Contribution from the School of Chemical Sciences,
University of East Anglia, Norwich NR4 7TJ, England

Solid-State Studies. 8. Raman Spectra of Mixed Crystals of Transition Metal Hexacarbonyls[1]

DAVID A. KARIUKI and SIDNEY F. A. KETTLE*

Received January 14, 1977

In mixed crystals derived from $M(CO)_6$ (M = Cr, Mo, W) and for $Mo(^{13}CO)_x(^{12}CO)_{6-x}$ the Raman spectra in the molecular ν(CO) A_{1g}-derived region show features corresponding to the individual components while in the E_g-derived region the spectrum is clearly similar to that of a pure component but the frequencies observed are composition-sensitive. It is concluded that intermolecular vibrational coupling occurs for the latter but not the former modes.

It is now recognized that the interpretation of the vibrational spectra of crystalline metal carbonyls and their derivatives in the 2000-cm^{-1} region requires the use of a factor group model. This model is appropriate whenever there is appreciable coupling between similar vibrators in different molecules (or ions) within a crystal lattice. In this situation the vibrators lose their individuality and what is observed is a collective, translationally in-phase (k = 0) mode of these vibrators. However, this interpretation gives rise to an apparent problem and it is the resolution of this problem which forms the motivation of the present and subsequent papers in this series.

The problem arises as a consequence of the presence of approximately 1% of ^{13}CO vibrators in metal carbonyls. In solution studies weak peaks associated with the presence of these vibrators are usually clearly resolved and may be used to provide additional data for vibrational analyses. It seems reasonable, then, that analogous weak peaks in crystalline samples should be similarly assigned. But if the observed spectral features correspond to *collective* vibrational modes one would expect no separate ^{13}CO features. Alternatively, if the zeroth-order frequency difference of the ^{13}CO vibrators is sufficient to completely uncouple them, then one would expect their spectral position to bear little relationship to those of modes of the, vibrationally coupled, majority of the ^{12}CO vibrators. Indeed, there would be no reason at all to expect that there should be a 1:1 correspondence between the *number* of factor group ^{12}CO components and the number of (effectively isolated) ^{13}CO modes, let alone any evident correspondence of frequencies. In contrast, the assignment—albeit, usually tentatively—of weak peaks in the vibrational spectra of crystalline metal carbonyl derivatives as ^{13}CO features has usually been made with an implicit assumption of a 1:1 correspondence between them and ^{12}CO factor group modes, even though all the isotopic peaks required by such a correspondence may not have been observed.

The most evident way of clarifying this situation is to prepare crystalline metal carbonyls with varying degrees of ^{13}CO enrichment and to correlate this enrichment with changes in the corresponding spectra. We report such studies in the present paper. However, we preceded these studies by a more general study of the vibrational coupling between chemically different species present in the same lattice and we report these studies as a prelude to our ^{13}CO results. Specifically, the present paper is devoted to hexacarbonyl species (Cr, Mo, $W(CO)_6$ and $Mo(^{12}CO)_n(^{13}CO)_{6-n}$). The phenomena observed are rather simpler than those found for some of the other systems which we shall describe in subsequent publications. Unfortunately, the infrared spectra (KBr disk) of the crystalline hexacarbonyls in the 2000-cm^{-1} region consist of one broad band with a shoulder on either side. Attempts to resolve this band by recording the spectra at low temperatures (−196 °C) and using different alkali halides for making the disks, or grinding for longer periods, all proved unsuccessful. Fortunately, the Raman spectra in this region show quite sharp peaks. In the present study we have therefore concentrated our attention on these spectra. Figures 1–3 show the Raman spectra of crystalline $Cr(CO)_6$ (that of $Mo(CO)_6$ is given in Figure 5; that of $W(CO)_6$ is also very similar but with peak positions differing by a few wavenumbers), of a crudely ground 1:1 mixture of $Cr(CO)_6$ and $W(CO)_6$, and of a mixed crystal of the same composition after repeated vacuum sublimation. It is evident from Figure 3 that in the mixed crystal the distinction between pure Cr- and pure W-containing vibrators in the 2000 ± 40-cm^{-1} region is lost. A detailed study of the behavior of the peaks in this region reveals that the band shape is unchanged with change of x in $Cr_xW_{1-x}(CO)_6$ but the peak positions all vary smoothly with x (Table III). Concomitant x-ray studies showed a smooth variation of unit-cell parameters with x. Before giving our explanation of these and related phenomena it is appropriate to first review the vibrational properties of these hexacarbonyls.

There is a considerable body of work reported in the literature on the infrared and Raman spectra of the metal hexacarbonyls of chromium, molybdenum, and tungsten. Of particular importance for the present work is the Adams et al.[2] recent report and detailed assignment of the single-crystal Raman spectra of the three hexacarbonyls.

The molecular symmetry of these $M(CO)_6$ complexes is O_h and the 33 normal vibrations belong to the species $2A_{1g} + 2E_g + 4T_{1u} + 2T_{2g} + T_{1g} + 2T_{2u}$. These normal vibrations can be approximately described as follows: carbon stretching (ν_{CO}) modes ($A_{1g} + E_g + T_{1u}$), metal–carbon stretching (ν_{MC}) modes ($A_{1g} + E_g + T_{1u}$), metal–carbon–oxygen bending (δ_{MCO}) modes ($T_{1g} + T_{2g} + T_{1u} + T_{2u}$), carbon–metal–carbon bending (δ_{CMC}) modes ($T_{1u} + T_{2g} + T_{2u}$). With the exception of the T_{1g} and T_{2u} modes all species are active either in the infrared or Raman spectra.

In solution, the carbonyl stretching modes (ν_{CO}) yield two Raman-active ($A_{1g} + E_g$) and one infrared-active (T_{1u}) bands. It is to be noted that the frequency corresponding to the totally symmetric A_{1g} mode is well separated from the E_g and T_{1u} frequencies. This is because there is a strong interaction between the individual CO vibrators in an individual molecule. It is the existence of corresponding intermolecular interactions which give rise to the additional splittings observed in the solid-state vibrational spectra of these compounds and which necessitate the factor group method of analysis.

Crystallographic studies of the metal hexacarbonyls have indicated that all three crystallize in the orthohombic space group *Pnma* (D_{2h}^{16}) with four molecules per unit cell (Z = 4).[3] The octahedral (O_h) symmetry of the free molecule is retained to a very good approximation in the crystal although the four molecules lie on mirror planes and hence have a site symmetry of C_S.

As shown in Table I, a site group analysis predicts that the degeneracies of the T_{1u} and of the E_g modes should be lifted.

0020-1669/78/1317-0141$01.00/0

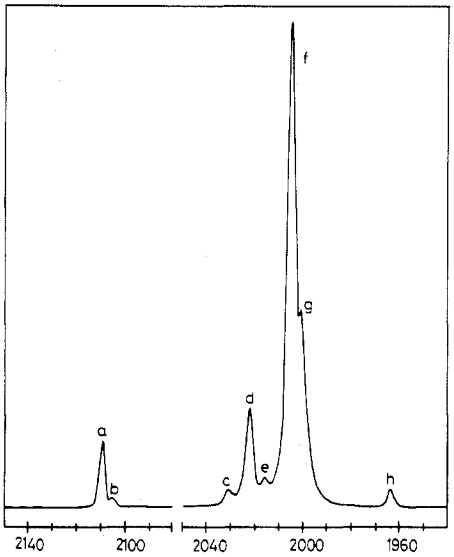
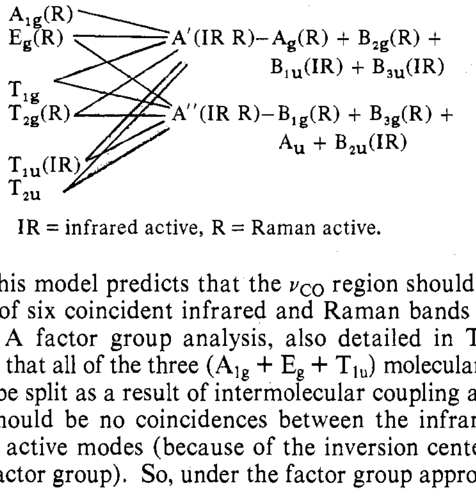


Figure 1. The room temperature Raman spectrum of polycrystalline $Cr(CO)_6$ in the 2000-cm^{-1} region.

Table I. Correlation Table for $M(CO)_6$ (M = Cr, Mo, W)[a]

Molecular symmetry O_h	Site group symmetry C_s	Factor group symmetry D_{2h}^{16} ($Z = 4$)



[a] Key: IR = infrared active, R = Raman active.

Thus, this model predicts that the ν_{CO} region should consist in toto of six coincident infrared and Raman bands (4A′ + 2A″). A factor group analysis, also detailed in Table I, predicts that all of the three (A_{1g} + E_g + T_{1u}) molecular modes should be split as a result of intermolecular coupling and that there should be no coincidences between the infrared and Raman active modes (because of the inversion center coset in the factor group). So, under the factor group approach the nondegenerate A_{1g} mode should generate two Raman (A_g + B_{2g}) and two infrared (B_{1u} + B_{3u}) active modes. The E_g mode should give rise to four Raman (A_g + B_{1g} + B_{2g} + B_{3g}) and three infrared (B_{1u} + B_{3u} + B_{2u}) active modes. Likewise, the T_{1u} molecular mode should give rise to six Raman ($2A_g$ + $2B_{2g}$ + B_{1g} + B_{3g}) and five infrared ($2B_{1u}$ + $2B_{3u}$ + B_{2u}) active modes. However, some of the vibrations which are formally predicted to be active may have very low or even zero intensities.

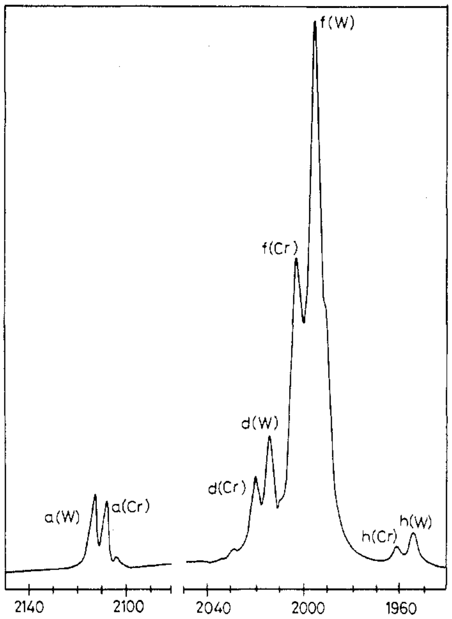


Figure 2. The room temperature Raman spectra of a 1:1 coarsely ground mixture of polycrystalline $Cr(CO)_6$ and $W(CO)_6$ in the 2000-cm^{-1} region.

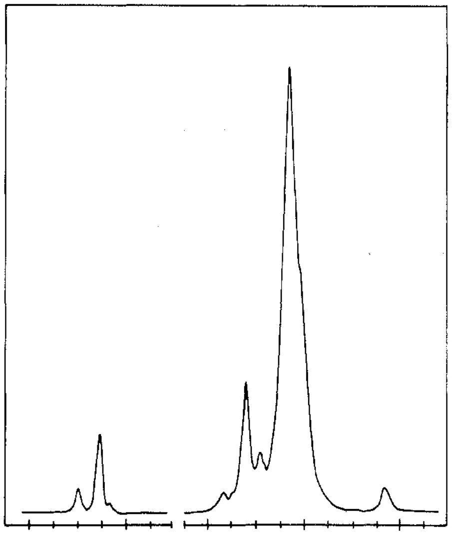


Figure 3. The liquid nitrogen Raman spectra of a sublimed 1:1 mixture of $Cr(CO)_6$ and $W(CO)_6$ in the 2000-cm^{-1} region.

This is most clearly seen for the case of the (molecular) A_{1g}-derived modes. Since, in the crystal, each molecule retains its octahedral shape to a very good approximation, each molecular contribution to a crystal mode will be, essentially, a zero derived dipole vector and a spherical derived polarizability tensor. It follows that the A_{1g}-derived crystal B_{1u} and

Table II. Assignment of Modes in the 2000-cm^{-1} Region of the Raman Spectra of Crystalline Hexacarbonyl Species[a]

Symmetry	Assignment	Design	Freq (rel intens)		
			$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
A_g	Factor fundamental	a	2110 (14)	2114 (18)	2116 (18)
A	^{13}CO of a	b	2105 (2)	2111 (4)	2111 (3)
B_{1g}	?^{13}CO	c	2032 (3)	2033 (3)	2029 (2)
B_{3g}	Factor fundamental	d	2023 (20)	2023 (21)	2018 (21)
B_{2g}	?^{13}CO	e	2016 (?, w)	2018 (?, w)	2013 (?, w)
B_{2g} B_{1g}	Factor fundamental Factor fundamental	f	2006 (100)	2006 (100)	1999 (100)
A_g	Factor fundamental	g	2002 (?, sh)	2002 (?, sh)	1995 (?, sh)
B_{3g}	?^{13}CO	h	1964 (4)	1966 (4)	1957 (4)

[a] Data from present work, assignments from ref 2, modified to remove inconsistencies (D. M. Adams, personal communication).

Table III. $Cr_xW_{1-x}(CO)_6$ Mixed Crystal Raman Frequencies (cm^{-1}) $\nu(CO)$ Region

Sample	a(W)	a(Cr) + b(w)	b(Cr)	c	d	e	f	g	h	Approx x value
$W(CO)_6$	2116 (17.6)	2111 (3.4)		2029	2018 (21.1)	2013	1999 (100)	1995	1957	0.0
1	2115 (17.0)	2110 (4.7)		2029	2016 (22.6)	2012	1998 (100)	1994	1957	0.05
2	2116 (15.1)	2111 (4.5)		2029	2018 (23.0)	2013	1999 (100)	1995	1957	0.10
3	2117 (15.3)	2111 (6.6)		2030	2019 (22.0)	2014	1999 (100)	1996	1959	0.17
4	2116 (14.9)	2111 (7.4)	2105	2030	2019 (22.8)	2014	2000 (100)	1996	1959	0.22
5	2117 (14.7)	2111 (8.4)		2030	2018 (22.8)	2014	2000 (100)	1996	1958	0.33
6	2117 (12.8)	2111 (13.4)	2105	2031	2020 (26.0)	2015	2001 (100)	1996	1960	0.42
7	2117 (9.8)	2110 (12.3)	2104	2030	2020 (26.8)	2017	2002 (100)	1996	1961	0.45
8	2118 (9.7)	2111 (17.8)	2106	2031	2021 (29.1)	2016	2003 (100)		1962	0.48
8[a]	2120	2112	2108	2033	2023	2017	2003	1998	1961	0.48
9	2119 (8.3)	2111 (19.5)	2107	2032	2022 (28.9)	2016	2005 (100)		1964	0.62
10	2118 (7.3)	2110 (20.3)	2106	2030	2022 (28.6)	2016	2005 (100)		1963	0.66
11	2118 (7.7)	2111 (20.9)	2106	2031	2021 (30.4)	2016	2004 (100)	1996	1963	0.63
12	2119 (6.6)	2111 (18.8)	2107	2032	2022 (29.6)	2016	2005 (100)		1964	0.72
13	2118 (5.1)	2111 (17.2)	2107	2032	2022 (29.6)	2017	2005 (100)	2000	1965	0.75
14	2118 (3.4)	2110 (16.9)	2104	2032	2023 (26.5)	2017	2006 (100)	2001	1965	0.83
15	2120 (1.8)	2111 (16.9)	2107	2033	2024 (27.8)	2017	2006 (100)	2001	1965	0.90
16	2120 (0.5)	2110 (14.9)	2107	2033	2023 (24.0)	2017	2006 (100)	2002	1965	0.95
17		2110 (17.6)	2105	2033	2024 (23.4)	2018	2007 (100)	2002	1965	0.98
$Cr(CO)_6$		2110 (14.4)	2105 (2.0)	2032	2023 (20.3)	2016	2006 (100)	2002	1964	1.0

[a] Recorded at liquid nitrogen temperature. Figures in parentheses in this and following tables indicate band heights based on 100 for the strongest band (f).

Table IV. Mixed Crystal Raman Frequencies (cm^{-1}), for $Cr_xMo_{1-x}(CO)_6$ in the $\nu(CO)$ Region

Sample	a(Mo)	a(Cr) + b(Mo)	b(Cr)	c	d	e	f	g	h	Approx x value
1	2114 (12.2)	2109 (8.5)		2031	2021 (22.0)	2016	2005 (100)	2001	1964	0.3
1[a]	2117 (10.2)	2112 (13.6)	2106	2034	2023 (20.6)	2017	2005 (100)	2000	1964	0.5
2	2115 (4.7)	2109 (8.5)		2030	2021 (20.5)	2015	2005 (100)	1999	1964	0.6
3	2115 (4.7)	2109 (11.8)	2106	2030	2022 (20.2)	2015	2005 (100)	2001	1964	0.7
4	2115 (3.6)	2109 (13.3)	2107	2029	2021 (18.2)	2014	2004 (100)	2000	1963	0.8

[a] Recorded at liquid nitrogen temperatures.

Table V. Mixed Crystal Raman Frequencies (cm^{-1}) for $Mo_xW_{1-x}(CO)_6$ in the $\nu(CO)$ Region

	a		b	c	d	e	f	g	h	Approx x value
1	2117	2114 (16.6)	2110	2030	2019 (22.1)	2014	2000 (100)		1959	0.2
2		2115 (19.2)	2111	2029	2019 (21.3)	2012	2000 (100)		1962	0.3
3		2115 (18.3)	2109	2030	2020 (22.5)	2014	2002 (100)	1997	1962	0.4
4	2118	2113 (23.0)	2110	2030	2020 (27.5)	2015	2002 (100)		1962	0.5
4[a]	2120	2116	2112	2032	2022	2017	2001	1998	1960	0.6
5	2120	2115 (20.6)	2110	2031	2022 (23.0)	2016	2003 (100)	1999	1964	0.7
6		2114 (20.4)	2110	2031	2021 (21.4)	2016	2003 (100)		1963	0.8

[a] Recorded at liquid nitrogen temperatures.

B_{3u} modes, although formally allowed in the infrared, will have very little strength. Similarly, for the B_{2g} Raman mode, the activity derives from a sum of four essentially spherical components with signs $++--$ so that the resultant will be close to zero and the feature will be very weak. However, there is no doubt that it is generally appropriate to use a factor group model in the present approach. Table II lists assignments, frequencies and relative intensities relevant to the Raman spectra in the 2000-cm^{-1} region.

In Figure 1 we distinguish the eight peaks occurring in the Raman spectra of $Cr(CO)_6$ by the labels a to h. As all of these peaks persist throughout the spectra reported in this paper we shall use these same labels (see also Table II). Sometimes, however, it will be necessary to distinguish thus: a(Cr) and a(W).

Adams et al.[2] reported single-crystal Raman studies of the three metal hexacarbonyls and thus enabled assignments of most of the bands observed in the four spectral regions. Although in the 2000-cm^{-1} region Adams et al. assigned band h to a ^{13}CO vibration, thus agreeing with the earlier tentative assignment of Stamper and Keeling,[4] they also found that bands a and b correspond to vibrations of A_g symmetry and so both of them could not be derived from the A_{1g} molecular mode (Table II). Adams et al. assigned the weaker of the two bands (band b) as arising from a vibration associated with the presence of ^{13}CO-containing species.

There is a small correction to be made to the report of Adams et al. (personal communication). As indicated by the very close similarity between the polycrystalline Raman spectra and very clear intensity correlations between the bands 2023 (Cr), 2023 (Mo), and 2018 (W) (band d) all of which are an order of magnitude more intense than the proximate 2016 (Cr), 2018 (Mo), and 2013 (W) (band e), the former set should be assigned as of B_{3g} symmetry and the latter as B_{2g}. Adams et al. suggested that the series of weaker bands might originate in ^{13}CO isotopic species. Adams et al. also found another weak feature, essentially coincident with band f in all the spectra, which they also suggested could possibly have an isotopic origin. The other main features, bands d, f, and g were found to have symmetries which were readily accounted for as the predicted site-plus-correlation-split components of the molecular E_g mode (Table II). It was suggested that band c might be isotopic in origin.

The Raman spectra obtained in our mixed crystal studies followed a general pattern, and although the results discussed below were obtained from crystals of composition Cr_xW_{1-x}-

Table VI. Mixed Crystal Raman Frequencies (cm^{-1}) for $Cr_xMo_yW_{1-x-y}(CO)_6$ in the ν(CO) Region

										Approximate	
Sample	a(Mo) + a(W)	a(Cr)	b	c	d	e	f	g	h	x	y
1	2117 (11.2)	2111 (11.2)		2031	2023 (26.6)	2016	2005 (100)		1964	0.5	0.25
2	2118 (13.1)	2112 (9.3)		2031	2022 (25.3)	2016	2003 (100)		1962	0.3	0.3
2[a]	2120 (13.2)	2114 (9.6)		2033	2023 (27.5)	2016	2003 (100)	1998	1961	0.3	0.3
3	2117 (18.6)	2112 (13.3)		2031	2023 (22.6)	2016	2005 (100)		1964	0.3	0.4

[a] Recorded at liquid nitrogen temperature.

$(CO)_6$ where $0 < x < 1$, *mutatis mutandis* similar behavior was observed for species $Cr_xMo_{1-x}(CO)_6$ (1), $Mo_xW_{1-x}(CO)_6$ (11), $Cr_xMo_yW_{1-x-y}(CO)_6$ (111) (where $0 < x + y < 1$). The data for $Cr_xW_{1-x}(CO)_6$ are detailed in Table III. The data refer to room temperature measurements but the spectra of an approximately 1:1 mixture showed no additional features at liquid nitrogen temperature (Figure 2). Data for crystals (1), (11), and (111) are given in Tables IV–VI, respectively. The series $Cr_xW_{1-x}(CO)_6$ was studied in more detail than the others because the separation of a(Cr) from a(W) in the pure compounds—6 cm^{-1}—is larger than a(Mo)–a(Cr) and a(W)–a(Mo). In studies of $Mo_xW_{1-x}(CO)_6$ mixed crystals, and the three-component mixture, some of the a bands were too close together to permit a general clear separation.

For the mixed crystals $Cr_xW_{1-x}(CO)_6$ two bands are observed in the high-frequency band (a) region. One of the bands lies at frequencies close to the frequency of the mode derived from the molecular A_{1g} vibration for pure $W(CO)_6$, denoted [a(W)], while the other band lies at frequencies close to the frequency of the molecular A_{1g}-derived mode of $Cr(CO)_6$, denoted [a(Cr)]. The strength of each band depends upon the composition of the mixed crystal, the a(W) band increasing linearly with $1 - x$ and a(Cr) with x.

In the region corresponding to the molecular E_g vibration, an intermediate spectrum is observed. That is, for each of the corresponding modes of W and Cr derived from E_g vibrations, only a single Raman-active mode is observed in the mixed crystal spectrum. The frequency of each mode varies with x. As the amount of $Cr(CO)_6$ in the mixed crystal is increased the bands shift from frequencies characteristic of $W(CO)_6$ toward frequencies characteristic of $Cr(CO)_6$. The intensity pattern of the bands in this region is the same as for either parent crystal.

For comparison purposes, an approximately 1:1 mechanical mixture of $W(CO)_6$ and $Cr(CO)_6$ was prepared by grinding the two components together, and its Raman spectrum was recorded. This is shown in Figure 2. As expected, the spectrum is a superposition of the spectra of pure Cr and W hexacarbonyls and clearly confirms that the spectra obtained for mixed crystals are not superpositions of the spectra of the pure components.

A qualitative interpretation of the results reported is relatively straightforward and provides a basis for the discussion of our results involving isotopic substitution (vide infra). Firstly, it is clear that in the (molecular) E_g-derived region the intermolecular vibrational coupling is of a sufficient magnitude to swamp the zeroth-order frequency differences between the chromium, molybdenum, and tungsten species and to give a spectrum for which the peak frequencies are usually intermediate between those of the components. Secondly, it is clear that in the (molecular) A_g-derived region each component in the mixed crystal gives rise to a unique feature, the intensity of which, to within experimental error, is proportional to the value of x (the contribution of b(W) to the a(Cr) + b(W) column of Table III may be estimated by proportionality from the spectra of pure $W(CO)_6$).

Both single-crystal Raman and our results concur in the presence of factor group splitting in the (molecular) E_g-derived region. The single-crystal Raman data of Adams et al. left unclear the status of the A_{1g}-derived region. No factor group splitting was observed but this could have been a consequence of the inherently low intensity of the B_{1g} mode (vide supra). Our data strongly suggest that an alternative explanation, that there is very little, if any, factor group splitting in the A_{1g}-derived region, is more appropriate (although in no way invalidating the intensity argument). Our argument finds some theoretical support. If each $M(CO)_6$ molecule retains full O_h symmetry in the crystal then the lowest multiple term connecting two e_g modes is quadrupole–quadrupole. In contrast the lowest term connecting two a_{1g} modes is hexadecapole–hexadecapole and so of extremely short relative range (the term of the form $(14/5)^{1/2}Y_4{}^0 + Y_4{}^4 + Y_4{}^{-4}$ is the first totally symmetric spherical harmonic in the crystal field expansion apart from the $Y_0{}^0$ term). Reduction in symmetry from O_h and cross-coupling with other vibrations render this argument only valid as a first approximation, but it seems reasonable to anticipate that factor group effects will be very much smaller for the A_{1g}-derived mode than for the E_g-derived mode.

A study of Tables III–VI reveals that some peaks fall marginally outside the limits of those of the corresponding bands of the pure components. The spectral data we report are, we believe, accurate to ca. ±1 cm^{-1} and so such discrepancies may just be significant. We shall report in subsequent publications cases where such discrepancies are clearly significant and so we prefer not to dismiss them in the present one. Rather, we suspect, they indicate that the static field contribution to the observed frequencies may vary with composition of the crystal, a not unreasonable situation since the unit cell parameters certainly vary in this way.

Studies of Isotopically Enriched $Mo(CO)_6$ Crystals

There are two important features which distinguish our studies on isotopically enriched crystals from those reported above. An important qualitative difference is that some of the zeroth-order frequency differences are greater between $M(CO)_6$ and $M(^{12}CO)_x(^{13}CO)_{6-x}$ than between $M(CO)_6$ and $M'(CO)_6$. An important quantitative difference is that the symmetry of $M(^{12}XO)_x(^{13}CO)_{6-x}$ $1 \leq x \leq 5$ will be much lower than that of $M(CO)_6$. Furthermore, these lower symmetry species will be randomly scattered and oriented in the lattice, subject only to the requirement that the molecular axes coincide with those of $M(CO)_6$ in the parent lattice. Both of these features suggest that the extent of vibrational uncoupling will generally be greater in ^{13}CO isotopic studies than in M,M′ mixed crystal studies.

Because $Mo(CO)_6$ undergoes ^{13}CO isotopic substitution much more readily than either Cr or W hexacarbonyls, we have studied this compound in detail.

The infrared solution spectrum of $Mo(CO)_6$ (ν_{CO} region) with natural abundance of ^{13}CO shows the very strong triply degenerate fundamental of $Mo(^{12}CO)_6$ at 1987 cm^{-1} and a weak, ^{13}CO-derived band at 1957 cm^{-1}. In more concentrated solutions another isotopic band appears at 2010 cm^{-1}. With isotopic enrichment studies these two bands associated with $Mo(^{12}CO)_5(^{13}CO)$ become more intense and were used to monitor the extent of isotopic substitution. With progressive enrichment two more satellites were observed at ca. 1945 and

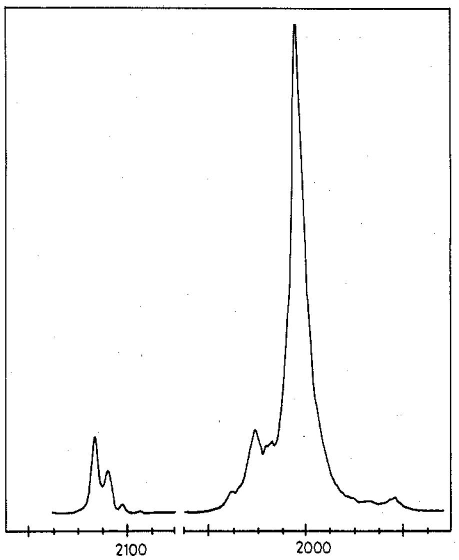


Figure 4. The room temperature Raman spectra of a sample of $Mo(CO)_6$ containing ca. 7% ^{13}CO in the 2000-cm^{-1} region.

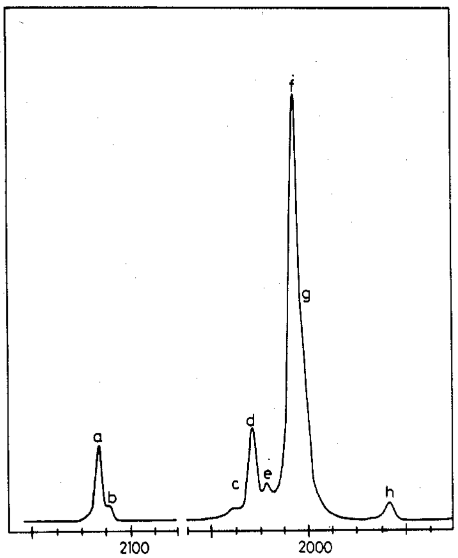


Figure 5. The room temperature Raman spectra of polycrystalline $Mo(CO)_6$ in the 2000-cm^{-1} region.

2110 cm^{-1} and correlate well with those observed by Harrill and Kaesz[5] and Bor and Jung[6] for ^{13}CO-substituted derivatives of $Mo(CO)_6$.

Substitution of one ^{13}CO group into $Mo(CO)_6$ lowers the molecular symmetry to C_{4v}, while substitution of two ^{13}CO groups lowers the molecular symmetry either to D_{4h} (*trans*-bis(^{13}CO)) or to C_{2v} (*cis*-bis(^{13}CO)). The relative concentrations of these molecular species as a function of isotropic substitution was obtained using the binomial distribution formula. This shows that for a ^{13}CO concentration of approximately 7%, the limit reached in this work, the relative concentrations of the components of the mixture are 65% $Mo(^{12}CO)_6$, 30% $Mo(^{12}CO)_5(^{13}CO)$, and 5% $Mo(^{12}CO)_4(^{13}CO)_2$. The natural abundance of ^{13}C is 1.1%, corresponding to 93% $Mo(^{12}CO)_6$ and 7% $Mo(^{12}CO)_5(^{13}CO)$.

The Raman spectra of a series of mixed crystals of ^{13}CO isotopically labeled $Mo(CO)_6$ are shown in Figure 4 where they are compared with the spectrum of an unenriched sample (Figure 5). The peak labels used in Figure 4 correspond to those of Figures 1 and 5. It is to be recalled that the peaks labeled b, c, e, and h have been assigned as isotopic in origin.

It is clear from Figure 4 that isotopic enrichment leads to an increase in number of peaks and to specific peak intensity changes in the 2110-cm^{-1} region, that corresponding to molecular A_{1g}-derived modes. The 1:1 correspondence observed between the number of peaks in this region and the number of isotopic species in the crystal is particularly striking. These observations are entirely in accord with our previous conclusion that factor group coupling is very small in this region so that the observations are best interpreted on a site group model. Because the modes occurring in this region are, for all molecular species, totally symmetric there is no question of site symmetry splitting and only a static field effect will be seen in the spectrum. The spectra also suggest, however, that the "molecular" frequencies are largely independent of the orientation adopted on the crystal site (there are several ways of placing a C_{4v}, D_{4h}, or C_{2v} species on any one site) because the bandwidths of the isotopic peaks do not generally seem to be very much greater than that of the $Mo(^{12}CO)_6$ peak. However, the lower height but apparently greater width of the band at 2095 cm^{-1} than that at 2103 cm^{-1} may be a consequence of the different number of ways of replacing an O_h by a D_{4h} or C_{2v} molecule (3 and 12, respectively). One aspect remains unclear, however. The observed intensity of band b is up to three times that expected from the natural abundance of ^{13}CO. There are several possible explanations for this observation but we have no evidence to indicate which is appropriate.

In the 2000-cm^{-1} region the effects of isotopic substitution are manifest more in peak broadening than in the selective enhancement of intensity of any peak. Certainly, in the 2000-cm^{-1} region the variation of intensity of bands c and h with isotopic substitution clearly excludes their assignment as isotopically derived. Rather than increasing in intensity they appear to marginally decrease (although this may be a consequence of peak broadening).

Band h is particularly interesting. Adams et al. in their single crystal work on $M(CO)_6$ (M = Cr, Mo, W) found that this band corresponds to a mode of B_{3g} symmetry. We therefore suggest that band h is a genuine factor group component derived from the molecular T_{1u} mode.[30] Both its frequency and polarization make this a reasonable assignment (although it was excluded by Adams et al). As shown in Table II the molecular T_{1u} mode should give rise to six Raman ($2B_{3g} + 2B_{1g} + A_g + B_{2g}$) active modes. Although, formally Raman active modes originating in an inactive molecular mode are expected to be weak, examples are known where they are quite strong. In the infrared solid-state spectrum (Table I) the center of the broad band associated with the T_{1u}-derived modes occurs at 1976 cm^{-1} which is to be compared with the frequency of band h (1966 cm^{-1}).

Figure 4 shows that there is a general slight broadening of the Raman bands associated with modes derived from the molecular E_g mode; this broadening almost certainly causes the apparent increase in intensity of band e on isotopic enrichment. Certainly, the contour of this peak provides no indication of isotopic enhancement. If this conclusion is correct then peak e is difficult to assign—its symmetry excludes the possibility that it is a factor group fundamental. We believe that it most probably originates in a multiphonon mode. Studies which we have made of such modes (which may involve $k \neq 0$ critical points) in very simple crystals[7] suggest that they are manifest in the spectrum when intensity can be stolen from a proximate intense fundamental. In the present case the relevant fundamental is band f, which has a B_{2g} component. Adams' work indicates that band f contains a B_{1g} feature, of about the same intensity as the B_{2g}. It therefore seems reasonable that band c (of B_{1g} symmetry) should also be tentatively assigned as a multiphonon feature.

In addition to the features already discussed, two additional, very weak features are to be seen in the isotopically labeled crystals at ca. 1980 cm^{-1}. It is tempting to assign these as isotopic in origin but this appears to us to be inconsistent with the results and arguments we have presented above. Rather, we suspect that they may be molecular, T_{1u}, derived in origin, their intensity originating in a weak relaxing of the translational invariance requirement. We plan further studies, involving C–^{18}O and ^{13}C–^{18}O labeled species, to investigate inter alia the origin of these features.

In this paper we have been particularly concerned with the ν(CO) spectral region. We have made a preliminary study of the other regions and there find that, with the probable exception of the lattice mode region below about 60 cm^{-1}, the spectral features of mixed crystals $M_xM_{1-x}(CO)_6$ are, essentially, superpositions of the spectral features of the pure components, with only minor frequency changes. In particular, both the 387-cm^{-1} (Cr) and 433-cm^{-1} (W) bands, which are quite strong, are observed close to their respective frequencies but with intensities varying with composition. Little can be said about the behavior of the bands in the δ_{CMC} and lattice mode region. These bands, especially the T_{2g}-derived bending mode (which is the strongest in the whole spectrum), are very broad thus making it difficult to separate them even in the 1:1 mixture. From the spectra recorded at low temperatures, however, it does appear that the bending mode region spectral features are a superposition of molecular features while the lattice mode bands show an averaging. This indicates that intermolecular vibrational coupling is small for other internal modes and a factor group analysis inappropriate. This is in accord with the results of the single-crystal work of Adams et al.[2] A similar situation seems to hold for the species $Mo(^{13}CO)_x(^{12}CO)_{6-x}$ but here there are no data for the pure components available. Hrostowski and Pimental[8] have suggested that the introduction of different molecular species into a crystal lattice may uncouple the various molecular vibrations thus causing factor group splittings to diminish. Underlying this belief was the assumption that the host and guest molecular vibrations did not couple together. Indeed, several mixed crystal systems have been observed which show such changes in factor group splittings.[9-11] However, the present work indicates that the assumption that host–guest interactions may be neglected is not generally true.

The vibrational spectra of the mixed crystals which we have studied show a remarkable simplicity and may evidently be interpreted on the same basis as the spectra of the pure crystals. Thus, although the $k = 0$ selection rule breaks down formally, it appears that the "effective vibrational unit cell" in the mixed crystal is not very different from the unit cell of the pure crystals. The only obvious indications of disorder and lack of translational symmetry are in the increase of line widths of the bands in the mixed crystals as compared to those in the pure crystals. There is a marked broadening especially of the strong band, band f, in $M_xM'_{1-x}(CO)_6$ crystals reaching a maximum when $x \simeq 0.5$.

It is generally true that studies of the spectroscopic properties of mixed crystals have been more extensively made by physicists than by chemists. As a consequence, in the field of vibrational spectroscopy such work has tended to be more concerned with lattice than internal modes. In this context the situation in which there appears a spectral feature corresponding to each of the (two) components is referred to as "two mode" behavior, whereas the appearance of a single feature, usually intermediate in position, is referred to as "one mode" behavior. Relevant to the results presented in the present paper is the work of Aggarwal and Saksena,[12] of Matossi,[13] of Martin,[14] of Bauhofer, Genzel, and Jahn,[15] and of Dean.[16] Recent data indicating the need for extensions to the general theory are to be found in the work of Murahashi and Koda[17] and of Laulicht and Ofek.[18] The effects of isotopic substitution have been discussed in a particularly pertinent paper by Hoshen and Jortner[19] and by Bates and Stidham[20] while the occurrence of weak isotopic features associated with ν(CN) vibrations has been discussed by Nitsch and Claus[21] and, in related systems, by us.[22] The consequence of some disorder (and possible clustering) has been treated theoretically by Klug and Whalley,[23] by Whalley and Bertie,[24] and by De Fontaine.[25] An interesting case of isotopically induced order–disorder has been reported by Ching and Krimm.[26] An example of a mixed crystal in which very little coupling occurs between the vibrations of octahedral complex anions is provided by $(n\text{-}Bu_4N)_2Ir_xSn_{1-x}Cl_6$;[27] in contrast, coupling occurs between the metal–ligand stretching vibrations of cation and anion in $[Co(NH_3)_6][FeF_6]$.[28]

Conclusions

In this paper we have demonstrated that studies of mixed crystals containing isotopic species can be of considerable value in factor group studies. In this context one may regard the substitution of $Cr(CO)_6$ host molecules by, for instance, $W(CO)_6$ as akin to an isotopic substitute (thus paralleling but extending the work of Nakamoto[29] and co-workers on metal isotopes). The phenomenon which we have reported, that the same vibrator (ν(CO) in the present case) can give rise, in one combination, to two-mode behavior and in another to one-mode behavior does not describe all of the phenomena which may arise in mixed crystal studies. In future communications we shall report on intensity-transfer and peak gross-contour-change phenomena which may also occur.

Experimental Section

Chromium and tungsten hexacarbonyls, purchased from Strem Chemicals Inc., and molybdenum hexacarbonyl, purchased from BDH, were purified by vacuum sublimation at 40 °C before use.

The $Cr_xMo_{1-x}(CO)_6$, $Cr_xW_{1-x}(CO)_6$, $Mo_xW_{1-x}(CO)_6$, and $Cr_xMo_yW_{1-x-y}(CO)_6$ ($0 < x < 1$, $0 < y < 1$) mixed crystals were prepared by a cosublimation method. Weighed amounts of the metal hexacarbonyls were ground together and then sublimed under vacuum at 60 °C. Although the three pure carbonyls sublime easily at ca. 40 °C a higher temperature was employed for the mixed crystal preparations to make sure that the hexacarbonyls in the mixture sublimed at the same (or nearly the same) rate. The grinding and sublimation process was repeated at least five times to ensure as far as possible uniform mixed crystals.

Two other methods were also tried for preparing these mixed crystals. These were (1) recrystallizing mixtures of the hexacarbonyls from dichloromethane or diisopropyl ether solutions and (2) sealing mixtures of the hexacarbonyls in an ampule under vacuum and then heating the ampule to 60 °C for 24 h. This sealed-tube method gave large clear crystals.

Mixed crystals obtained by either of the three methods gave essentially identical Raman spectra. However, the cosublimation method was much simpler and faster and hence it was used for the data reported here.

In order to determine whether more than one crystalline form was present in the mixed crystals, powder x-ray diffraction photographs of some of the mixed crystals were obtained using a Phillips camera employing nickel-filtered copper Kα radiation. The x-ray powder photographs thus obtained were compared with those obtained for the pure compounds. The patterns obtained for the mixed crystals unambiguously indicated that the mixed crystals were isomorphic with crystals of the pure compounds.

For the ^{13}CO substitution of $Mo(CO)_6$, carbon monoxide enriched to 97.4% ^{13}C (B.O.C.) was used. The exchange experiment was performed on a high-vacuum line. The carbonyl complex was dissolved in degassed hexane, the enriched carbon monoxide added, the reaction vessel kept in sunlight, and the solution stirred magnetically at room temperature for ca. 5 days.

Infrared spectra were recorded on a Perkin-Elmer 325 double-beam spectrometer while the Raman spectra were recorded using a Spex 1401 double monochromator with photon counting and Ar$^+$/Kr laser excitation.

The spectra reported are those with the sample at room temperature. Cooling to liquid nitrogen temperature led to some band sharpening but in no case did any additional features appear or any significant change in band intensity occur.

In all cases the value of x (and y) quoted refers to the molar ratios of components in the initial mixture from which mixed crystals were made.

Acknowledgment. D.A.K. is indebted to the British Council for financial support.

Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

References and Notes

(1) A preliminary account of part of this work has been given: D. A. Kariuki and S. F. A. Kettle, *J. Organomet. Chem.*, **105**, 209 (1976).

(2) D. M. Adams, W. S. Fernando, and M. A. Hopper, *J. Chem. Soc., Dalton Trans.*, 2264 (1973).

(3) A. Whitaker and J. W. Jeffrey, *Acta Crystallogr.*, **23** 977 (1967).

(4) G. Keeling and P. J. Stamper, Ph.D. Theses, University of Sheffield, 1970.

(5) R. W. Harrill and H. D. Kaesz, *J. Am. Chem. Soc.*, **90**, 1449 (1968).

(6) G. Bor and G. Jung, *Inorg. Chim. Acta*, **3**, 69 (1969).

(7) S. S. Ti, S. F. A. Kettle, and Ø Ra, *Spectrochim. Acta, Part A*, **32a**, 1603 1765 (1976).

(8) H. J. Hrostowski and G. C. Pimentel, *J. Chem. Phys.*, **19**, 661 (1951).

(9) D. P. Craig, *Adv. Chem. Phys.*, **8**, 27 (1965).

(10) A. S. Barker and A. J. Sievers, *Rev. Mod. Phys.*, **47**, S(2)1 (1975).

(11) H. Takeuchi, I. Harada, and T. Shimanouchi, *Chem. Phys. Lett.*, **43**, 516 (1976).

(12) R. R. Aggarwal and B. D. Saksena, *J. Chem. Phys.*, **19**, 1480 (1951).

(13) F. Matossi, *J. Chem. Phys.*, **19**, 161 (1951).

(14) T. P. Martin, *Phys. Status Solidi B*, **67**, 137 (1975).

(15) W. Bauhofer, L. Genzel, and I. R. Jahn, *Phys. Status Solidi B*, **63**, 465 (1974).

(16) P. Dean, *Rev. Mod. Phys.*, **44**, 127 (1972).

(17) T. Murahashi and T. Koda, *J. Phys. Soc. Jpn.*, **40**, 747 (1976).

(18) I. Laulicht and R. Ofek, *J. Raman Spectrosc.*, **4**, 41 (1975).

(19) J. Hoshen and J. Jortner, *J. Chem. Phys.*, **56**, 933 (1972).

(20) J. B. Bates and H. D. Stidham, *Solid State Commun.*, **16**, 1223 (1975).

(21) W. Nitsch and R. Claus, *Z. Naturforsch. A*, **29**, 1017 (1974).

(22) S. S. Ti, Ø Ra, and S. F. A. Kettle, *Spectrochim. Acta, Part A*, **33a**, 111 (1977).

(23) D. D. Klug and E. Whalley, *J. Chem. Phys.*, **56**, 553 (1972).

(24) E. Whalley and J. E. Bertie, *J. Chem. Phys.*, **46**, 1264 (1967).

(25) D. De Fontaine, *J. Appl. Crystallogr.*, **8**, 81 (1975).

(26) J. H. C. Ching and S. Krimm, *J. Appl. Phys.*, **46**, 4181 (1975).

(27) J. E. Fergusson and T. W. Tee, *Inorg. Nucl. Chem. Lett.*, **12**, 297 (1976).

(28) S. L. Barker and S. F. A. Kettle, *Spectrochim. Acta*, in press.

(29) K. Nakamoto, *Angew. Chem., Int. Ed. Engl.*, **11**, 666 (1972).

(30) We are indebted to a referee for pointing out that this assignment is in accord with the observation of L. J. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969), that band h shifts to 1922 cm^{-1} in $Cr(^{13}CO)_6$ and 1918 cm^{-1} in $Cr(C^{18}O)_6$ demonstrating that it is not to be associated with a mode of $Cr(^{12}CO)_5(^{13}CO)$. Further these shifts correspond rather well to those observed for the T_{1u} mode, ν_6, in solution.

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

Photolysis and Spectroscopy with Polarized Light: Key to the Photochemistry of $Cr(CO)_5$ and Related Species[1]

JEREMY K. BURDETT, JOSEPH M. GRZYBOWSKI, ROBIN N. PERUTZ, MARTYN POLIAKOFF, JAMES J. TURNER,* and ROBERT F. TURNER

Received April 26, 1977

A photochemical mechanism is proposed which accounts for almost all the experimental data on matrix-isolated $M(CO)_5$ (M = Cr, Mo, W), $N_2M(CO)_5$, and $M(CO)_4CS$. The mechanism is based on evidence obtained by polarized photolysis and polarized spectroscopy of square-pyramidal (spy) $L\cdots M(CO)_5$ (L = Ar, Xe, N_2 etc.) species. Polarized photolysis of $Ar\cdots Mo(CO)_5$ in mixed Ar/N_2 matrices leaves oriented $Ar\cdots Mo(CO)_5$, but the photoproduct $N_2Mo(CO)_5$ is randomly oriented. Other reactions of this type also exhibit dichroic photodepletion without dichroic photoproduction. In pure matrices polarized photolysis of $m\cdots M(CO)_5$ (m = matrix) with visible light causes reorientation to positions less favorable to absorption. These results can be understood from a three-step mechanism consisting of (1) photochemical ejection of the sixth ligand m from spy $m\cdots M(CO)_5$, (2) internal rearrangements of the resulting *naked* $M(CO)_5$ via a trigonal-bipyramidal (tbp) intermediate and decay back to the spy ground state in one of several orientations, (3) recombination with an alternative ligand, CO, Ar, N_2 etc. This spy → tbp → spy process represents an inverse Berry mechanism and also accounts for many other aspects of the photochemistry (e.g., recombination with CO to $M(CO)_6$). A similar mechanism also explains the initial formation of $M(CO)_5$ from $M(CO)_6$. The details of the mechanism are developed from an assignment of the photochemically active absorption and from molecular orbital arguments using both extended Hückel and angular overlap methods.

On ultraviolet photolysis of metal hexacarbonyls of chromium, molybdenum, and tungsten in low-temperature matrices, CO and square-pyramidal metal pentacarbonyls are generated. Irradiation of the pentacarbonyl in its visible absorption band results in the reversal of this reaction (eq 1).[2]

$$M(CO)_6 \underset{h\nu\ (\text{visible})}{\overset{h\nu\ (\text{UV})}{\rightleftharpoons}} m\cdots M(CO)_5 + CO \tag{1}$$

(M = Cr, Mo, W; m = matrix)

The infrared and UV/visible spectra and the photochemical properties of the metal pentacarbonyls have been studied under a wide variety of conditions.[2-7] These experiments and those on the analogous system $M(CO)_5CS$ (M = Cr,W)[8,9] have been summarized in a recent review.[10] In this paper we describe in detail the additional information obtained by using polarized photolysis and detection (a short communication was published earlier[11]). We use a molecular orbital treatment to suggest a photochemical pathway which accounts for almost all the data, both new and old.

I. Experiments with Polarized Light

Although the use of polarized photolysis and detection in low-temperature glasses was described many years ago,[12] the technique is still new for matrix isolation.[11] A detailed analysis of other applications of the method and a description of the experimental technique will be given elsewhere.[13]

If a nonrotating molecule (of lower symmetry than cubic) is photolyzed with plane-polarized light in a matrix, the preferential absorption of the photolyzing light by molecules in some orientations will lead to partial orientation of the *remaining* starting material (*dichroic photodepletion*). If there were no rotation in the photochemical reaction, the product would be preferentially oriented in the opposite direction

0020-1669/78/1317-0147$01.00/0