Spectroscopic Studies on Matrix-isolated Metal Carbonyls. Part I. Use of $C^{18}O$ Enrichment to obtain Characteristic Frequency and Intensity Patterns

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This paper is concerned with a general method of characterising simple binary carbonyls produced under matrix isolation conditions, where i.r. spectroscopy is often the only means of detection. I.r. band frequency and intensity patterns are calculated for a number of isotopically mixed carbonyls, and in particular, it is shown that if one were to use a mixture of $C^{16}O$ and $C^{18}O$ in the metal-atom synthesis of these compounds, then the species MCO, $M(CO)_2$, $M(CO)_3(D_{3h})$, $M(CO)_4(D_{4h}$ or $T_d)$, and $M(CO)_6(O_h)$ would each give rise to a characteristic frequency and intensity pattern. These patterns not only reveal the stoicheiometry and symmetry of the species, but also yield the appropriate Cotton–Kraihanzel force constants. The calculations are displayed as line spectra and cover a wide range of force constants.

INFRARED spectroscopy has been used for several years in the characterisation of stable transition-metal carbonyls and their derivatives,[1] and the information obtained has frequently been combined with molecular-weight data to arrive at a probable molecular geometry before a detailed structural determination. Quite recently, however, a number of papers have appeared describing the synthesis of new binary carbonyls by use of matrix-isolation techniques.[2-7] These new species are prepared by co-condensing carbon monoxide at low temperatures (typically *ca.* 4—20 K) with metal atoms produced in a high-temperature furnace, and they are detected by i.r. spectroscopy.

By use of these techniques, it has been possible to demonstrate the formation of new binary carbonyls of nickel and tantalum,[2] uranium,[3] germanium and tin,[4] copper and silver,[5] palladium and platinum,[6] and aluminium.[7] However, in the absence of any additional experimental data, the characterisation of many of these new species has been based solely upon changes in

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[6] H. Huber, P. Kundig, M. Moskovits, and G. A. Ozin, *Nature*, 1972, **235**, 98.

[7] A. J. Hinchcliffe, J. S. Ogden, and D. D. Oswald, *J.C.S. Chem. Comm.*, 1972, 338.

relative band intensities which can be brought about by varying the operating conditions: *e.g.*, by changing the proportion of carbon monoxide present, or by warming the deposit in controlled diffusion studies. In this way, DeKock [2] was able to identify the species $Ni(CO)_n$ with $n = 1$—4 by interpreting changes in band intensities in terms of the stepwise addition of CO to NiCO in an argon matrix. It would be very useful to have some additional criteria to aid band assignments, and isotopic substitution is an obvious possibility.

From a spectroscopic point of view, binary metal carbonyls can be grouped according to the number of i.r.-active fundamental CO stretching vibrations. Thus there are at least six well known geometries which would yield only one such vibration: MCO ($C_{\infty v}$), $M(CO)_2$ ($D_{\infty h}$), $M(CO)_3$ (D_{3h}), $M(CO)_4$ (T_d or D_{4h}), and $M(CO)_6$ (O_h). Carbonyls with these stoicheiometries, but possessing a lower symmetry, will usually give rise to a greater number of i.r.-active fundamentals, and in particular, the species $M(CO)_2$ (C_{2v}), $M(CO)_3$ (C_{3v}), and $M(CO)_4$ (D_{2d}) would be included with $M(CO)_5$ (D_{3h}) in a group of molecules characterised by two i.r.-active CO stretching modes.

This division on the basis of the number of i.r.-active fundamentals is very useful, since by varying the experimental conditions in the matrix synthesis it is usually possible to determine the number of CO stretching modes associated with any given species. The main difficulty in completing an assignment is then one of distinguishing between several possible structures each of which, for example, is characterised by a single i.r.-active CO fundamental.

This paper, which is an extension of the work of Haas and Sheline [8] and Bor,[9] shows how the use of $C^{16}O$–$C^{18}O$ mixtures in the matrix-isolation synthesis of metal carbonyls leads to characteristic frequency and intensity patterns from which one can deduce the molecular symmetries of a number of simple binary carbonyls in addition to obtaining force-constant data. We shall be primarily concerned with a method of distinguishing between the six important species listed above which possess only one i.r.-active CO stretching vibration.

EXPERIMENTAL

Procedure.—Within the framework of the high-frequency separation approximation, it is relatively straightforward to calculate carbonyl stretching vibration frequencies from atomic masses and Cotton–Kraihanzel force constants.[10] However, only a few calculations have been carried out on the relative band intensities of isotopically substituted carbonyls. In their paper on the i.r. spectra of metal carbonyls, Haas and Sheline [8] show how it is possible to calculate both the frequencies and relative intensities of numerous weak bands in the spectra of stable metal carbonyls which arise from molecules containing ^{13}CO in natural abundance.

If one assumes [1] that all CO bond dipole derivatives are equal in magnitude, the basic equation for the intensity of a carbonyl band ν_k in terms of symmetry co-ordinates S and transformation coefficients L is given [11] by equation (1).

$$I_k = \sum_{k'k''} \frac{\partial\mu}{\partial S_{k'}} \cdot \frac{\partial\mu}{\partial S_{k''}} L_{k'k} L_{k''k} \qquad (1)$$

The transformation coefficients can conveniently be obtained from the relationships (2) and (3), and thus depend

$$\sum_{k} L_{k'k} L_{k''k} = G_{k'k''} \qquad (2)$$

$$\sum_{k'k''} L_{k'k} F_{k'k''} L_{k''k} = \lambda_k \qquad (3)$$

only upon a knowledge of the F and G matrix elements and upon the frequencies ($\lambda = 4\pi^2\nu^2$).

By using these equations in conjunction with the Wilson FG method [11] for calculating vibration frequencies, we have computed typical spectra which one expects to observe if $C^{16}O$ and $C^{18}O$ are present in equimolar proportions in the matrix synthesis of metal carbonyls.

Apart from the superposition of a frequency scale, it turns out that the patterns so produced depend on the *ratios* of the principal and interaction CO force constants and not their absolute values, and as we are concerned with the recognition of a characteristic pattern in addition to numerical results, our calculations are displayed as line spectra (Figures 1—5) over a range of force-constant ratios. However, since many terminal CO stretching vibrations lie near 2000 cm^{-1} it is convenient to choose this frequency for the single i.r.-active mode in the group of molecules under examination. This places the calculated pattern on a realistic frequency scale, and allows one to relate the calculated line spectra to experimental results, where finite band widths may limit the number of distinct absorptions which can be observed.

In order to emphasise the characteristic patterns associated with each of the species studied, calculations have been carried out for several different ratios of principal and interaction force constants. Thus the species $M(CO)_2$ ($D_{\infty h}$), $M(CO)_3$ (D_{3h}), and $M(CO)_4$ (T_d) each have two such force constants: a principal CO force constant K_{CO} and an interaction constant $K_{CO,CO}$. The ratios $R = K_{CO} : K_{CO,CO}$ employed in the calculations on these molecules are $R = 10$, 20, 50, and 100. The D_{4h} tetracarbonyl and the hexacarbonyl require three force constants: a principal constant K_{CO} and two interaction constants K_{cis} and K_{trans}, and the effect of varying both the $K_{CO} : K_{cis}$ and $K_{CO} : K_{trans}$ ratios independently is considered.

Although the frequency patterns depend only upon these force constants and the atomic masses, and are independent of the $C^{16}O : C^{18}O$ ratio, the intensity pattern is a product of the 'intrinsic' intensities I_k [equation (1)] and the appropriate relative abundance for each molecule. This pattern thus depends strongly upon the isotope ratio. The choice of a $C^{16}O : C^{18}O$ ratio of 1 : 1 in the spectra shown is made partly for convenience and partly to highlight any symmetry in the resulting patterns. Experimentally, this ratio is often obtainable directly from the i.r. spectrum, as unchanged carbon monoxide is usually present in the matrix in addition to the species of interest.

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[8] H. Haas and R. K. Sheline, *J. Chem. Phys.*, 1967, **47**, 2996.

[9] G. Bor, *J. Organometallic Chem.*, 1967, **10**, 343.

[10] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[11] E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955, pp. 191—192.

RESULTS AND DISCUSSION

Tables 1—5 and the accompanying Figures summarise our frequency and intensity calculations for the species $M(CO)_2$—$M(CO)_6$. Several papers have described how one can set up *F* and *G* matrices for these molecules,[1] and this aspect will therefore not be discussed in detail. It is convenient, however, to identify in each Figure the symmetry and source of every band of significant intensity, and this is done for each of the molecules considered. For the square planar and octahedral geometries, accidental band overlap frequently occurs, and we have arbitrarily chosen to represent this as a single line where the frequency separation is less than 0·5 cm^{-1}. For these molecules also, it is convenient to list the statistical weights of the isotopically mixed species.

Monocarbonyls.—The calculations for a monocarbonyl are rather trivial in that only two species $MC^{16}O$ and $MC^{18}O$ can be produced in the $C^{16}O$–$C^{18}O$–metal atom synthesis. Each of these molecules has only one CO stretching vibration, and for a $C^{16}O : C^{18}O$ ratio of 1 : 1, the relative intensities of the two bands should be 1 : 0·952. In addition to NiCO, which was characterised by DeKock,[2] several other monocarbonyls have been detected recently, notably of tin,[4] germanium,[4] gold,[12] and aluminium.[13] This result is valid for monocarbonyls of any symmetry.

Dicarbonyls (*Table* 1).—A linear dicarbonyl $M(CO)_2$ ($D_{\infty h}$) has two CO stretching vibrations with symmetries Σ^+_g and Σ^+_u. Only the Σ^+_u mode is i.r.-active, and thus $M(C^{16}O)_2$ and $M(C^{18}O)_2$ each give rise to only one band.

TABLE 1

CO Vibration frequencies (ν) and i.r. intensities (*I*) for linear dicarbonyls $M(CO)_2$

Molecule	Relative abundance *	Mode	$R = 10$ ν_k (I_k)	$R = 20$ ν_k (I_k)	$R = 50$ ν_k (I_k)	$R = 100$ ν_k (I_k)
			Force-constant ratios $R = K_{CO} : K_{CO,CO}$			
$M(C^{16}O)_2$ $D_{\infty h}$	1	Σ_g^+	2211·1(0·00)	2102·6(0·00)	2040·4(0·00)	2020·1(0·00)
		Σ_u^+	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
$M(C^{16}O)(C^{18}O)$ $C_{\infty v}$	$2x$	Σ^+	2187·5(0·03)	2083·0(0·11)	2027·3(0·38)	2012·0(0·63)
		Σ^+	1972·9(1·92)	1970·2(1·84)	1964·4(1·58)	1959·7(1·32)
$M(C^{18}O)_2$ $D_{\infty h}$	x^2	Σ_g^+	2157·8(0·00)	2052·0(0·00)	1991·2(0·00)	1971·4(0·00)
		Σ_u^+	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)

* For a $C^{16}O : C^{18}O$ ratio of 1 : *x*.

The partially substituted molecule $M(C^{16}O)(C^{18}O)$ belongs to point-group $C_{\infty v}$ and both CO stretching modes now have Σ^+ symmetry and are i.r.-active. Figure 1 shows spectra calculated for a range of ratios *R*. For all values of *R*, three prominent bands are expected, and these can readily be identified as (1) Σ^+_u $M(C^{18}O)_2$, (2) Σ^+ $M(C^{16}O)(C^{18}O)$, and (3) Σ^+_u $M(C^{16}O)_2$. Band (4) is the higher Σ^+ mode in $M(C^{16}O)(C^{18}O)$ and only has significant intensity for high *R* values. For this reason, it is omitted from the first two spectra.

The spectra for the corresponding bent (C_{2v}) dicarbonyls differ only in the respect that both CO vibrations are now active in each of the three molecules produced. A six-line spectrum should therefore be observed, and this has been found for aluminium dicarbonyl.[7]

Tricarbonyls (*Table* 2).—The planar D_{3h} molecule $M(CO)_3$ has two CO stretching modes with symmetries A_1' and E'. Only the E' mode is i.r.-active, and thus $M(C^{16}O)_3$ and $M(C^{18}O)_3$ each give rise to only one band. The partially substituted molecules $M(C^{16}O)_2(C^{18}O)$ and $M(C^{16}O)(C^{18}O)_2$ have C_{2v} symmetry, and the CO vibrations are now $2A_1 + B_2$, all of which are i.r.-active.

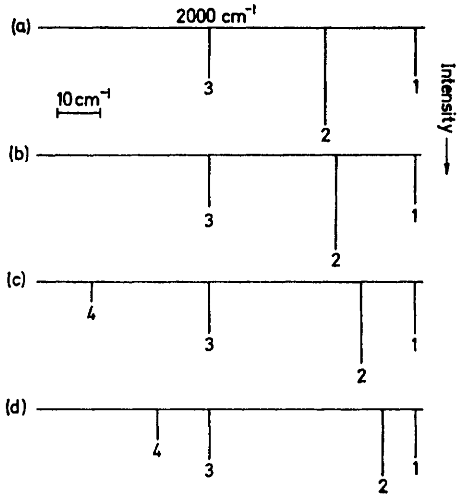

FIGURE 1 Calculated i.r. spectra for linear $C^{16}O$–$C^{18}O$ dicarbonyl species; (a) $R = 10$, (b) $R = 20$, (c) $R = 50$, and (d) $R = 100$

However, it can readily be shown that the symmetry co-ordinate for the B_2 vibration of, for example, $M(C^{16}O)(C^{18}O)_2$ is identical to that for one of the components of the E' vibration in $M(C^{18}O)_3$. Since the corresponding *G* matrix elements are also identical, it follows that the B_2 vibration in $M(C^{16}O)(C^{18}O)_2$ must, within the high frequency separation approximation, occur at *exactly* the same frequency as the E' mode in $M(C^{18}O)_3$. Similar considerations apply to the B_2 mode in $M(C^{16}O)_2(C^{18}O)$ which overlaps with the E' mode of $M(C^{16}O)_3$.

It is for this reason that one sees in Figure 2 a strong four-line spectrum in which the outer bands are more intense than the central pair. As in the case of the $C_{\infty v}$ dicarbonyl, the high-frequency symmetric modes in the

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[12] D. R. Bevis, personal communication.

[13] D. D. Oswald, personal communication.

TABLE 2

CO Vibration frequencies (ν) and i.r. intensities (I) for planar tricarbonyls $M(CO)_3$

			Force-constant ratios $R = K_{CO} : K_{CO,CO}$			
Molecule	Relative abundance *	Mode	$R = 10$ ν_k (I_k)	$R = 20$ ν_k (I_k)	$R = 50$ ν_k (I_k)	$R = 100$ ν_k (I_k)
$M(C^{16}O)_3$ D_{3h}	1	A_1'	2309·4(0·00)	2152·1(0·00)	2060·3(0·00)	2030·1(0·00)
		E'	2000·0(3·00)	2000·0(3·00)	2000·0(3·00)	2000·0(3·00)
$M(C^{16}O)_2(C^{18}O)$ C_{2v}	$3x$	B_2	2000·0(1·50)	2000·0(1·50)	2000·0(1·50)	2000·0(1·50)
		A_1	2292·7(0·01)	2138·1(0·03)	2050·2(0·11)	2023·2(0·22)
		A_1	1966·0(1·44)	1964·6(1·42)	1961·4(1·34)	1958·4(1·23)
$M(C^{16}O)C^{18}O)_2$ C_{2v}	$3x^2$	B_2	1951·8(1·43)	1951·8(1·43)	1951·8(1·43)	1951·8(1·43)
		A_1	2274·4(0·01)	2121·6(0·05)	2037·2(0·25)	2014·6(0·55)
		A_1	1981·9(1·46)	1979·9(1·43)	1974·0(1·23)	1966·8(0·93)
$M(C^{18}O)_3$ D_{3h}	x^3	A_1'	2253·7(0·00)	2100·2(0·00)	2010·7(0·00)	1981·2(0·00)
		E'	1951·8(2·86)	1951·8(2·86)	1951·8(2·86)	1951·8(2·86)

* For a $C^{16}O : C^{18}O$ ratio of 1 : x.

TABLE 3

CO Vibration frequencies (ν) and i.r. intensities (I) for tetrahedral carbonyls $M(CO)_4$

			Force-constant ratios $R = K_{CO} : K_{CO,CO}$			
Molecule	Relative abundance *	Mode	$R = 10$ ν_k (I_k)	$R = 20$ ν_k (I_k)	$R = 50$ ν_k (I_k)	$R = 100$ ν_k (I_k)
$M(C^{16}O)_4$ T_d	1	A_1	2403·7(0·00)	2200·5(0·00)	2080·0(0·00)	2040·0(0·00)
		T_2	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)
$M(C^{16}O)_3(C^{18}O)$ C_{3v}	$4x$	E	2000·0(2·67)	2000·0(2·67)	2000·0(2·67)	2000·0(2·67)
		A_1	2390·5(0·01)	2189·4(0·01)	2071·7(0·05)	2034·1(0·11)
		A_1	1962·6(1·28)	1961·7(1·27)	1959·7(1·23)	1957·5(1·17)
$M(C^{16}O)_2(C^{18}O)_2$ C_{2v}	$6x^2$	B_1	2000·0(1·33)	2000·0(1·33)	2000·0(1·33)	2000·0(1·33)
		B_2	1951·8(1·27)	1951·8(1·27)	1951·8(1·27)	1951·8(1·27)
		A_1	2376·5(0·01)	2177·1(0·02)	2062·0(0·11)	2027·0(0·25)
		A_1	1974·1(1·29)	1972·7(1·28)	1968·9(1·19)	1964·3(1·05)
$M(C^{16}O)(C^{18}O)_3$ C_{3v}	$4x^3$	E	1951·8(2·54)	1951·8(2·54)	1951·8(2·54)	1951·8(2·54)
		A_1	2361·7(0·01)	2163·4(0·02)	2049·8(0·15)	2018·0(0·45)
		A_1	1986·5(1·31)	1985·2(1·29)	1980·6(1·17)	1973·1(0·87)
$M(C^{18}O)_4$ T_d	x^4	A_1	2345·8(0·00)	2147·4(0·00)	2029·9(0·00)	1990·8(0·00)
		T_2	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)

* For a $C^{16}O : C^{18}O$ ratio of 1 : x.

TABLE 4

CO Vibration frequencies (ν) and i.r. intensities (I) for square planar tetracarbonyls $M(CO)_4$

			Force-constant ratios $K_{CO} : K_{cis} : K_{trans}$				
Molecule	Relative abundance *	Mode	20 : 1 : 2 ν_k (I_k)	50 : 1 : 2 ν_k (I_k)	100 : 1 : 2 ν_k (I_k)	50 : 1 : 4 ν_k (I_k)	50 : 1 : 1·33 ν_k (I_k)
$M(C^{16}O)_4$ D_{4h}	1	A_{1g}	2309·4(0·00)	2121·3(0·00)	2060·3(0·00)	2206·7(0·00)	2093·7(0·00)
		B_{2g}	2108·2(0·00)	2041·2(0·00)	2020·3(0·00)	2126·4(0·00)	2013·7(0·00)
		E_u	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)
$M(C^{16}O)_3(C^{18}O)$ C_{2v}	$4x$	B_2	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
		A_1	2297·3(0·01)	2112·1(0·03)	2053·5(0·06)	2196·5(0·01)	2085·0(0·04)
		A_1	2097·4(0·05)	2033·4(0·20)	2015·1(0·39)	2114·4(0·04)	2009·9(0·44)
		A_1	1972·1(1·90)	1967·8(1·73)	1963·4(1·50)	1972·0(1·90)	1963·5(1·47)
$M(C^{16}O)_2(C^{18}O)_2$ D_{2h}	$2x^2$	A_g	2285·1(0·00)	2103·0(0·00)	2047·3(0·00)	2187·9(0·00)	2075·6(0·00)
		A_g	2079·3(0·00)	2009·4(0·00)	1984·2(0·00)	2093·0(0·00)	1982·3(0·00)
		B_{1u}	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)
		B_{2u}	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
$M(C^{16}O)_2(C^{18}O)_2$ C_{2v}	$4x^2$	A_1	2283·8(0·02)	2100·7(0·08)	2044·2(0·24)	2183·2(0·03)	2074·6(0·13)
		A_1	1973·7(1·93)	1971·0(1·87)	1967·1(1·72)	1972·8(1·92)	1969·7(1·83)
		B_2	2088·2(0·10)	2028·0(0·37)	2012·2(0·62)	2105·6(0·08)	2007·8(0·74)
		B_2	1970·4(1·85)	1964·5(1·58)	1959·7(1·33)	1971·1(1·87)	1957·5(1·22)
$M(C^{16}O)(C^{18}O)_3$ C_{2v}	$4x^3$	B_2	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)
		A_1	2269·8(0·01)	2088·5(0·07)	2034·7(0·26)	2171·1(0·03)	2062·4(0·11)
		A_1	2071·9(0·06)	2007·9(0·26)	1986·5(0·41)	2087·7(0·03)	1987·3(0·79)
		A_1	1971·9(1·88)	1966·8(1·63)	1961·6(1·28)	1971·9(1·89)	1959·3(1·05)
$M(C^{18}O)_4$ D_{4h}	x^4	A_{1g}	2253·7(0·00)	2070·2(0·00)	2010·7(0·00)	2153·5(0·00)	2043·2(0·00)
		B_{2g}	2057·4(0·00)	1992·0(0·00)	1971·6(0·00)	2075·2(0·00)	1965·1(0·00)
		E_u	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)

* For a $C^{16}O : C^{18}O$ ratio of 1 : x.

isotopically mixed molecules only gain significant intensity at high R values. The maximum number of distinct bands which can be observed is six, and these are identified as follows: (1) overlap of B_2 $M(C^{16}O)(C^{18}O)_2$ and E' $M(C^{18}O)_3$, (2) A_1 $M(C^{16}O)_2(C^{18}O)$, (3) A_1 $M(C^{16}O)(C^{18}O)_2$, (4) overlap of B_2 $M(C^{16}O)_2(C^{18}O)$ and E' $M(C^{16}O)_3$, (5) A_1 $M(C^{16}O)(C^{18}O)_2$, and (6) A_1 $M(C^{16}O)_2(C^{18}O)$.

Tetracarbonyls (*Tables* 3 *and* 4).—Both tetrahedral (T_d) and square planar (D_{4h}) tetracarbonyls give rise to only one i.r.-active CO stretching mode. However, apart from some very recent evidence[14] that $V(CO)_4$ and $Cr(CO)_4$ may be square planar, simple binary carbonyl species with this stoicheiometry [*e.g.*, $Ni(CO)_4$, $Co(CO)_4^-$] are usually found to be tetrahedral.

A large number of studies have been carried out on $Ni(CO)_4$ by use of both ^{13}C and ^{18}O enrichment,[15] and in particular, Day *et al.*[16] have observed and assigned the frequency pattern which is produced for a mixture of the molecules $Ni(C^{16}O)_4$, $Ni(C^{16}O)_3(C^{18}O)$, $Ni(C^{16}O)_2(C^{18}O)_2$, $Ni(C^{16}O)(C^{18}O)_3$, and $Ni(C^{18}O)_4$. The i.r.-active CO stretching mode in $Ni(C^{16}O)_4$ has T_2 symmetry, and this three-fold degeneracy is removed in the isotopically mixed species. Once again, however, there is band overlap as a result of identical F and G matrix elements,[9] and the effect of this is to produce a characteristic five-line pattern (Figure 3) in which the outer bands are significantly more intense than the central triplet. This pattern is produced for a wide range of ratios R, and is only modified at high values of R by the appearance of the high-frequency symmetric modes of the isotopically mixed species. The maximum number of distinct bands is now eight, and these are identified as follows: (1) overlap of T_2 $M(C^{18}O)_4$, E $M(C^{16}O)(C^{18}O)_3$, and B_2 $M(C^{16}O)_2(C^{18}O)_2$, (2) A_1 $M(C^{16}O)_3(C^{18}O)$, (3) A_1 $M(C^{16}O)_2(C^{18}O)_2$, (4) A_1 $M(C^{16}O)(C^{18}O)_3$, (5) overlap of T_2 $M(C^{16}O)_4$, E $M(C^{16}O)_3(C^{18}O)$, and B_1 $M(C^{16}O)_2(C^{18}O)_2$ (6) A_1 $M(C^{16}O)(C^{18}O)_3$, (7) A_1 $M(C^{16}O)_2(C^{18}O)_2$, and (8) A_1 $M(C^{16}O)_3(C^{18}O)$.

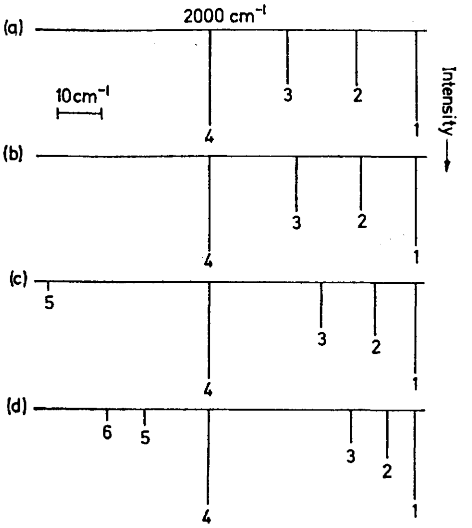

FIGURE 2 Calculated i.r. spectra for planar $C^{16}O-C^{18}O$ tricarbonyl species; (a) $R = 10$, (b) $R = 20$, (c) $R = 50$, and (d) $R = 100$

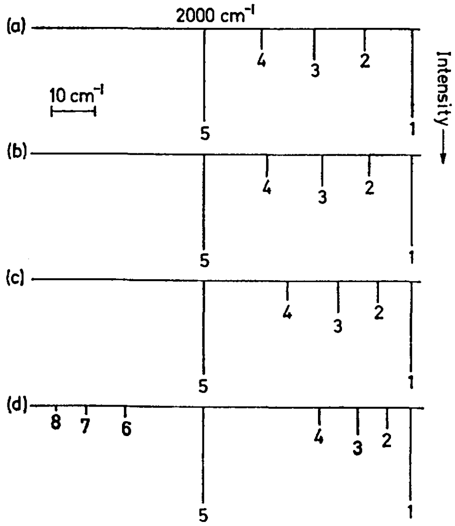

FIGURE 3 Calculated i.r. spectra for tetrahedral $C^{16}O-C^{18}O$ carbonyl species; (a) $R = 10$, (b) $R = 20$, (c) $R = 50$, and (d) $R = 100$

It is noteworthy that the new species $Pd(CO)_4$ was first shown to be tetrahedral[17] by use of this technique.

Figure 4 shows corresponding spectra calculated for square planar molecules. Here, a 1 : 1 ratio of $C^{16}O : C^{18}O$ in the metal atom synthesis would lead to six molecular species: $M(C^{16}O)_4$ (D_{4h}), $M(C^{16}O)_3(C^{18}O)$

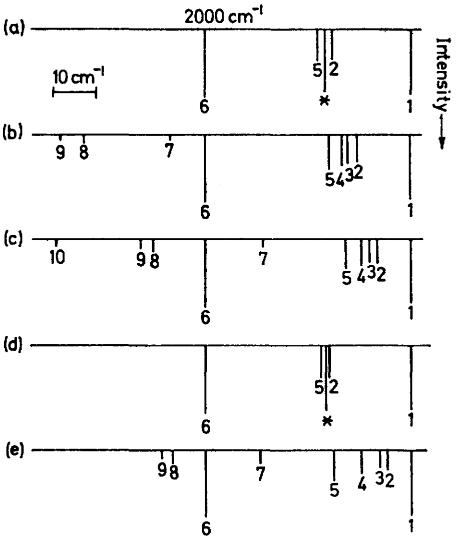

FIGURE 4 Calculated i.r. spectra for square planar $C^{16}O-C^{18}O$ tetracarbonyls in which the ratios $K_{CO} : K_{cis} : K_{trans}$ are (a) 20 : 1 : 2, (b) 50 : 1 : 2, (c) 100 : 1 : 2, (d) 50 : 1 : 4, and (e) 50 : 1 : 1·33. * Accidental overlap of bands 3 and 4

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(C_{2v}), *trans*-$M(C^{16}O)_2(C^{18}O)_2$ (D_{2h}), *cis*-$M(C^{16}O)_2(C^{18}O)_2$ (C_{2v}), $M(C^{16}O)(C^{18}O)_3$ (C_{2v}), and $M(C^{18}O)_4$ (D_{4h}) with statistical weights 1 : 4 : 2 : 4 : 4 : 1 respectively. Two interaction constants K_{cis} and K_{trans} are now employed in the Cotton–Kraihanzel force field, and it is clearly not practicable to consider the large number of permutations of the ratios $K_{CO} : K_{cis} : K_{trans}$. It is found experimentally [8] that in molecules of the general formula *trans*-$M(CO)_4L_2$ the ratio $K_{cis} : K_{trans}$ is very close to the expected ratio [10] of 1 : 2, and we have therefore displayed three spectra [Figure 4(a)—(c)] calculated for a range of ratios $K_{CO} : K_{cis}$ whilst maintaining $K_{cis} : K_{trans}$ at 1 : 2. The remaining two spectra show the effect of varying $K_{cis} : K_{trans}$ at a constant $K_{CO} : K_{cis}$ ratio of 50 : 1.

TABLE 5

CO Vibration frequencies (ν) and i.r. intensities (I) for octahedral carbonyls $M(CO)_6$

Molecule	Relative abundance *	Mode	Force-constant ratios $K_{CO} : K_{cis} : K_{trans}$				
			20 : 1 : 2	50 : 1 : 2	100 : 1 : 2	50 : 1 : 4	50 : 1 : 1·33
			ν_k (I_k)	ν_k (I_k)	ν_k (I_k)	ν_k (I_k)	ν_k (I_k)
$M(C^{16}O)_6$ O_h	1	A_{1g}	2403·7(0·00)	2160·2(0·00)	2080·0(0·00)	2245·8(0·00)	2132·6(0·00)
		E_g	2108·2(0·00)	2041·2(0·00)	2020·3(0·00)	2126·4(0·00)	2013·7(0·00)
		T_{1u}	2000·0(6·00)	2000·0(6·00)	2000·0(6·00)	2000·0(6·00)	2000·0(6·00)
$M(C^{16}O)_5(C^{18}O)$ C_{4v}	$6x$	B_1	2108·2(0·00)	2041·2(0·00)	2020·3(0·00)	2126·4(0·00)	2013·7(0·00)
		E	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)
		A_1	2395·1(0·00)	2153·6(0·01)	2074·9(0·03)	2238·6(0·01)	2126·2(0·02)
		A_1	2094·4(0·06)	2031·6(0·25)	2014·0(0·46)	2111·6(0·05)	2009·1(0·54)
		A_1	1971·8(1·88)	1967·1(1·69)	1962·7(1·46)	1971·9(1·89)	1962·1(1·39)
$M(C^{16}O)_4(C^{18}O)_2$ C_2	$12x^2$	B_2	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
		B_1	2088·2(0·10)	2028·0(0·37)	2012·2(0·62)	2105·6(0·08)	2007·8(0·74)
		B_1	1970·4(1·85)	1964·5(1·58)	1959·7(1·33)	1971·1(1·87)	1957·5(1·22)
		A_1	2386·0(0·01)	2146·3(0·03)	2069·0(0·07)	2230·6(0·01)	2119·2(0·04)
		A_1	2101·0(0·03)	2035·9(0·13)	2016·6(0·26)	2118·4(0·03)	2011·0(0·30)
		A_1	1973·0(1·91)	1969·7(1·80)	1965·8(1·62)	1972·6(1·91)	1966·7(1·62)
$M(C^{16}O)_4(C^{18}O)_2$ D_{4h}	$3x^2$	E_u	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)	2000·0(4·00)
		B_{1g}	2108·2(0·00)	2041·2(0·00)	2020·3(0·00)	2126·4(0·00)	2013·7(0·00)
		A_{2u}	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)
		A_{1g}	2386·5(0·00)	2147·0(0·00)	2070·0(0·00)	2232·1(0·00)	2119·5(0·00)
		A_{1g}	2072·2(0·00)	2004·3(0·00)	1981·2(0·00)	2087·9(0·00)	1977·3(0·00)
$M(C^{16}O)_3(C^{18}O)_3$ C_{3v}	$8x^3$	A_1	2376·5(0·01)	2138·1(0·05)	2062·0(0·16)	2221·4(0·03)	2111·5(0·07)
		A_1	1974·1(1·94)	1972·0(1·90)	1968·9(1·79)	1973·2(1·93)	1971·3(1·88)
		E	2088·2(0·20)	2028·0(0·74)	2012·2(1·25)	2105·6(0·16)	2007·8(1·47)
		E	1970·4(3·70)	1964·5(3·17)	1959·7(2·66)	1971·1(3·75)	1957·5(2·43)
$M(C^{16}O)_3(C^{18}O)_3$ C_{2v}	$12x^3$	B_1	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)
		B_2	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
		A_1	2377·0(0·00)	2139·0(0·02)	2063·3(0·05)	2223·4(0·01)	2111·8(0·02)
		A_1	1971·6(1·88)	1966·4(1·62)	1961·4(1·30)	1971·8(1·89)	1959·2(1·08)
		A_1	2098·6(0·04)	2034·0(0·17)	2015·3(0·36)	2115·7(0·03)	1980·5(0·44)
		A_1	2069·0(0·03)	2004·0(0·14)	1982·8(0·25)	2085·3(0·02)	2010·1(0·41)
$M(C^{16}O)_2(C^{18}O)_4$ C_{2v}	$12x^4$	B_2	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)	1951·8(1·90)
		B_1	2088·2(0·10)	2028·0(0·37)	2012·2(0·62)	2105·6(0·08)	2007·8(0·74)
		B_1	1970·4(1·85)	1964·5(1·58)	1959·7(1·33)	1971·1(1·87)	1957·5(1·22)
		A_1	2366·9(0·01)	2129·7(0·04)	2054·9(0·16)	2213·0(0·02)	2103·1(0·06)
		A_1	2067·2(0·04)	2003·7(0·25)	1984·5(0·56)	2083·9(0·03)	1984·0(0·96)
		A_1	1972·7(1·90)	1968·2(1·65)	1962·9(1·24)	1972·5(1·91)	1960·3(0·93)
$M(C^{16}O)_2(C^{18}O)_4$ D_{4h}	$3x^4$	E_u	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)
		B_{1g}	2057·4(0·00)	1992·0(0·00)	1971·6(0·00)	2075·2(0·00)	1965·1(0·00)
		A_{2u}	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)	2000·0(2·00)
		A_{1g}	2367·5(0·00)	2130·9(0·00)	2056·9(0·00)	2215·5(0·00)	2103·6(0·00)
		A_{1g}	2088·9(0·00)	2019·5(0·00)	1993·8(0·00)	2103·5(0·00)	1992·0(0·00)
$M(C^{16}O)(C^{18}O)_5$ C_{4v}	$6x^5$	B_1	2057·4(0·00)	1992·0(0·00)	1971·6(0·00)	2075·2(0·00)	1965·1(0·00)
		E	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)	1951·8(3·81)
		A_1	2356·7(0·00)	2120·1(0·03)	2045·8(0·15)	2203·4(0·01)	2093·4(0·04)
		A_1	2077·4(0·08)	2015·1(0·32)	1995·3(0·52)	2093·7(0·05)	1995·0(0·80)
		A_1	1971·5(1·87)	1966·0(1·60)	1960·9(1·28)	1971·8(1·89)	1958·6(1·11)
$M(C^{18}O)_6$ O_h	x^6	A_{1g}	2345·8(0·00)	2108·2(0·00)	2029·9(0·00)	2191·7(0·00)	2081·2(0·00)
		E_g	2057·4(0·00)	1992·0(0·00)	1971·6(0·00)	2075·2(0·00)	1965·1(0·00)
		T_{1u}	1951·8(5·71)	1951·8(5·71)	1951·8(5·71)	1951·8(5·71)	1951·8(5·71)

* For a $C^{16}O : C^{18}O$ ratio of $1 : x$.

As indicated in the assignment below, the two most prominent bands in the spectrum owe their enhanced intensity to exact band overlap, but in addition one finds that for certain force-constant ratios a number of closely spaced bands are expected. Band widths in matrix-isolation i.r. studies are typically *ca.* 0·5—2·0 cm^{-1}, and in those cases where the calculated band separations are less than 0·5 cm^{-1}, they are drawn superposed as it is unlikely that they would be resolved experimentally. It is interesting to note that the pattern calculated for $K_{CO} : K_{cis} : K_{trans} = 50 : 1 : 4$ is very similar to that obtained for the ratios 20 : 1 : 2, and that the pattern for 50 : 1 : 1·33 resembles that for 100 : 1 : 2. This suggests that the patterns displayed in

Figure 4(a)—(c) may typify spectra for a wide range of $K_{CO} : K_{cis} : K_{trans}$ ratios. The detailed band assignment is: (1) overlap of E_u $M(C^{18}O)_4$, B_{1u} *trans*-$M(C^{16}O)_2(C^{18}O)_2$, and B_2 $M(C^{16}O)(C^{18}O)_3$, (2) B_2 *cis*-$M(C^{16}O)_2(C^{18}O)_2$, (3) A_1 $M(C^{16}O)(C^{18}O)_3$, (4) A_1 $M(C^{16}O)_3(C^{18}O)$, (5) A_1 *cis*-$M(C^{16}O)_2(C^{18}O)_2$, (6) overlap of E_u $M(C^{16}O)_4$, B_{2u} *trans*-$M(C^{16}O)_2(C^{18}O)_2$, and B_2 $M(C^{16}O)_3(C^{18}O)$, (7) A_1 $M(C^{16}O)(C^{18}O)_3$, (8) B_2 *cis*-$M(C^{16}O)_2(C^{18}O)_2$, (9) A_1 $M(C^{16}O)_3(C^{18}O)$, and (10) A_1 $M(C^{16}O)(C^{18}O)_3$. Two bands remain which are not shown in Figure 4 as their intensities are very low. These are the high-frequency A_1 modes in $M(C^{16}O)_3(C^{18}O)$ and *cis*-$M(C^{16}O)_2(C^{18}O)_2$.

Hexacarbonyls (*Table* 5).—Ten hexacarbonyl species would be produced in the mixed $C^{16}O$–$C^{18}O$ synthesis. These are $M(C^{16}O)_6$ (O_h), $M(C^{16}O)_5(C^{18}O)$ (C_{4v}), *cis*-$M(C^{16}O)_4(C^{18}O)_2$ (C_{2v}), *trans*-$M(C^{16}O)_4(C^{18}O)_2$ (D_{4h}), *sym*-$M(C^{16}O)_3(C^{18}O)_3$ (C_{3v}), *asym*-$M(C^{16}O)_3(C^{18}O)_3$ (C_{2v}), *cis*-$M(C^{16}O)_2(C^{18}O)_4$ (C_{2v}), *trans*-$M(C^{16}O)_2(C^{18}O)_4$ (D_{4h}), $M(C^{16}O)(C^{18}O)_5$ (C_{4v}), and $M(C^{18}O)_6$ (O_h). These are more conveniently referred to as species H_1—H_{10} respectively, and for a $C^{16}O : C^{18}O$ ratio of 1 : 1, they are produced in the proportions 1 : 6 : 12 : 3 : 8 : 12 : 12 : 3 : 6 : 1.

Figure 5 shows a series of spectra calculated for a range of force-constant ratios. As in the previous case, three spectra are shown in which the ratio $K_{cis} : K_{trans}$ is 1 : 2. The stable carbonyls $Cr(CO)_6$ and $Mo(CO)_6$ both have force-constant ratios $K_{CO} : K_{cis} : K_{trans}$ very close [8] to 60 : 1 : 2, and if these ratios are typical for hexacarbonyls in general, it should be possible to characterise the recently detected [2,3] $Ta(CO)_6$ and $U(CO)_6$ by reference, for example, to Figure 5(b). The detailed band assignment is: (1) overlap of T_{1u} H_{10}, E H_9, E_u H_8, B_2 H_7, B_1 H_6, and A_{2u} H_4, (2) overlap of B_1 H_7, E H_5, and B_1 H_3, (3) A_1 H_9, (4) A_1 H_6, (5) A_1 H_2, (6) A_1 H_7, (7) A_1 H_3, (8) A_1 H_5, (9) overlap of T_{1u} H_1, E H_2, B_2 H_3, E_u H_4, B_2 H_6, and A_{2u} H_8, (10) A_1 H_7, (11) overlap of B_1 H_7, E H_5, and B_1 H_3, (12) A_1 H_6, (13) A_1 H_9, (14) A_1 H_2, (15) A_1 H_6, (16) A_1 H_3. In addition to these bands, each of the species H_2, H_3, H_5, H_6, H_7, and H_9 has one A_1 mode of very low intensity and these bands have not been included in the Figures.

Conclusions.—Several important features emerge from these calculations, and can be summarised as follows: (i) The spectral features which characterise the six molecular species considered here usually lie entirely between the i.r.-active fundamental of $M(C^{16}O)_n$ and the corresponding band in $M(C^{18}O)_n$. This represents a frequency range of *ca.* 50 cm^{-1} for a species absorbing near 2000 cm^{-1}. The only exceptions to this occur when there is significant intensity borrowing by high-frequency vibrations, and this becomes important when interaction constants are very small. (ii) Only dicarbonyls produce a strong central band. (iii) Planar tricarbonyls and tetrahedral tetracarbonyls give very characteristic four- and five-line patterns respectively. These are quite unambiguous, and would be well resolved in virtually any matrix. (iv) Under conditions of poor resolution, the distinction between a square planar tetracarbonyl and a hexacarbonyl would not be very clear. However, the hexacarbonyl would always give a strongly asymmetric pattern of overlapping bands in the centre, whereas the centre of the tetracarbonyl pattern would be symmetrical and relatively weaker. In the event of poor resolution, characterisation would be assisted by varying the $C^{16}O : C^{18}O$ ratio and thus altering the relative proportions of the isotopically mixed molecules. (v) Although the calculations have been carried out for $C^{16}O$–$C^{18}O$ molecules, the patterns are equally valid for ^{13}CO–^{12}CO carbonyls, and quite generally for *any* new molecule produced by the reaction of metal atoms with a mixture of isotopically different ligands L–L′, provided that the high-frequency separation approximation is valid.

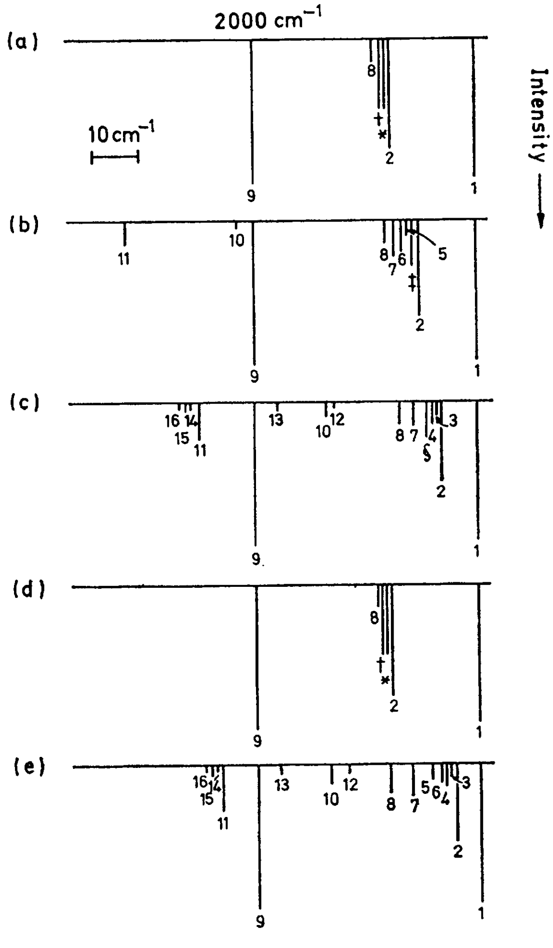

FIGURE 5 Calculated i.r. spectra for octahedral $C^{16}O$–$C^{18}O$ hexacarbonyls in which the ratios $K_{CO} : K_{cis} : K_{trans}$ are (a) 20 : 1 : 2, (b) 50 : 1 : 2, (c) 100 : 1 : 2, (d) 50 : 1 : 4, and (e) 50 : 1 : 1·33. Accidental overlap of bands * 3, 4, and 5; † 6 and 7; ‡ 3 and 4; § 5 and 6

One additional point may also be made in connection with the use of these results. When one synthesises new metal carbonyls by use of the matrix-isolation technique, one often produces several different molecular species, and the resultant bands often lie within rather a narrow frequency range, *e.g.*, 50—100 cm^{-1}. It is then quite probable that considerable band overlap will occur when using either ^{13}C or ^{18}O enrichment, and this can make spectral identification on the basis of frequency position impossible. In this event it is a considerable advantage to know relative band intensities.

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