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A new method for assigning the C–O stretching bands in *cis*-disubstituted octahedral metal carbonyl complexes

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Abstract

The paper describes a method for assigning the C–O stretching bands in *cis*-disubstituted metal carbonyls of the types $L_2M(CO)_4$, $(L-L)M(CO)_4$, $LL'M(CO)_4$ and $(L-L')M(CO)_4$. The method was based on the parameter δ, defined as $\delta = (\lambda_1 - \lambda_2)/(\lambda_1 + \lambda_2 - 2\lambda_4)$ where λ_1, λ_2 and λ_4 are the λ parameters of the $a_1^{(1)}$, $a_1^{(2)}$ and b_2 modes, respectively. For a large number of complexes with the above general formulas, the average value of δ was found to be 0.62, with a standard deviation of 0.02. It was shown that this range of δ can be used as a criterion of the correct band assignment for the complexes understudy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tetracarbonyls; Vibrational spectra; Band assignment; CO-factored force field

1. Introduction

For *cis*-disubstituted carbonyl complexes of the types $L_2M(CO)_4$, $(L-L)M(CO)_4$, $LL'M(CO)_4$ and $(L-L')M(CO)_4$, under the C_{2v} local symmetry of the carbonyl groups, group theory predicts four C–O stretching modes ($2a_1+b_1+b_2$). All the modes are both infrared and Raman-active [1,2]. Several methods that enable us to assign C–O stretching bands of the mentioned complexes have been reported in the literature. In the theory of local oscillating dipoles [3–6] based on the assumption that each vibrating carbonyl group can be considered as an oscillating dipole, the relative order of the C–O stretching modes is established by a simple electronic interaction between the dipoles. This method purely qualitative has particularly been useful in assigning the mode with the highest energy.

The assignment of C–O stretching frequencies for many carbonyl compounds has been based on the intensity considerations [7–10]. In this method, the relative intensities of the fundamental C–O stretching bands in the infrared spectra were compared with those estimated theoretically. However, the method requires the dipole moment derivatives, which depend on bond angles to be determined. ‘Correlation curves’ have also been used to assign C–O stretching bands [11–13]. However, the application of this method to the complexes understudy necessitates the use of C–O stretching frequencies of all $M(CO)_{6-n}L_n$, ($n = 0$–6), species, not only those of the *cis*-disubstituted molecule.

Cotton and Kraihanzel developed a method that has proved to be of value in the band assignment [14–16]. In the application of this method to *cis*-disubstituted octahedral metal carbonyls, it was suggested the relationship $1/2k_t = k_c = k_c' = k_i$ and two criteria $k_2 > k_1$ and $k_i > 0$, derived from elementary bonding considerations [15,17]. Using this relationship and three C–O stretching frequencies, force constants and the remaining frequency were calculated for six possible assignments. The assignment for which there was tolerable agreement between observed and calculated frequencies and for which the above criteria were upheld was considered the correct assignment. However, it was shown that in the application of the method to certain complexes real roots cannot be obtained and agreement between observed and calculated frequencies was poor, with the use of the relationship mentioned above. In order to overcome this problem, some authors [18–20] have employed various relationships among the interaction constants.

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Another method which can be used to assign C–O stretching bands in *cis*-disubstituted octahedral metal carbonyl complexes has been developed by Timney [21]. However, this method is restricted to complexes whose ligand effect constants and bond angles are known because the relationships suggested for calculating force constants are expressed in terms of the mentioned parameters.

The availability of the correct band assignment through use of isotopic data allows various methods to be tested. A 'valid' method would be one, which yields the result consistent with that obtained from isotopic enrichment studies. This report presents a method for determining the correct band assignment of *cis*-disubstituted octahedral metal carbonyls. The method is based on the δ parameter defined as $\delta=(\lambda_1-\lambda_2)/(\lambda_1+\lambda_2-2\lambda_4)$ where λ_1, λ_2 and λ_4 are the λ parameters of the $a_1^{(1)}$, $a_1^{(2)}$ and b_2 modes, respectively.

2. Definition of the parameter δ

The secular equations for tetracarbonyls with C_{2v} symmetry derived by employing a CO-factored force field, which are given elsewhere [14,22,23], are presented in Table 1. When these equations are rearranged so that four of the five force constants are expressed in terms of the fifth and the observed frequencies, the following relations are obtained:

$$k_1=\alpha(\lambda_1+\lambda_2+2\lambda_4-\beta) \tag{1}$$

$$k_2=\alpha(\lambda_1+\lambda_2+2\lambda_3+\beta) \tag{2}$$

$$k_c'=\alpha(\lambda_1+\lambda_2-2\lambda_4-\beta) \tag{3}$$

$$k_t=\alpha(\lambda_1+\lambda_2-2\lambda_3+\beta) \tag{4}$$

where $\alpha=1/(4\mu)$; $\beta=[(\lambda_1-\lambda_2)^2-16\mu^2k_c^2]^{1/2}$ and λ_1, λ_2, λ_3 and λ_4 are the λ parameters of the $a_1^{(1)}$, $a_1^{(2)}$, b_1 and b_2 modes, respectively. Since all the above relations contain the square root term β, it is mathematically evident that in order to obtain real values for the force constants, the term $[(\lambda_1-\lambda_2)^2-16\mu^2k_c^2]$ in the square root must be equal to or greater than zero. With the use of $(\lambda_1-\lambda_2)^2-16\mu^2k_c^2=0$, we have:

$$k_c(\max)=\alpha(\lambda_1-\lambda_2) \tag{5}$$

where $k_c(\max)$ is the maximum value of k_c. In an our previous work [23] we have derived Eq. (6) for *cis*-$L_2M(CO)_4$ molecules by an analytical approach.

$$k_c=\frac{\alpha(\lambda_1-\lambda_2)[(\lambda_1+\lambda_2-2\lambda_4)^2-(\lambda_1-\lambda_2)]^{1/2}}{\lambda_1+\lambda_2-2\lambda_4} \tag{6}$$

Combining Eqs. (5) and (6) gives:

$$\frac{k_c}{k_c(\max)}=\left[1-\left(\frac{\lambda_1-\lambda_2}{\lambda_1+\lambda_2-2\lambda_4}\right)^2\right]^{1/2} \tag{7}$$

The term $(\lambda_1-\lambda_2)/(\lambda_1+\lambda_2-2\lambda_4)$ in Eq. (7) was defined as the parameter δ. According to this, the expression for δ can be written as follows:

$$\delta=(\lambda_1-\lambda_2)/(\lambda_1+\lambda_2-2\lambda_4) \tag{8}$$

where λ_1, λ_2 and λ_4 are the λ parameters of the $a_1^{(1)}$, $a_1^{(2)}$ and b_2 modes, respectively.

Table 1
Secular equations for tetracarbonyls with C_{2v} symmetry

Symmetry species	Secular equations [a]
$a_1^{(1)}$ $a_1^{(2)}$	$\begin{vmatrix}\mu(k_1+k_2)-\lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_1+k_c')\end{vmatrix}=0$
b_1	$\lambda=\mu(k_2-k_1)$
b_2	$\lambda=\mu(k_1-k_c')$

[a] The various force constants are defined in Fig. 1; μ represents the reciprocal of the reduced mass of the CO group; $\lambda=4\pi^2c^2v^2$ where v is the frequency in cm^{-1}.

3. Results and discussion

Eq. (8) shows that the value of the δ parameter depends on both the frequencies and the assignment of C–O stretching bands. In order words, in order for the δ parameter to be determined from Eq. (8) it is necessary to assign C–O stretching frequencies.

In this work, we have assumed that the δ parameter for the correct band assignment of *cis*-disubstituted octahedral metal carbonyl complexes remains unchanged from one complex to another. In order to test the validity of this assumption, Eq. (8) was applied to a large number of complexes of the types $L_2M(CO)_4$, $(L-L)M(CO)_4$, $LL'M(CO)_4$ and $(L-L')M(CO)_4$. The complexes selected were those whose correct band assignments have previously been reported by many authors, using various methods [9,14,20,24,25]. The calculated values of δ are given in Table 2, together with observed C–O stretching frequencies of the complexes. Inspection of Table 2 reveals that the δ parameter does not differ significantly from one complex to another. The average value of δ and the standard deviation measured as $(\sigma^2/n)^{1/2}$ were found to be 0.62 and 0.02, respectively. From this result one can conclude that the δ value for the correct band assignment is in the range of 0.62±0.02. It

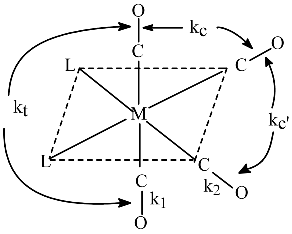

Fig. 1. Definition of carbonyl stretching force constants and interaction constants for *cis*-disubstituted octahedral metal carbonyl complexes.

Table 2
Calculated values of the δ parameter for some tetracarbonyls belonging to the C_{2v} point group

Complex [a]	Frequencies (cm^{-1})					δ
	Reference	$a_1^{(1)}$	$a_1^{(2)}$	b_1	b_2	
$(tmen)Cr(CO)_4$	[22]	2005	1879	1868	1839	0.62
$(diphos)Cr(CO)_4$	[22]	2009	1918	1903	1887	0.60
$(P\text{-}en)Cr(CO)_4$	[22]	2018	1932	1907	1907	0.64
$(diars)Cr(CO)_4$	[22]	2005	1914	1894	1885	0.62
$(dto)Cr(CO)_4$	[22]	2013	1902	1893	1867	0.62
$(PMe_3)_2Cr(CO)_4$	[26]	2001	1901	1873	1866	0.60
$(AsMe_2Ph)_2Cr(CO)_4$	[26]	2008	1904	1893	1873	0.63
$(PrSeCH_2)_2Cr(CO)_4$	[27]	2015	1900	1900	1860	0.60
$[(acac)Cr(CO)_4]^-$	[28]	2005	1848	1877	1795	0.61
$[Me_2P(CH_2)_2PMe_2]Cr(CO)_4$	[29]	2009	1921	1900	1894	0.63
$[(C_6H_{11})_2P(CH_2)_2P(C_6H_{11})_2]Cr(CO)_4$	[29]	2002	1912	1890	1886	0.64
$[(C_4H_9)_2PPh]_2Cr(CO)_4$	[30]	2002	1906	1893	1874	0.61
$(diphos)Mo(CO)_4$	[22]	2020	1925	1912	1894	0.61
$(dpae)Mo(CO)_4$	[22]	2022	1925	1912	1894	0.62
$(diars)Mo(CO)_4$	[22]	2018	1922	1907	1894	0.64
$(dth)Mo(CO)_4$	[22]	2023	1911	1903	1878	0.64
$(tmpa)Mo(CO)_4$ [b]	[22]	2013	1881	1881	1837	0.61
$(tmpa)Mo(CO)_4$ [c]	[25]	2015.9	1890.6	1885.8	1853.0	0.63
$(bipy)Mo(CO)_4$	[15]	2017	1878	1909	1829	0.60
$(en)Mo(CO)_4$	[15]	2015	1864	1890	1818	0.63
$(NH_3)_2Mo(CO)_4$	[31]	2010	1837	1915	1780	0.62
$(PPh_3)_2Mo(CO)_4$ [d]	[32]	2023	1927	1908	1897	0.62
$(PPh_3)_2Mo(CO)_4$ [c]	[25]	2023.4	1930.2	1911.2	1900.2	0.62
$(PPh_3)_2Mo(CO)_4$ [c]	[33]	2021	1926	1908	1897	0.63
$(PMe_3)_2Mo(CO)_4$	[26]	2016	1910	1896	1874	0.60
$(PMe_2Ph)_2Mo(CO)_4$ [e]	[26]	2011	1912	1895	1878	0.60
$(PMe_2Ph)_2Mo(CO)_4$ [d]	[32]	2018	1920	1900	1891	0.64
$(PPhCy_2)_2Mo(CO)_4$	[32]	2012	1908	1890	1877	0.63
$[P(n\text{-}Bu)_3]_2Mo(CO)_4$	[32]	2013	1910	1895	1879	0.63
$(SbPh_3)_2Mo(CO)_4$	[32]	2025	1934	1919	1905	0.62
$[P(OPh)_3]_2Mo(CO)_4$	[25]	2045.6	1965.5	1945.2	1940.4	0.62
$(PrSeCH_2)_2Mo(CO)_4$	[27]	2012	1900	1900	1864	0.62
$(Et_2NPF_2)_2Mo(CO)_4$	[34]	2055	1974	1942	1950	0.63
$(C_5H_{10}NPF_2)_2Mo(CO)_4$	[34]	2053	1977	1942	1952	0.61
$[(C_4H_9)_2PPh]_2Mo(CO)_4$	[30]	2016	1917	1902	1888	0.64
$[(C_4H_9)PPh_2]_2Mo(CO)_4$	[30]	2021	1924	1904	1892	0.61
$[(CF_3)_2PF]_2Mo(CO)_4$	[34]	2093	2033	2033	2013	0.61
$(Me_2P(CH_2)_2PMe_2)Mo(CO)_4$	[29]	2020	1929	1909	1903	0.64
$(Ph_3P)(NC_5H_5)Mo(CO)_4$	[33]	2017	1909	1896	1872	0.60
$(Ph_3P)(AsPh_3)Mo(CO)_4$	[33]	2022	1927	1910	1897	0.62
$(Ph_3P)[P(OCH_2)_3CC_2H_5]Mo(CO)_4$	[33]	2036	1940	1923	1907	0.60
$(Ph_3P)(SbPh_3)Mo(CO)_4$	[33]	2023	1929	1909	1902	0.64
$(diphos)W(CO)_4$	[22]	2017	1918	1903	1888	0.63
$(dpae)W(CO)_4$	[22]	2017	1918	1903	1887	0.62
$(tmpa)W(CO)_4$	[22]	2006	1873	1866	1832	0.63
$(dth)W(CO)_4$	[22]	2016	1906	1891	1874	0.64
$(bipy)W(CO)_4$	[15]	2010	1873	1899	1826	0.61
$(o\text{-}Phen)W(CO)_4$	[9]	2007.1	1871.0	1895.4	1824.0	0.60
$[(acac)W(CO)_4]^-$	[28]	2001	1818	1869	1754	0.61
$(Me_3P)_2W(CO)_4$	[26]	2008	1898	1880	1862	0.61
$[Ph_3PC(OC_2H_5)CH_3]W(CO)_4$	[9]	2019.1	1925.0	1912.4	1894.9	0.62
$[P(OCH_2)_3CC_2H_5]C(OC_2H_5CH_3W(CO)_4$	[9]	2033.1	1940.7	1931.6	1912.5	0.63
$[Ph_3AsC(OC_2H_5)CH_3]W(CO)_4$	[9]	2020.6	1924.5	1909.8	1896.8	0.64

[a] See Refs. [15,22,28,32] for abbreviations of ligands.
[b] In carbondisulfide.
[c] In hexane.
[d] In tetrachloroetylene.
[e] In chloroform.

Table 3
Calculated δ values for six possible assignments in some *cis*-disubstituted octahedral metal carbonyls

Complex	Assignment [a]					δ
	Number	$a_1^{(1)}$	$a_1^{(2)}$	b_1	b_2	
(diphos)W(CO)$_4$	1	2016	1912	1901	1876	0.60
	2	2016	1912	1876	1901	0.83
	3	2016	1901	1902	1876	0.71
	4	2016	1901	1876	1912	1.23
	5	2016	1876	1912	1901	1.53
	6	2016	1876	1901	1912	2.00
Mo(CO)$_4$ (in CH$_4$ matrix)	1	2057.2	1944.7	1927.2	1887.2	0.51
	2	2057.2	1944.7	1887.2	1927.2	0.77
	3	2057.2	1927.2	1944.7	1887.2	0.63
	4	2057.2	1927.2	1887.2	1944.7	1.34
	5	2057.2	1887.2	1944.7	1927.2	1.84
	6	2057.2	1887.2	1927.2	1944.7	2.87
(diphos)Mo(CO)$_4$	1	2023.1	1931.4	1917.1	1904.0	0.63
	2	2023.1	1931.4	1904.0	1917.1	0.78
	3	2023.1	1917.1	1931.4	1904.0	0.81
	4	2023.1	1917.1	1904.0	1931.4	1.36
	5	2023.1	1904.0	1931.4	1917.1	1.27
	6	2023.1	1904.0	1917.1	1931.4	1.82
(bipy)W(CO)$_4$	1	2007.6	1896.7	1871.5	1826.2	0.45
	2	2007.6	1896.7	1826.2	1871.5	0.70
	3	2007.6	1871.5	1896.7	1826.2	0.61
	4	2007.6	1871.5	1826.2	1896.7	1.56
	5	2007.6	1826.2	1896.7	1871.5	1.93
	6	2007.6	1826.2	1871.5	1896.7	4.08

[a] Frequencies were taken from Refs. [9,14,24,25].

should also be noted that for a given complex the use of various solvents does not lead to a value of δ beyond this range, as can be seen from the data in Table 2 for (tmpa)Mo(CO)$_4$, (PPh$_3$)$_2$Mo(CO)$_4$ and (PPhMe$_2$)$_2$Mo(CO)$_4$ complexes.

To determine how the δ parameter varies with the assignment of C–O stretching frequencies and to ascertain whether or not the range of 0.62 ± 0.02 is a valid criterion for the correct band assignment, the δ parameter was calculated for all possible assignments in some complexes whose correct band assignments have previously been established by other methods. It has undoubtedly been shown that for octahedral metal carbonyl complexes belonging to the C_{2v} point group one of the two a_1 modes corresponds to the highest frequencies [2,14], which is represented by $a_1^{(1)}$ in this work. For the three remaining modes, $a_1^{(2)}$, b_1 and b_2, there are then six possible assignments. The δ values calculated by Eq. (8) for each of these possible assignments are summarised in Table 3. From the data in Table 3 two conclusions can be drawn: (1) in a given complex the δ parameter has a different value for each possible assignment; (2) for only one of the possible assignments the value of δ is in the range of 0.62 ± 0.02. These results in conjunction with the δ values found for the complexes given in Table 2 enable us to conclude that the correct band assignment for (diphos)W(CO)$_4$, and (diphos)Mo(CO)$_4$ is $a_1^{(1)} > a_1^{(2)} > b_1 > b_2$ and for Mo(CO)$_4$ and (bipy)W(CO)$_4$ is $a_1^{(1)} > b_1 > a_1^{(2)} > b_2$. It is worth noting that the assignments suggested for the mentioned complexes are consistent with those established by other methods, the Cotton–Kraihanzel method [14], isotopic substitution [24,25] and intensity considerations [9].

In conclusion, the values of the δ parameter for the correct band assignments was found to be in the range of 0.62 ± 0.02 for *cis*-disubstituted complexes of the types L$_2$M(CO)$_4$, (L–L)M(CO)$_4$, LL′M(CO)$_4$ and (L–L′)M(CO)$_4$. The fact that our conclusions about the complexes given in Table 3 are in agreement with those obtained from other methods, especially from isotopic substitution, indicates that the δ parameter can be used as a criterion of the correct band assignment. It should also be noted that the method presented here makes it easy to assign C–O stretching bands, using a parameter which depends only on the fundamental C–O stretching frequencies of the complex considered.

References

[1] L.E. Orgel, Inorg. Chem. 1 (1962) 25.
[2] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.
[3] M.A. El-Sayed, H.D. Kaesz, J. Mol. Spectry. 9 (1962) 310.

[4] M.A. El-Sayed, H.D. Kaesz, Inorg. Chem. 2 (1963) 158.
[5] L.E. Orgel, Inorg. Chem. 4 (1964) 389.
[6] B.L. Ross, J.G. Graselli, W.M. Ricthey, H.D. Kaesz, Inorg. Chem. 2 (1963) 1023.
[7] S.F.A. Kettle, I. Paul, Adv. Organomet. Chem. 10 (1972) 199 (and references contained therein).
[8] A. Poietti, Foffani, R. Cataliotti, Spectrochim. Acta Part A 26 (1969) 1063.
[9] C.L. Hyde, D.J. Darensbourg, Inorg. Chem. 12 (1973) 1075.
[10] J. Darensbourg, J.E. Tappan, H.H. Nelson, Inorg. Chem. 16 (1977) 535.
[11] M. Bigorgne, R. Poilblanc, Bull. Soc. Chim. France (1962) 1301.
[12] M. Bigorgne, J. Organomet. Chem. 1 (1963) 101.
[13] M. Bigorgne, G. Bouquet, Bull. Soc. Chim. France (1962) 433.
[14] F.A. Cotton, C.S. Kraihanzel, J. Am. Chem. Soc. 84 (1962) 4432.
[15] C.S. Kraihanzel, F.A. Cotton, Inorg. Chem. 2 (1963) 533.
[16] E.W. Abel, I.S. Butler, Trans. Faraday Soc. 63 (1967) 45.
[17] L.H. Jones, in: S. Kirscher (Ed.), Advances in the Chemistry of the Coordination Compounds, MacMillan, 1961.
[18] J. Dalton, I. Paul, J.G. Smith, F.G.A. Stone. J. Chem. Soc. A (1968) 1195.
[19] E.W. Abel, J. Dalton, I. Paul, J.G. Smith, F.G.A. Stone, J. Chem. Soc. A. (1968) 1203.
[20] F.T. Delbeke, E.G. Claeys, G.P. van der Kelen, J. Organomet. Chem. 25 (1970) 219.
[21] J.A. Timney, Inorg. Chem. 18 (1979) 2502.
[22] R.T. Jernigan, R.A. Brawn, G.R. Dobson, J. Coord. Chem. 2 (1972) 47.
[23] C. Kaya, Spectrochim. Acta Part A 50 (1994) 1101.
[24] R.N. Perutz, J.J. Turner, J. Am. Chem. Soc. 97 (1975) 4800.
[25] D.J. Darensbourg, A. Salzer, J. Am. Chem. Soc. 100 (1978) 4119.
[26] J.M. Jenkis, J.R. Moss, B.L. Shaw, J. Chem. Soc. A 2518 (1969).
[27] R. Donaldson, G. Hunter, R.C. Massey, J. Chem. Soc. Dalton Trans. (1974) 288.
[28] G. Doyle, J. Organomet. Chem. 61 (1973) 235.
[29] R.L. Cook, J.G. Morse, Inorg. Chem. 23 (1984) 2332.
[30] S.O. Grim, D.A. Wheatland, Inorg. Chem. 8 (1969) 1716.
[31] C.G. Barlow, G.C. Holywell, J. Organomet. Chem. 16 (1969) 439.
[32] D.J. Darensbourg, R.L. Kump, Inorg. Chem. 17 (1978) 2680.
[33] C.L. Hyde, D.J. Darensbourg, Inorg. Chem. 12 (1973) 1286.
[34] C.G. Barlow, J.F. Nixon, M. Webster, J. Chem. Soc. A (1968) 2216.