Table VI. Rates of Reaction of *mer*-$[Mn(CO)_3dpeBr]^+$ at 25 °C

Solvent	k_{obsd}, s^{-1}	k_{solv}, s^{-1}	k_{red}, s^{-1}
CH_3CN (0.1 M Et_4NClO_4)	$(4.12 \pm 0.03) \times 10^{-4}$	$(7.4 \pm 0.2) \times 10^{-5}$	3.38×10^{-4}
CH_2Cl_2 (0.1 M Et_4NClO_4)	$(5.8 \pm 0.2) \times 10^{-4}$	$(8.9 \pm 0.3) \times 10^{-5}$	4.91×10^{-4}

the other steps, so that k_{solv} can be measured in this experiment, k_{red} therefore can be calculated by subtraction of k_{solv} from k_{obsd}. Results obtained by linear least-squares analysis are summarized in Table VI.

During the course of the above measurements it was observed that *mer*-Mn(II) complexes are extremely light (visible) sensitive and on exposure to sunlight the purple *mer*-$[Mn(CO)_3(L\text{-}L')Br]^+$ or red *mer*-$[Mn(CO)_3(L\text{-}L')Cl]^+$ species are very rapidly reduced on the second time scale to yellow *mer*-$Mn(CO)_3(L\text{-}L')X$. In acetonitrile, yields of less than 100% are obtained but in dichloromethane close to 100% yield is found. Clearly, manganese(II) carbonyl species are extremely reactive and can undergo a large number of very interesting reactions which are considerably more complex than simple solvent reduction as has been proposed previously.[3,4] Many carbonyl complexes have been shown to be light sensitive.[10] Speculation of the light-sensitive pathway for catalyzing the redox reaction would in normal circumstances probably be that.[10]

$$mer\text{-Mn(II)} \xrightarrow{h\nu} fac\text{-Mn(II)}$$

Since the facial form is a much more powerful oxidant than the meridional one this would be consistent with the observations. However, reduction of *fac*-Mn(II) by solvent or water impurity should lead to the *fac*-Mn(I) complex, not the *mer*-Mn(I) form as found experimentally. An explanation of the transition state in the light-sensitive reaction must therefore await further detailed experimental examination.

Regardless of the mechanism of these reactions it seems clear that in addition to being kinetically labile with respect to isomerism (as noted previously) the 17-electron systems are labile with respect to a wide range of reactions. Studies of other manganese and rhenium 17-electron systems[11,12] also indicate that facile substitution of CO is a characteristic of their chemistry so this observation may be of fairly general applicability.

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Registry No. $[Mn(CO)_3dpmCl]^+$ (*mer*), 60305-99-9; $[Mn(CO)_3dpmBr]^+$ (*mer*), 60325-42-0; $[Mn(CO)_3dpeCl]^+$ (*mer*), 65634-87-9; $[Mn(CO)_3dpeBr]^+$ (*mer*), 65634-86-8; $[Mn(CO)_3apeCl]^+$ (*mer*), 65622-62-0; $[Mn(CO)_3apeBr]^+$ (*mer*), 65622-61-9; $[Mn(CO)_3daeCl]^+$ (*mer*), 65622-60-8; $[Mn(CO)_3daeBr]^+$ (*mer*), 65622-59-5; $[Mn(CO)_3dpmCl]^+$ (*fac*), 65634-85-7; $[Mn(CO)_3dpmBr]^+$ (*fac*), 47752-42-1; $[Mn(CO)_3dpeCl]^+$ (*fac*), 65622-58-4; $[Mn(CO)_3dpeBr]^+$ (*fac*), 47768-35-4; $[Mn(CO)_3apeCl]^+$ (*fac*), 65634-91-5; $[Mn(CO)_3apeBr]^+$ (*fac*), 65634-90-4; $[Mn(CO)_3daeCl]^+$ (*fac*), 65634-89-1; $[Mn(CO)_3daeBr]^+$ (*fac*), 65634-88-0.

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Solid-State Studies. 10. Vibrational Spectra of Mixed and Isotopic Crystals of Manganese and Rhenium Pentacarbonyl Iodides

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The Raman spectra of mixed crystals of manganese and rhenium pentacarbonyl iodides and of ^{13}CO-enriched manganese pentacarbonyl iodide are interpreted in terms of one-mode, intermediate, and two-mode behaviors, notwithstanding the absence of overt factor group splitting in the individual spectra of the pure compounds.

The majority of work which has been reported on the composition dependence of the vibrational spectra of crystals containing components of which the relative proportions may be varied over a wide range has been concerned with semiconductor, alloy, and ionic crystals.[2] Such studies have therefore been concerned with the behavior of the long-wavelength optical phonons. Two types of behavior have been recognized. In the first, cases exhibiting so-called one-mode behavior, the frequency of the spectral feature varies continuously and approximately linearly with concentration from the frequency characteristic of one pure component to that of the other. The band intensity remains approximately constant. Examples of mixed crystals belonging to this class include compounds which might normally be regarded as ionic.[2b-10]

In the other class of mixed-crystal vibrational behavior, the so-called two-mode type, two phonon features are observed, each frequency being close to that associated with one of the pure components. The intensity of each varies continuously from its maximum (for one end member) to zero as its fractional contribution varies from 1 to 0 or from 0 to 1. Examples of mixed crystals belonging to this category tend to be those that might be regarded as covalent materials.[11-15] In some cases both one- and two-mode behaviors have been found.[16] For both types it has been observed that spectral line widths increase with concentration exhibiting a maxium near

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Table I. ν(CO) Frequencies (cm^{-1}) for M(CO)$_5$I

	Mn(CO)$_5$I					Re(CO)$_5$I				
	Infrared					Infrared				
Assignment	Solution^a	Designation^b	Solid	Designation^b	Raman Solid	Solution^a	Designation^b	Solid	Designation^b	Raman Solid
A$_1$ (radial)	2128 m	g	2133 ms	a	2130 s	2148 mw	g	2151 ms	a	2148 s
	2120 w	h	2124 w	b	2124 w	2140 w	h	2142 w	b	2139 w
B$_1$				c	2072 s				c	2073 s
E		j	2055 sh			2044 s	j	ca. 2055 sh		
	2046 s	k	2045 s				k	2035 vs		
			2037 sh			2015 w		2007 sh	d	2028 w
A$_1$ (axial)		l	2014 s				l	1990 s		
	2018 w					1989 ms				
		m	2005 sh	e	2005 s				e	1982 s
	2005 s					1975 w				
		n	1970 w	f	1972 w		n	1949 w	f	1950 w

^{a} CCl$_4$ as solvent. ^{b} See Figure 1.

the 1:1 mixture. Qualitatively, this is not unexpected since at this composition, assuming random mixing, there is a maximum departure from full translational symmetry and so a breakdown of the $k = 0$ selection rule is not unexpected. Quantitatively, however, there is no entirely adequate theory for the variation of line width with concentration.

The report that for the system (NH$_4$)Cl$_{1-x}$Br$_x$[17] new peaks occur which are not related to peaks in the spectra of the pure components suggests, however, that the full range of extant spectral phenomena may not be covered by an explanation solely in terms of one- and two-mode behaviors.

In previous communications[18-21] we have described studies on the vibrational spectra of the ν(CO) region of mixed molecular crystals containing metal carbonyl species. In this work we have found evidence not only for one- and two-mode behaviors but also for an intermediate behavior, characterized by broad spectral features. The distinction that was made between these behavioral types was one dependent upon the magnitude of coupling between ν(CO) vibrators. When this is negligible, two-mode behavior is observed; when very large, leading to effective coupling over large distances, one-mode behavior results. Intermediate behavior may be associated with the existence of a statistical variety of small interpenetrating packets of molecules within the crystal, the intermolecular vibrational coupling being relatively weak so that it dies away quickly from each central reference molecule. Mixed crystals of manganese/rhenium pentacarbonyl bromides, of manganese/rhenium pentacarbonyl chlorides, and of ^{13}CO-enriched Mn(CO)$_5$Br showed all of these types of behavior.[20]

Results and Discussion

In the present communication we report our studies of mixed crystals of manganese/rhenium pentacarbonyl iodides and of ^{13}CO-enriched Mn(CO)$_5$I. Despite their chemical similarity to the bromides and chlorides, the pentacarbonyl iodides are not isomorphous with them (although isomorphous to each other), necessitating a quite separate discussion. Although the solution spectra in the ν(CO) region of the iodides are very similar to those of the chloro and bromo complexes, the solid-state spectra are very different. The iodides present a simpler picture for only three strong bands are observed both in solution and in solid-state infrared and Raman spectra.

The simplicity of the solution spectra, together with the excellent understanding of the isolated C_{4v} M(CO)$_5$ system makes band assignment of the crystal spectra quite unambiguous in contrast to the corresponding chlorides and bromides. Comparison of the infrared and Raman ν(CO) spectra makes it possible to assign the highest and lowest frequency strong bands denoted a and g, e and l in Figure 1 and Table I—to the a$_1$(radial)- and a$_1$(axial)-derived modes, respectively. Band c (Raman) is assignable to the b$_2$-derived mode while in the infrared spectra the remaining strong band k must then be assigned to the e-derived mode. The e-derived mode, though Raman allowed in theory, apparently has little or no intensity for the iodides. This is interesting because for the chlorides and bromides there were two strong bands (one showing splitting) in this b$_2$/e-derived mode region and the molecular parentage was uncertain.[19] The factor group analysis for the chlorides and bromides indicates that there are only two b$_2$ mode derived fundamentals so some additional mechanism must be sought to explain the third peak. Intensity stealing by an e mode is an obvious explanation but one which is weakened because the iodide data suggest that no significant Raman intensity is transferred to this mode in crystalline phases. For the iodide it may be possible to correlate that molecular e mode with a very weak band (d) which occurs between the a$_1$(axial)- and b$_2$-derived modes in Re(CO)$_5$I spectra. The weak bands b and f (Raman) and h and n (infrared) are assigned to ^{13}CO modes, assignments confirmed by our ^{13}CO enrichment data. It is to be noted that band d does not appear to be isotopic in origin (vide infra). Spectral data for crystalline samples in the ν(CO) region are given in Table I and spectra shown in Figure 1. Data for the other regions showing significant features, that below 650 cm^{-1}, are given in Table II.

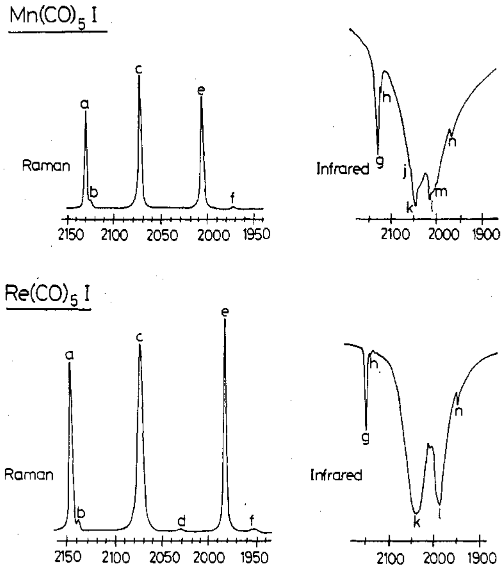

Figure 1. Room temperature infrared and Raman spectra of crystalline M(CO)$_5$I, M = Mn or Re, in the 2000-cm^{-1} region.

Mixed crystals of Mn$_x$Re$_{1-x}$(CO)$_5$I ($0 < x < 1$) were prepared by cocrystallizing appropriate mixtures of the components from acetone at 0 °C under nitrogen. The re-

Table II. Low-Frequency Region for $M(CO)_5I$

	$Mn(CO)_5I$		$Re(CO)_5I$	
Assignment	Infrared solid	Raman solid	Infrared solid	Raman solid
δ(MCO) + ν(MC)	630 s	632 m	587 s	590 m
				580 w
		543 w		547 w
				530 vw
				497 m
		464 m		475 vs
		426 mw		440 s
	419 s	412 vw		413 vw
	406 m	389 s		370 m
			360 m	354 ms
		233 vw		233 w
ν(MI)		189 s		163 s
δ(CMC), δ(CMI), lattice		132 s		128 s
		121 s		120 vs
		61 s		55 s
		45 m		40 s
				33 w

sulting crystals were dried under vacuum. Infrared spectra were recorded as KBr and KI disks on a Perkin-Elmer 325 spectrometer. The resolution was 1 cm^{-1} or better. Spectra obtained with either disk material were essentially identical, although of somewhat better quality in KBr, indicating that no halogen exchange occurred in this medium. Raman spectra of polycrystalline samples were recorded on a Spex 1401 monochromator with red-enhanced optics and a Spectra Physics 165 Ar/Kr laser at ca. 10 mW incident power using one of the red lines. The resolution employed was between 1 and 2 cm^{-1} and usually closer to the former value. Exchange of $Mn(CO)_5I$ with ^{13}CO was carried out in hexane solution in the dark with magnetic stirring. Each exchange was judged essentially complete after ca. 24 h.

The Raman spectra of $Mn_xRe_{1-x}(CO)_5I$ mixed crystals were recorded for ten different values of x and are detailed in Table III. Typical spectra are shown in Figure 2. In Table III, approximate intensity ratios (calculated from band heights of $I(ReI)/I(MnI)$ and $I(a(Re))/I(a(Mn))$ are included. The former refers to the ratio of the bands corresponding to the M–I stretching (A_1) vibration (i.e., bands at 163 and 180 cm^{-1} for Re and Mn, respectively) and the latter refers to the ratio of the bands corresponding to the a_1(radial) C–O stretching vibration. These two ratios give independent estimates of the relative concentrations in the mixed crystals and were in general accord with the crystal composition expected from the component ratios (given in the final column of Table III).

The pentacarbonyl iodides are very good scatterers and, as such, their spectra in the low-frequency region are superior to those of most other mixed-crystal species which we have studied, allowing more definite observations in this region. Thus, two-mode behavior is clearly found for the bands corresponding to ν(MC) and δ(MCO) vibrations. Those bands with frequencies between ca. 120–200 cm^{-1} show a two-mode behavior, whereas the three bands (or each compound) occurring below 61 cm^{-1} show a one-mode behavior. One-mode behavior would generally be expected for lattice modes. Although Butler et al.[23] assigned all the bands below 61 cm^{-1} as corresponding to the δ(MCO) and δ(CMX) bending modes only, it is possible that these bands either are at higher frequencies or are strongly mixed with lattice modes.

If the pattern found for the ν(CO) features of the pentacarbonyl bromides and chlorides is followed in the iodides, it would be expected that the a_1(radial)-derived modes will give rise to two-mode behavior (indicating, inter alia, that octupole–octupole coupling is negligible). Similarly, the e- and b_2-mode derived features are expected to show one-mode behavior and, while the a_1(axial)-derived features will show evidence of coupling, the zeroth-order frequency difference between the pure component peaks may mean that it is intermediate mode behavior which is manifest. In general, these expectations are fulfilled. Because of their greater clarity (Figure 2) we shall confine our detailed discussion to the Raman spectra. Infrared spectra of the mixed crystals were generally broader and even less informative than those of the pure compounds.

For the a_1(radial) region two bands are found at ca. 2148 and 2130 cm^{-1} in all mixed crystals studied. The frequencies of these bands correspond to those of the a_1(radial) modes of the pure rhenium and manganese species, respectively. The

Table III. ν(CO) Raman Frequencies (cm^{-1}) for $Mn_xRe_{1-x}(CO)_5I$ Mixed Crystals[a]

Sample	a(Re)	b(Re)	a(Mn)	b(Mn)	c	d	e	
$Re(CO)_5I$	2148 (86.7)	2139 (5.2)			2073 (100)	2028		
1	2149 (90.1)	2141 (6.0)	2131 (3.9)		2073 (100)	2029		
2	2149 (81.3)	2141 (7.8)	2132 (9.6)		2074 (100)			
3	2148 (71.3)	2142 (4.5)	2131 (11.7)	2125	2073 (100)	2030	2010 (3.2)	
4	2149 (57.2)	2142 (3.7)	2131 (24.2)	2125	2073 (100)		2009 (6.8)	1995 sh
5	2148 (50.9)	2141 (4.8)	2130 (27.5)	2124	2073 (100)		2009 (10.2)	
6	2148 (36.5)	2141 (3.8)	2130 (37.7)	2124	2072 (100)		2007 (16.0)	1993 sh
7	2148 (22.3)		2130 (48.2)	2124	2073 (100)		2006 (30.2)	1993 sh
8	2149 (11.8)		2129 (57.9)	2124	2072 (100)		2005 (43.0)	1992 (13.4)
9	2149 (7.8)		2129 (56.4)	2125	2072 (100)		2005 (60.2)	1992 (13.1)
10	2149 (5.2)		2130 (64.9)	2125	2073 (100)		2005 (70.9)	1993 (11.6)
$Mn(CO)_5I$			2129 (119.5)	2124	2072 (100)		2005 (139.5)	

Sample	e	f(Mn)	f(Re)	I(ReI)/ I(MnI)	I(a(Re))/ I(a(Mn))	Actual Re:Mn
$Re(CO)_5I$	1982 (108.2)		1950 (1.9)			
1	1932 (147.9)		1949 (2.1)	19.8	23.1	95:5
2	1983 (112.4)			4.1	8.5	85:15
3	1983 (93.5)		1950 (1.6)	2.9	6.1	80:20
4	1983 (73.2)		1950 vw	0.97	2.4	70:30
5	1983 (62.9)	1969 vw		0.74	1.9	50:50
6	1985 (36.5)			0.39	0.96	40:60
7	1987 (24.8)	1970 vw		0.22	0.46	30:70
8	1988 (13.4)	1970 vw		0.10	0.20	15:85
9	1989 sh	1971 vw		0.075	0.14	10:90
10		1971 (3.3)		0.029	0.08	5:95
$Mn(CO)_5I$		1971 (5)				

[a] Numbers in parentheses indicate relative band heights based on 100 for band c (heights are not specified for some very weak bands).

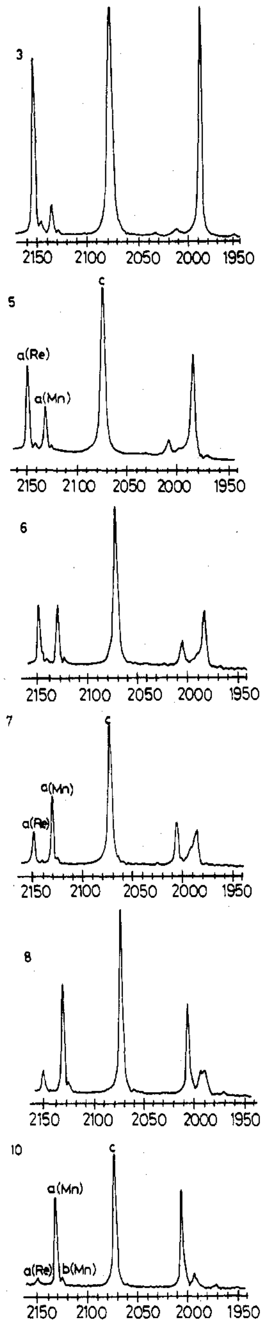

Figure 2. Room temperature Raman spectra of $Mn_xRe_{1-x}(CO)_5I$ mixed crystals in the 2000-cm^{-1} region. The numbers on spectra refer to the sample number in Table III.

intensities of these bands are dependent on the composition of the crystals, the a(Re) band increasing in strength essentially linearly with $1 - x$, while the a(Mn) band increases with x. The same behavior is displayed by bands b(Re) and b(Mn) which have been assigned as the corresponding bands arising from ^{13}CO species. This clear two-mode behavior is taken as indicative that the vibrational modes which are responsible for these bands are little affected by intermolecular interactions and so a factor group analysis is inappropriate (we note, however, that changes in the static field with x may cause small frequency changes of features exhibiting two-mode behavior).

Only one band is observed in the region corresponding to the b_2-derived modes. Although this may result from one-mode behavior of b_2-derived modes of Re and Mn, it could equally be interpreted as a superposition of the "c" bands of the manganese and rhenium compounds since these are ca. 1 cm^{-1} apart in the pure crystals. However, as we shall see, the ^{13}CO isotopic data confirm that one-mode behavior occurs. The weak band d corresponding possibly to an e-derived mode was only observed clearly in the spectra of two mixed crystal systems and so no definite conclusions can be drawn concerning its behavior. Similarly, no clear conclusions emerge from the infrared spectra. The original bands are broad and have maxima within 10 cm^{-1} of each other; it is therefore difficult to determine the effects of mixing and thus not possible to distinguish between one- and two-mode behaviors.

The a_1(axial)-mode-derived region is most interesting. The pattern observed is similar to that seen in the mixed crystals of rhenium and manganese pentacarbonyl chlorides and in the corresponding bromides. A broad unresolved band occurs at low frequency while a much sharper band occurs at high frequency. As the mixed-crystal composition varies, both bands show marked changes in frequency and intensity. The intensity distribution among the bands is not directly proportional to the concentrations of the mixed crystals as can be seen by comparing these two bands in Figure 2 with those associated with the a_1(radial)-derived modes. When x is very small, the lower frequency band is situated at frequencies characteristic of the pure rhenium compound (ca.1982 cm^{-1}). As the proportion of the manganese species is increased, this band moves toward higher frequencies. The band on the high-frequency side starts off at 2010 cm^{-1} as x increases. In other words, this band occurs at frequencies which are outside the limits set by the frequencies of band e in either pure species (1982–2005 cm^{-1}). As the manganese proportion is increased, the band both grows in intensity and shifts toward frequencies characteristic of the a_1(axial)-derived peak of manganese pentacarbonyl iodide.

We believe that the behavior of the a_1(axial)-mode-derived features provide insight into the situation in which there is near-two-mode behavior but with significant residual intermolecular vibrational coupling. In particular, we note the rather large zeroth-order frequency difference of ca. 23 cm^{-1} between the corresponding features in the Raman spectra of the pure compounds (in the bromides, the separation is 25 cm^{-1}; differences in behavior are therefore presumably to be attributed to smaller intermolecular vibrational couplings in the iodides). The spectra suggest that such residual coupling may broaden two-mode features unsymmetrically (cf. spectra of samples 6, 7, and 8 in Figure 2). Closer examination, however, reveals that this unsymmetrical broadening may occur because of the appearance of a third peak (close to one of the "original" features). It may be that such new features are associated with the statistical distribution of composition of the packets of molecules referred to earlier; peaks are associated with packets occurring in high abundance. Although, as spectra 5 and 6 indicate, there is a suspicion of similar broadening of the "manganese" peak in the rhenium-rich compound, there seems little doubt that, in the transition from two-mode to intermediate mode behavior, the individual features associated with two-mode behavior may behave rather differently, in frequency, intensity, and contour.

^{13}CO-Enriched Iodopentacarbonylmanganese $Mn(^{12}CO)_{5-x}(^{13}CO)_xI$ ($0 \leq x \leq 5$)

Two ^{13}CO-enriched samples of $Mn(CO)_5I$ were prepared. The ^{13}CO concentrations in these samples were estimated to be approximately 15 and 33% based on a statistical analysis of the bands appearing in the solution infrared spectra, which showed that $x = 0, 1, 2,$ and 3 substituted species can occur. Raman spectra of polycrystals of both samples and the infrared spectrum of the second are illustrated in Figure 3.

The isotopic enrichment studies confirm the lack of vibrational coupling in the a_1(radial)-derived region, a multimode

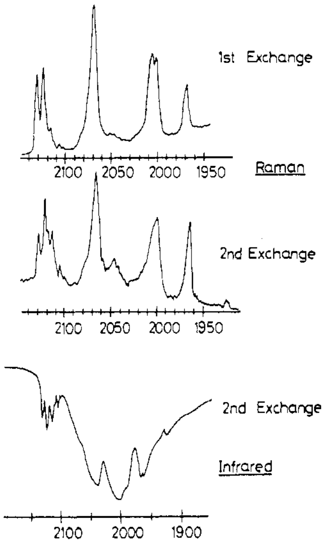

Figure 3. Room temperature Raman and infrared spectra of ^{13}CO-enriched crystalline $Mn(CO)_5I$ in the 2000-cm^{-1} region.

behavior being observed. Infrared and Raman coincidences occur, with similar intensity patterns and a peak count in accord with the number of species expected (but with neglect of site occupancy differences, in accord with previous observations). ^{13}CO isotopic frequency shifts are, in general, considerably greater than those associated with change in metal atom so that modes which in the latter situation display one-mode behavior may well show intermediate or even two-mode in the former. Evidently, the b_2-derived mode falls in the latter category. Comparison between Figures 1 and 3 shows that the dominant effect of ^{13}CO substitution on band c is one of broadening; a weak peak appears at ca. 2045 cm^{-1}, which may be indicative of additional putative two-mode behavior. The broadening of band c is indicative of intermolecular vibrational coupling, resolving the ambiguity of the mixed manganese–rhenium spectra. The ^{13}CO substitution spectra also show broadening in the a_1(axial)-derived region (band e in Figure 1); there are similarities with the mixed manganese–rhenium spectra, presumably another indication that for this mode near-two-mode behavior occurs.

The differences between the two a_1 regions are illuminating. In the absence of intermolecular vibrational coupling each molecular species gives a characteristic spectral feature. Its presence may be sufficient to swamp molecular frequency differences consequent on different extents of isotopic substitution and symmetries. In the intermediate case it may be possible only to define two regions: one, loosely, ^{12}CO and the other, equally loosely, ^{13}CO. It is by no means clear, for instance, whether the splitting on the ca. 2050-cm^{-1} band (Figure 3, first exchange) is in any way a parallel to that at ca. 2125 cm^{-1}. We incline to the view it is not.

Conclusion

Manganese and rhenium pentacarbonyl iodides provide an interesting example of the isomorphous substitution method used as a probe in vibrational spectroscopy. Their crystal structures are unknown, but the similarity of the vibrational spectra of their crystals led to the conclusion that they are isomorphous, a conclusion confirmed in that they form a continuous range of mixed crystals with vibrational spectra related to those of the pure components and subsequently by x-ray powder photography. Although the crystal infrared spectra are very broad and so yield little information, as is so often the case the Raman spectra of the pure crystals were correspondingly sharp. One method of testing for intermolecular vibrational coupling is a study of single-crystal Raman spectra; it is doubtful if such a study would be worthwhile in the present case because either the site symmetry is high or the effective vibrational site symmetry is high. The outcome is that the Raman spectra are very simple, the pure compounds showing no overt factor group splitting. Nonetheless, the combined use of metal atom and ^{13}CO isotopic replacement studies has led to a definite conclusion on the existence of intermolecular vibrational coupling in each of the Raman features. Only the infrared-active e-mode derived features remain undiscussed but the general breadth of the infrared spectra of the substituted crystals in the e-mode region surely implies that such coupling occurs. In any case it seems highly improbable that coupling should be manifest in Raman-active modes (where the coupling may be quadrupole–quadrupole) and not in the infrared where a dipolar mechanism is expected to dominate.

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Registry No. $Mn(CO)_5I$, 14879-42-6; $Re(CO)_5I$, 13821-00-6.

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