has no permanent dipole moment and/or the symmetry species of the vibrations over which the intensity sum is calculated is not the same as a rotation which moves the permanent dipole, then the sums, for isotopic species of the same symmetry, are independent of isotope. Thus, strictly speaking, the rules disallow the sum and product rules for $M(CO)_5$. However for CO intensities practically all calculations assume that the total intensity is derived from the sum of CO dipole derivatives (plus M–C derivatives if necessary). Thus on *this model*, coupling with rotation is irrelevant; the fact that a good intensity fit is obtained for $Cr(CO)_5$ demonstrates the usefulness of the model and hence that the rules may be ignored. Moreover it can be demonstrated that coupling with rotation would produce a negligible effect even on more sophisticated models because the moment of inertia is so large.

2. **Methods of Calculation.** Frequencies and eigenvectors were calculated by diagonalizing the unsymmetrized $[G^{1/2}FG^{1/2}]$ matrix.[4] Intensities were calculated from the eigenvectors using the equations

$$\mathbf{O} = \mathbf{P}\left(\frac{1}{\mu_{12}}\mathbf{G}\right)^{1/2} \mathbf{L}$$

$$I_j = \sum_{i=1}^{3} O_{ji}^2$$

where $\mathbf{L}$ is the $(n \times n)$ eigenvector matrix, $\mathbf{G}$ and μ have their usual meaning, $\mathbf{P}$ is a $(3 \times n)$ matrix which contains the components of the CO vectors in the cartesian directions and the bond moment ratio, I_j is the intensity of the *jth* band, and $\mathbf{O}$ contains the sum of the components of the eigenvectors in each cartesian direction for each eigenvalue.

The force constants were refined by a least-squares method in which each force constant was perturbed in turn by a small amount and the error, $|\Delta\lambda|^2$, calculated for all isotopic molecules for which bands were observed. (No observed band was entered more than once in the refinement.) The force constants were perturbed cyclically until no further improvement was obtained; the perturbation was then reduced and the refinement continued. This process was repeated until no more improvement was obtained. This method, although slow, was bound to converge whereas more sophisticated methods tended to produce divergence because of the overdetermined nature of the problem and the strong correlation of the force constants.

3. **Force Constants of $Cr(CO)_5$ for the D_{3h} Structure.** There are no simple approximations for predicting a starting set of force constants for a D_{3h} pentacarbonyl. The bands of the parent molecule were assigned as A_1' 2088 cm^{-1}, A_2'' 1932 cm^{-1}, and E' 1961 cm^{-1} using intensity arguments and assuming that the A_1' was made active by a matrix effect. In order to obtain an extra frequency the weak bands in the isotopic spectrum at 1992 and 1971 cm^{-1} were assigned to the isotopic bands derived essentially from the second forbidden A_1' band of the parent molecule. This assignment is quite unambiguous. From these wave numbers the position of the parent A_1' band was estimated to be 2005 cm^{-1}. With four observed bands the force constants could be plotted as a function of $\cos \beta$ following Bor's method.[37,38] The complete isotopic spectrum was calculated for five sets of force constants corresponding to points taken over the entire range of $\cos \beta$.

4. **Structure and Dipole Moment Values.** For octahedral $Cr(CO)_6$ a good fit to the intensities of the isotopic molecules is obtained simply by assuming that each CO group has the same dipole moment derivative irrespective of the symmetry of the normal mode.

For $M(CO)_5X$ systems, the picture is more complex. Assuming only mechanical and electrical harmonicity[36] then the intensity of the *kth* normal mode for a molecule is given by

$$I_k \propto \left(\frac{\partial \mu_g}{\partial Q_k} \frac{\partial \mu_g}{\partial Q_k} \right)$$

($g = x$, y, and z; $\partial\mu_g/\partial Q_k$ is the change of molecular dipole moment in the *gth* molecule-fixed axes with normal coordinates Q_k). Since the normal coordinates are related to symmetry coordinates by

$$\mathbf{S} = \mathbf{L}\mathbf{Q}, \quad \frac{\partial S_i}{\partial Q_k} = L_{ik} \qquad (1)$$

and the symmetry coordinates to internal coordinates by

$$\mathbf{R} = \mathbf{U}^{-1}\mathbf{S}, \frac{\partial R_j}{\partial S_i} = U_{ji}^{-1} = U_{ij}$$

(because $\mathbf{U}$ is orthogonal)

we can obtain

$$I_k \propto \left[\sum_i \sum_j L_{ik} U_{ij} \left(\frac{\partial \mu_g}{\partial R_j} \right) \right]^2 \qquad (2)$$

Thus for $M(CO)_5$, assuming that the overall dipole moment change derives from changes in CO bonds (or M–C–O groups) and that the bond moment vectors lie along the axes of the CO groups

$$I_1(A_1{}^{\text{low}}) = G(\mu'{}_{\text{a}}{}^{(1)} \cos\phi - 2\mu'{}_{r}{}^{(1)} \sin\phi \cos\theta)^2$$

$$I_2(A_1{}^{\text{high}}) = G(\mu'{}_{\text{a}}{}^{(2)} \sin\phi + 2\mu'{}_{\text{r}}{}^{(2)} \cos\phi \cos\theta)^2$$

$$I_3(E) = 4G(\mu'{}_{\text{r}}{}^{(3)})^2 \sin^2\theta$$

The $\mathbf{L}$ matrix elements are taken from ref 15, and $\mu'{}_{a}{}^{(2)}$, for example, is the dipole moment derivative along the axial M–C–O group due to this group's motion during the A_1 vibration in which the CO groups are in phase. ϕ is defined by the expression $\tan 2\phi = 4k_c/(k_2 + 2k'_c + k_t - k_1)$[39] and the remaining terms are defined as in ref 17. We also make the following definitions

$$R_1 = I_2/I_1$$

$$R_2 = I_3/I_1$$

$$R_3 = I_3/(I_1 + I_2) = R_2/(1 + R_1)$$

The simplest approximation is to assume that all μ' values are identical.[19] There are then two observables and one unknown and θ may be determined from eq 3 or 4

$$\cos\theta = ((\cos\phi)\sqrt{R_1} - \sin\phi)/((\sin\phi)\sqrt{R_1} + \cos\phi) \qquad (3)$$

$$R_3 = 4\sin^2\theta/(5 - 4\sin^2\theta) \qquad (4)$$

Equation 4 is the more usual one to use since it is independent of the force field. However, this function becomes extremely insensitive at values of θ less than 95° and is then quite unsuitable. In such cases it is better to use eq 3 although R_1 may be less accurately known than R_3. This treatment suffers from the disadvantage that R_3 cannot exceed 4, a requirement which is inconsistent with the experimental results. If eq 1 is used to calculate θ for $Cr(CO)_5$ in CH_4, a value 93.18° is

Table VIII. Calculations of Hypothetical Dicarbonyl $M(CO)_2$ Anharmonicities: $X_{11} = -2, X_{22} = -7, X_{12} = -8$ cm^{-1} [a]

	Mode	ν_i	ω_i	$(\omega_i - \chi_i)$
$M(^{12}CO)_2$	Σ_g^+	2200.0	2208.0	2200.0
$D_{\infty h}$	Σ_u^+	2000.0	2018.0	2000.0
$M(^{12}CO)(^{13}CO)$	Σ^+	2178.2	2186.3	
$C_{\infty v}$	Σ^+	1975.0	1992.6	
$M(^{13}CO)_2$	Σ_g^+	2151.0	2158.8	2151.1
$D_{\infty h}$	Σ_u^+	1955.4	1973.0	1955.8

[a] ν_i, anharmonic wave numbers; ω_i, harmonic wave numbers; χ_i, anharmonicities. Couplings of bands of $M(^{12}CO)(^{13}CO)$ (see text): $\alpha_a = 2.7$ cm^{-1}; $\alpha_h = 2.9$ cm^{-1}.

obtained and R_2 is predicted to be 4.11 (observed value 5.34). Equation 2 cannot be used because $R_3 > 4$.

Brown and Darensbourg[21] argued that because of differing demands for π-electron density, the dipole moment derivatives will vary with the nature of the vibrational mode. They stated $\mu'_a{}^{(1)} = \mu'_a{}^{(2)}$ and $\mu'_r{}^{(1)} = \mu'_r{}^{(2)}$ and assumed that $\mu'_a{}^{(1)} = \mu'_r{}^{(1)}$; *i.e.*, $\mu'^{(1)} = \mu'^{(2)} \equiv \mu'_{A_1}$; $\mu'_r{}^{(3)} \equiv \mu'_E$. The value of θ obtained by this method is identical with that obtained from eq 1. The method surmounts the problem of the limit on the value of R_3

$$R_3 = \frac{4\mu'_E{}^2 \sin^2\theta}{(5 - 4\sin^2\theta)\mu'_{A_1}{}^2} \tag{5}$$

Only the positive value of (μ'_E/μ'_{A_1}) is considered. For $Cr(CO)_5$ in CH_4, $\theta = 93.18°$ and $\mu'_E/\mu'_{A_1} = 1.14$. However, since ^{13}CO substitution lowers the molecular symmetry and hence the symmetry of the normal coordinates, it is difficult to see how the method can be applied to the isotopic molecules. It should also be noted that the method assumes electrical *anharmonicity* whereas the approximation involved in calculating intensities assumes both mechanical and electrical harmonicity. Certainly the activity of overtone bands indicates the presence of electrical anharmonicity, but it would seem to be invalid to use this in the interpretation of intensity calculations which rely on its absence.

Braterman, *et al.*,[17] assumed for $M(CO)_5$ that μ'(axial) $\neq$ μ'(radial) but that these derivatives are independent of vibrational mode, implying that

$$\mu'_a{}^{(1)} = \mu'_a{}^{(2)} \equiv \mu'_a$$

$$\mu'_r{}^{(1)} = \mu'_r{}^{(2)} = \mu'_r{}^{(3)} \equiv \mu'_r$$

The particular advantage of this method is that intensity calculations on isotopic molecules are very straightforward. As in the method of Brown and Darensbourg there are no limits on R_3, but the chemical interpretation which this method places on the difference between μ'_a and μ'_r obviates the problems of electrical anharmonicity.

The expressions of Braterman, *et al.*,[17] may be rewritten as

$$\theta = \tan^{-1}[\sqrt{R_2}/((\cos\phi)\sqrt{R_1} - \sin\phi)] \tag{6}$$

$$\mu'_a/\mu'_r = 2\sin\theta(\cos\phi + \sqrt{R_1}\sin\phi)/\sqrt{R_2} \tag{7}$$

Both eq 3 and eq 6 are quoted for the solution in which the intensities of the A_1 modes are *in phase*; the *out-of-phase* solution is obtained by changing the sign of $R_1^{1/2}$. Equation 6 has two further solutions which are obtained by changing the sign of $R_2^{1/2}$. Obtuse angles become acute and *vice versa* and (μ'_a/μ'_r) becomes negative. Because of the negative value of (μ'_a/μ'_r) this solution is rejected. The values of θ obtained from this method (Table VII) are not substantially different from those obtained using eq 3, but this model is preferred because it offers a more complete description of the experimental results. The isotopic data are used as a check on the model and are used to choose between the in-phase and out-of-phase solution.

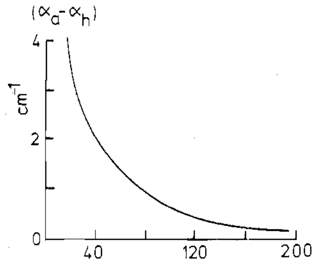

Figure 6. The effect of neglect of anharmonicity. Plot of coupling of bands of $M(^{13}CO)(^{12}CO)$ against separation of bands of $M(^{12}CO_2)$ $(\delta\nu)$. $(\alpha_a - \alpha_h)$ is difference in coupling in harmonic and anharmonic approximations.

5. The Effect of the Neglect of Anharmonicity. In order to assess the effect of neglecting anharmonicity we performed some calculations on a simple model system. Table VIII shows the results of such an investigation on $M(CO)_2$ ($D_{\infty h}$ geometry) using anharmonicities "estimated" from the Jones[30,40] data on $M(CO)_6$ and $M(CO)_5X$ systems. All the calculations were performed without recourse to force constants, by using the isotopic sum and product rules. The anharmonicities of the disubstituted molecules were calculated using the formula

$$X'_{ij} = X_{ij}\frac{\omega'_i\omega'_j}{\omega_i\omega_j}$$

where primes refer to disubstituted molecule. It can be seen from Table VIII that the neglect of anharmonicity produces an error <0.4 cm^{-1} in the prediction of the bands of the disubstituted molecule. The errors in the prediction of the frequencies in the intermediate molecule are estimated by comparing the coupling with and without anharmonicity. α is a measure of the coupling and is defined as

$$\alpha_a = \nu_3 - (\nu_1 + \nu_5)/2 = \nu_4 - (\nu_2 + \nu_6)/2$$

$$\alpha_h = \omega_3 - (\omega_1 + \omega_5)/2 = \omega_4 - (\omega_2 + \omega_6)/2$$

In the example in Table VIII $(\alpha_a - \alpha_h)$ is 0.2 cm^{-1}. It follows that errors in the calculations due to anharmonicity will be very small for such a molecule, provided that the anharmonicity of the bands of $M(^{12}CO)(^{13}CO)$ approximate to a linear function of the anharmonicities of the bands of $M(^{12}CO)_2$. Figure 6 shows the effect on $(\alpha_a - \alpha_h)$ of bringing the two bands of $M(^{12}CO)_2$ closer together. As they approach, the coupling increases rapidly, and the errors in the frequencies of the monosubstituted molecule mount. (Note, however, that the errors in the frequencies of the disubstituted molecule stay fixed.)

We cannot obtain an estimate of the errors for a linear dicarbonyl because the Σ_g^+ mode is ir inactive, but we can perform part of the calculation on the bent dicarbonyl $Al_x(CO)_2$ which has been studied with $C^{18}O$ substitution.[41] Recalculating the data we may fix the force constants to match the parent bands exactly and calculate the bands of the isotopically substituted molecules in the usual way. The errors $(\nu_{obsd} - \nu_{calcd})$ in the calculated positions of the bands of the totally substituted molecule are 1.0 and 0.4 cm^{-1}; those in the monosubstituted molecule, 0.4 and 0.8 cm^{-1}. The observed coupling α_a is 5.2 cm^{-1}. Although the bands of the parent molecule are only separated by about 100 cm^{-1}, the errors due to neglecting anharmonicity are within the experimental error of ±1.0 cm^{-1}.

Corresponding calculations on $M(CO)_5$ and $M(CO)_6$ are not possible because the force constant problem is underdetermined when the parent ir spectrum is taken alone. However, the evidence of the excellent fit of calculated and observed spectra suggest that they present a similar case to $Al_x(CO)_2$.

Registry No. $\mathrm{Cr(^{12}CO)_6}$, 13007-92-6; $\mathrm{Cr(^{12}CO)_5(^{13}CO)}$, 53109-01-6; *trans*-$\mathrm{Cr(^{12}CO)_4(^{13}CO)_2}$, 53109-00-5; *cis*-$\mathrm{Cr(^{12}CO)_4(^{13}CO)_2}$, 53108-99-9; *cis*-$\mathrm{Cr(^{12}CO)_3(^{13}CO)_3}$, 53108-98-8; *trans*-$\mathrm{Cr(^{12}CO)_3(^{13}CO)_3}$, 53109-02-7; *trans*-$\mathrm{Cr(^{12}CO)_2(^{13}CO)_4}$, 53042-53-8; *cis*-$\mathrm{Cr(^{12}CO)_2(^{13}CO)_4}$, 53109-11-8; $\mathrm{Cr(^{12}CO)(^{13}CO)_5}$, 53109-12-9; $\mathrm{Cr(^{13}CO)_6}$, 25941-09-7; $\mathrm{Mo(^{12}CO)_6}$, 13939-06-5; $\mathrm{Mo(^{12}CO)_5(^{13}CO)}$, 17594-07-9; *trans*-$\mathrm{Mo(^{12}CO)_4(^{13}CO)_2}$, 17594-08-0; *cis*-$\mathrm{Mo(^{12}CO)_4(^{13}CO)_2}$, 53042-52-7; *cis*-$\mathrm{Mo(^{12}CO)_3(^{13}CO)_3}$, 20529-45-7; *trans*-$\mathrm{Mo(^{12}CO)_3(^{13}CO)_3}$, 20529-46-8; *trans*-$\mathrm{Mo(^{12}CO)_2(^{13}CO)_4}$, 53042-49-2; *cis*-$\mathrm{Mo(^{12}CO)_2(^{13}CO)_4}$, 53042-50-5; $\mathrm{Mo(^{12}CO)(^{13}CO)_5}$, 53042-57-6; $\mathrm{Mo(^{13}CO)_6}$, 25941-10-0; $\mathrm{W(^{12}CO)_6}$, 14040-11-0; $\mathrm{W(^{12}CO)_5(^{13}CO)}$, 17594-12-6; *trans*-$\mathrm{W(^{12}CO)_4(^{13}CO)_2}$, 53109-09-4; *cis*-$\mathrm{W(^{12}CO)_4(^{13}CO)_2}$, 53042-47-0; *cis*-$\mathrm{W(^{12}CO)_3(^{13}CO)_3}$, 53042-48-1; *trans*-$\mathrm{W(^{12}CO)_3(^{13}CO)_3}$, 53109-10-7; *trans*-$\mathrm{W(^{12}CO)_2(^{13}CO)_4}$, 53042-45-8; *cis*-$\mathrm{W(^{12}CO)_2(^{13}CO)_4}$, 53042-46-9; $\mathrm{W(^{12}CO)(^{13}CO)_5}$, 53109-08-3; $\mathrm{W(^{13}CO)_6}$, 25941-11-1; $\mathrm{Cr(^{12}CO)_5}$, 53042-44-7; (C_{4v})-$\mathrm{Cr(^{12}CO)_4(^{13}Co)}$, 53109-06-1; ($C_s$)-$\mathrm{Cr(^{12}CO)_4(^{13}CO)}$, 53109-07-2; ($C_s$-ax-eq)-$\mathrm{Cr(^{12}CO)_3(^{13}CO)_2}$, 53109-76-5; ($C_s$-eq-eq)-$\mathrm{Cr(^{12}CO)_3(^{13}CO)_2}$, 53109-77-6; ($C_{2v}$)-$\mathrm{Cr(^{12}CO)_3(^{13}CO)_2}$, 53109-78-7; ($C_s$-ax-eq)-$\mathrm{Cr(^{12}CO)_2(^{13}CO)_3}$, 53129-38-7; ($C_s$-eq-eq)-$\mathrm{Cr(^{12}CO)_2(^{13}CO)_3}$, 53109-75-4; ($C_{2v}$)-$\mathrm{Cr(^{12}CO)_2(^{13}CO)_3}$, 53059-22-6; ($C_{4v}$)-$\mathrm{Cr(^{12}CO)(^{13}CO)_4}$, 53109-73-2; ($C_s$)-$\mathrm{Cr(^{12}CO)(^{13}CO)_4}$, 53109-74-3; $\mathrm{Cr(^{13}CO)_5}$, 53059-21-5; $\mathrm{Mo(^{12}CO)_5}$, 53109-70-9; (C_{4v})-$\mathrm{Mo(^{12}CO)_4(^{13}CO)}$, 53109-71-0; ($C_s$)-$\mathrm{Mo(^{12}CO)_4(^{13}CO)}$, 53109-72-1; ($C_s$-ax-eq)-$\mathrm{Mo(^{12}CO)_3(^{13}CO)_2}$, 53109-67-4; ($C_s$-eq-eq)-$\mathrm{Mo(^{12}CO)_3(^{13}CO)_2}$, 53109-68-5; ($C_{2v}$)-$\mathrm{Mo(^{12}CO)_3(^{13}CO)_2}$, 53109-69-6; ($C_s$-ax-eq)-$\mathrm{Mo(^{12}CO)_2(^{13}CO)_3}$, 53109-64-1; ($C_s$-eq-eq)-$\mathrm{Mo(^{12}CO)_2(^{13}CO)_3}$, 53109-65-2; ($C_{2v}$)-$\mathrm{Mo(^{12}CO)_2(^{13}CO)_3}$, 53109-66-3; ($C_{4v}$)-$\mathrm{Mo(^{12}CO)(^{13}CO)_4}$, 53109-61-8; ($C_s$)-$\mathrm{Mo(^{12}CO)(^{13}CO)_4}$, 53109-62-9; $\mathrm{Mo(^{13}CO)_5}$, 53109-63-0; $\mathrm{W(^{12}CO)_5}$, 53109-57-2; (C_{4v})-$\mathrm{W(^{12}CO)_4(^{13}CO)}$, 53109-58-3; ($C_s$)-$\mathrm{W(^{12}CO)_4(^{13}CO)}$, 53109-59-4; ($C_s$-ax-eq)-$\mathrm{W(^{12}CO)_3(^{13}CO)_2}$, 53109-60-7; ($C_s$-eq-eq)-$\mathrm{W(^{12}CO)_3(^{13}CO)_2}$, 53110-30-8; ($C_{2v}$)-$\mathrm{W(^{12}CO)_3(^{13}CO)_2}$, 53110-31-9; ($C_s$-ax-eq)-$\mathrm{W(^{12}CO)_2(^{13}CO)_3}$, 53110-27-3; ($C_s$-eq-eq)-$\mathrm{W(^{12}CO)_2(^{13}CO)_3}$, 53110-28-4; ($C_{2v}$)-$\mathrm{W(^{12}CO)_2(^{13}CO)_3}$, 53110-29-5; ($C_{4v}$)-$\mathrm{W(^{12}CO)(^{13}CO)_4}$, 53110-24-0; ($C_s$)-$\mathrm{W(^{12}CO)(^{13}CO)_4}$, 53110-25-1; $\mathrm{W(^{13}CO)_5}$, 53110-26-2.

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