Vibrational Studies of the Cluster Carbonyls of Ruthenium and Osmium. Part 1. Raman Solution Data for $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$, and $[Ru_4H_4(CO)_{12}]$ in the CO Stretching Region

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Hitherto unobtainable Raman solution data for $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$, and $[Ru_4H_4(CO)_{12}]$ in the carbonyl stretching region are presented. The results were obtained by careful choice of solvent and specialist instrumentation. They are shown to confirm previous assignments, by examining the special vibrational properties of cluster compounds. Preliminary results for $[Ru_5C(CO)_{15}]$ are also given.

Recent publications [1-3] involving vibrational studies of metal cluster carbonyls have commented on the difficulty of obtaining Raman solution data for these compounds, although some resonance spectra have been obtained.[4,†] Whilst impressive attempts have been made to overcome this limitation, involving i.r. overtone-combination band spectroscopy,[1] isotopic and mixed-metal substitution with detailed calculations,[1] and i.r. dichroism of single crystals,[2] it is clear that Raman polarisation and intensity data would provide a much simpler and more direct route to vibrational assignment. For this reason we have re-investigated the possibility of obtaining Raman solution data. We have also carried out a single-crystal Raman and i.r. study of the carbonyl stretching region of $[Ru_3(CO)_{12}]$, partly with a view to using the (much more complicated) solid-state polarisation data, as an aid to assignment for the solution phase molecule of unperturbed symmetry (see following paper). We report success on both fronts, to the extent that previous assignments for the CO stretching region now rest on a much firmer basis. It is clear that Raman spectroscopy is a worthwhile technique for both new and existing compounds in this area.

Preliminary results for $[Ru_5C(CO)_{15}]$ are also given, but we were unable entirely to remove a fluorescent impurity from this compound.

Experimental

Choice of Solvent.—Since lack of sensitivity is a common reason for failure to obtain Raman spectra, it has been widely assumed that methylene chloride, in which these compounds exhibit the greatest solubility at room temperature, is an appropriate Raman solvent for them. However, it became clear that these solutions exhibit an intrinsic fluorescence background, which is actually a greater limitation. Not surprisingly, solvent molecules with more complicated structures and a wider range of vibrational modes are much more efficient at quenching this fluorescence. For this work we chose cyclohexane as an acceptable compromise between quenching and solubility (it is also widely used for i.r. work on these compounds), and worked at temperatures up to and in some cases above the boiling point. For the higher temperatures, cells were allowed to pressurise at 2—3 atm (atm $\approx 10^5$ N m^{-2}). It is probably preferable to introduce carbon monoxide (and hydrogen for hydrogenated complexes) as the buffer atmosphere, although this was not done in all cases. For $[Ru_4H_4(CO)_{12}]$, we were unable to work above the boiling point without an apparently autocatalytic decomposition setting in. This behaviour has been noticed previously for concentrated, boiling octane solutions.[5]

Our choice of solvent limited us to studying the metal-metal and carbonyl stretching regions, although it is possible that this limitation could be partly overcome with, for example, deuteriated solvents or more ' exotic ' materials. In cyclohexane, the final limitation on detectivity is the general Raman background continuum with individual features due to overtone and combination bands; we note that this is likely to be worse where heavier atoms are present.

Preparation of Compounds.—Compounds were prepared according to literature methods.[5,6] In the case of $[Ru_5C(CO)_{15}]$ it was necessary to recrystallise several times from cyclohexane to remove a fluorescent impurity; this process was probably not complete. Ethyl violet microscopical stain was purchased from Hopkin and Williams.

Raman Instrumentation.—Spectra were obtained on both conventional and multiplex instruments, with parameters matched as closely as possible to notional requirements. For critical experiments such as these, a given instrument and laser may not be sufficiently flexible, and some of our success must be attributed to the wide range of lasers, monochromators/spectrographs, and detectors available in this department. This applies to an even greater extent to multiplex experiments, where the dispersion of grating or prism must match requirements; widening the slit is not useful as it is with a single photomultiplier detector. This objection could be partly overcome with a purpose-built ' zoom ' image transfer system; camera systems are unfortunately of limited and variable through-put.

In all cases a Dallmeyer 63-mm uncoated double meniscus collection optic was employed, with nominal aperture *f*/1.1. Depolarisation ratios were obtained by using a $\lambda/2$ plate in the (polarised) laser beam: the method for minimum signal loss. The resulting ratio approximates ρ_n for natural light, with a maximum value of 6/7.

Low-resolution Multiplex Experiments.—In view of the dark colours and problematic photochemical stabilities of $[Ru_3(CO)_{12}]$ and $[Ru_5C(CO)_{15}]$, we decided to use a comparatively low power red helium-neon laser in these cases in particular (50 mW nominal; Spectra-Physics 125). For the solution spectra, the resolution was deliberately held down, and the light throughput kept up, by using a Hilger and Watts E612.304 $\frac{3}{4}$-m Double Quartz spectrograph. In this way the available light was spread over the minimum number of channels of a Tracor Northern Intensified Diode Array (TN 1223-3GI). The dispersion and detector spacing resulted in a final sampling interval of *ca.* 7 cm^{-1} per channel, giving a theoretical resolution (*ca.* $3\frac{1}{2}$ channels for crosstalk of various origins) of *ca.* 25 cm^{-1}, to which the entrance slit was matched. Although this is comparatively coarse, it was mitigated by the data-handling capability of the TN 1 710 mainframe. Thus a

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† Substantial resonance enhancement is probably limited to the metal cage vibrations, since this is the chromophore.

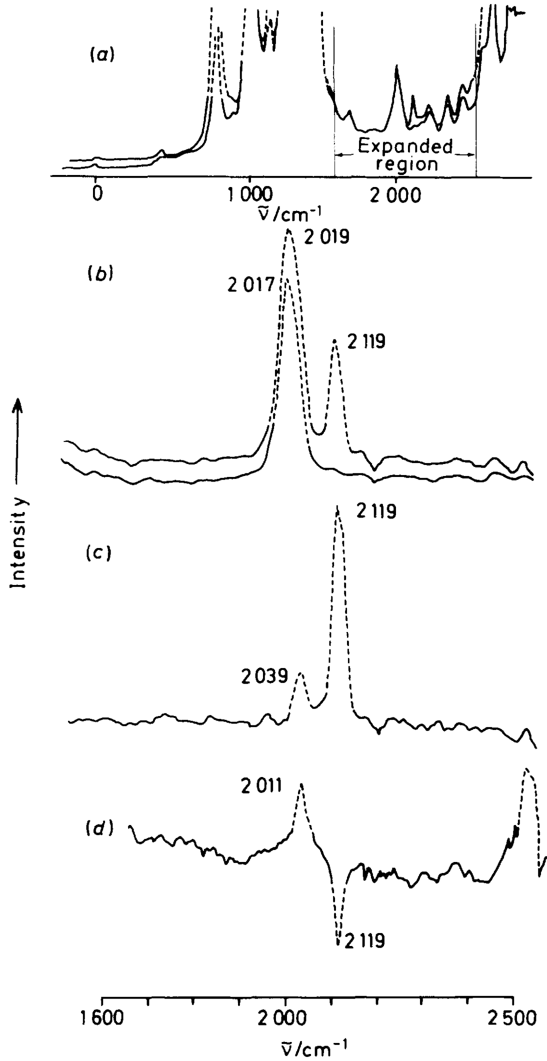

Figure 1. Raman solution spectra for $[Ru_3(CO)_{12}]$ in hot cyclohexane (*ca.* 90° C); 25 cm^{-1} resolution. (*a*) Unprocessed spectra; (*b*) CO stretching region with solvent background removed (upper trace = parallel spectrum, lower trace = perpendicular spectrum); (*c*) parallel spectrum with 7/6 perpendicular spectrum removed, giving position of polarised (p) bands; (*d*) perpendicular spectrum with spectrum (*c*) subtracted in ratio to give smoothest profile at 2 039 cm^{-1}, giving position of depolarised (dp) band

partially polarised band could be subtracted out of perpendicular spectra to leave only $\rho_n = 6/7$ features and *vice versa.* The solvent background could also be removed, although not in regions where it was of greater intensity than the solute spectrum.

This simple optical system requires a filter to remove the scattered laser light, and it was found that ethyl violet solution in isopropyl alcohol was particularly useful for the He/Ne line, cutting in sharply at about 800 cm^{-1}, and usable down to much lower shifts for intense lines.

Calibration was performed by removing the laser ' spike ' filter and superimposing the plasma lines on the spectrum. In this connection it should be noted that the laser contains ^3He, and the helium line at 728.1 nm therefore has an apparent Raman shift of 2 069.11 cm^{-1}, not 2 068.07 cm^{-1} as would be the case for ^4He. Other values were taken from Loader.[7] Calibration is not dependent on spectra output to the chart recorder. By appropriate manipulation of the cathode ray tube

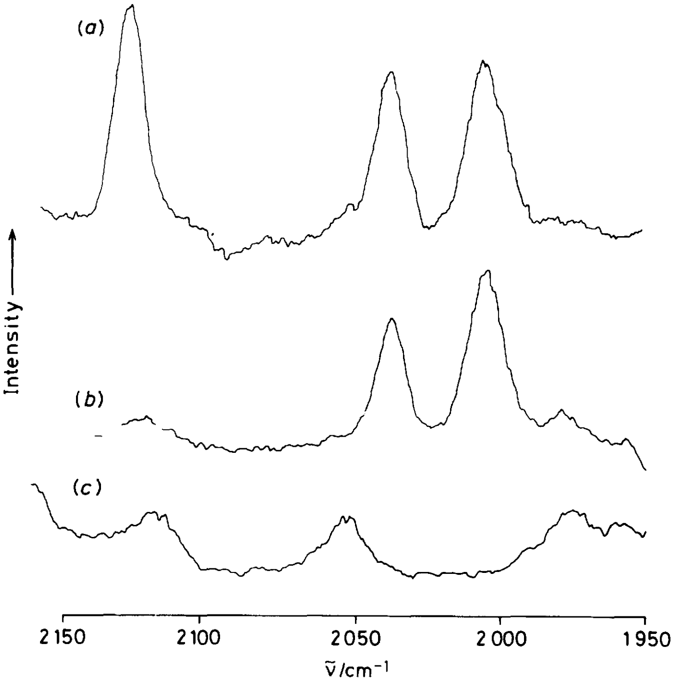

Figure 2. Raman solution spectra for $[Os_3(CO)_{12}]$ in hot cyclohexane (*ca.* 80 °C); resolution sample limited at *ca.* 10 cm^{-1}. (*a*) Parallel spectrum; (*b*) perpendicular spectrum; (*c*) parallel solvent background [perpendicular background is obvious in (*b*)]

display, positions were read to 0.2 channels or ± 1.5 cm^{-1}. Drift and non-linearities coarsened this to *ca.* ± 2 cm^{-1}.

Spectra taken using this system are shown in Figure 1.

The utility of the multiplex detector and data-handling system is evident in the clean background. We note however that the ultimate sensitivity of the intensified array does not at present match a good photomultiplier tube, which would therefore be the detector of choice for zero background (*e.g.* gas phase) spectra.

Scanning Raman System.—In the case of solutions able to withstand higher laser frequencies and powers {$[Ru_4H_4(CO)_{12}]$ and $[Os_3(CO)_{12}]$} we used a very conventional spectrometer system. Thus a double, rather than a triple monochromator, with ruled rather than holographic gratings, optimises throughput and provides adequate stray light rejection for solution spectroscopy. We used a 1-m Cary 81 monochromator, modified to have a conventional slit system, with gratings (1 200 lines per mm) blazed at 500 nm.

Our choice of laser was in this case unconventional, but there is no reason to suppose that a gas ion or Cu vapour laser would not produce equal results. We used a frequency doubled, Q switched Nd-doped Y–Al garnet laser with a 20-Hz repetition rate. The peak power used (dictated by the onset of non-linearities at the focus) was *ca.* 100 kW in the 10-ns pulse at 532 nm. Note that *average* power was *ca.* 40 mW, very little more than the He/Ne intensity at the sample.

This laser frequency was well suited to the compounds, the gratings, and the detector. The boxcar detection employed made it unnecessary to cool the photomultiplier tube, or indeed to shield the sample area.[8] This system is also noticeably more immune to electrical interference than a photon counter, and the surprisingly good signal-to-noise ratio for the laser power involved must be attributed to *complete* absence of ' dark noise '.

This spectrometer was calibrated carefully to ± 0.1 cm^{-1}

Table 1. Raman (this work) and i.r. (ref. 1) data (cm^{-1}) for the carbonyl stretching region of [$Ru_3(CO)_{12}$], with calculated values [1]

			Assignments	
			global	local
I.r.	Raman	Calculated	D_{3h}	C_{2v}
		1 994.5	e''	b_2 (axial)
		1 999.5	a_2'	b_1 (radial)
2 012.5m	2 011 ± 3 (dp)	2 012.5	e'	b_1 (radial)
2 018.7w		2 018.7	e'	a_1
2 031.3s br		2 031.3	a_2''	b_2 (axial)
	2 039 ± 3 ($\rho_n \approx 0.7$)	2 036.0	a_1'	a_1
2 061.2s		2 061.2	e'	a_1
	2 119 ± 2 ($\rho_n = 0$)	2 120.0	a_1'	a_1

Table 2. Raman (this work) and i.r. (ref. 1) data (cm^{-1}) for the carbonyl stretching region of [$Os_3(CO)_{12}$], with calculated values [1]

			Assignments	
			global	local
I.r.	Raman	Calculated	D_{3h}	C_{2v}
		1 987.0	a_2'	b_1 (radial)
		1 995.0	e''	b_2 (axial)
2 004.7	2 004.8 (dp)	2 004.7	e'	b_1 (radial)
2 015.6		2 015.6	e'	a_1
2 036.5		2 036.5	a_2''	b_2 (axial)
	2 037.3 ($\rho_n = 0.64$)	2 038.0	a_1'	a_1
2 069.0		2 069.0	e'	a_1
	2 128.2 ($\rho_n = 0$)	2 130.0	a_1'	a_1

with a neon lamp, and as may be seen, sufficiently well resolved lines indeed show this order of coincidence with calibrated i.r. frequencies. Spectra are shown in Figure 2.

Results

[$Ru_3(CO)_{12}$] *and* [$Os_3(CO)_{12}$].—These are shown in Figures 1 and 2 and Tables 1 and 2, where i.r. data and calculated frequencies for the carbonyl stretching region are also compared. It may be seen that only three ν(C–O) bands are observed in the Raman at the available sensitivity, $2a_1' + e'$. At first sight this is disappointing, but it is not inconsistent with a more detailed assessment of Raman activity (see Appendix). As shown there, the detailed assignment of Kettle and coworkers [1] is confirmed, with only the radial antisymmetric e' mode showing appreciable Raman activity. The depolarisation ratios of the a_1' modes confirm the conventional assignment to in-phase (higher frequency) and out-of-phase (lower). This is shown also in the single-crystal spectra for [$Ru_3(CO)_{12}$] (following paper) giving $c \approx -(a + b)$ for the out-of-phase mode.

The metal cage frequencies for [$Os_3(CO)_{12}$] were found at 158.9 (p) and *ca.* 113 (dp) cm^{-1} [*cf.* 158 (p) and 117 (dp) cm^{-1} previously reported [4]].

[$Ru_4H_4(CO)_{12}$].—Raman data for this compound were obtained on both instruments. The low-resolution multiplex spectra were of very high quality, superior to those for [$Ru_3(CO)_{12}$]. The high-resolution scanned spectra were poor in comparison to those of [$Os_3(CO)_{12}$], but still useful.

Table 3. Raman and i.r. solution data (cm^{-1}) for [$Ru_4H_4(CO)_{12}$]

		Assignment		
		global		local
I.r. (±0.1 cm^{-1})	Raman (±1 cm^{-1})	D_{2d}	T_d	C_{3v}
2 008.7w		e	f_1	
	2 023 (dp)	b_1	e	e
2 024.1s		e	f_2	
	2 029 (p) ($\rho_n \approx 0.6$)	a_1		
2 029.9m		b_2		
2 066.1vs		e	f_2	
2 080.6ms		b_2		a_1
	2 109 (p) ($\rho_n \approx 0.1$)	a_1	a_1	

Kettle *et al.*[3] have recently discussed the assignments and correlations for this molecule. As they point out, the Raman intensity correlations are not simple or straightforward. A treatment of the kind used for [$M_3(CO)_{12}$] would be complicated by the presence of independent components of the Raman tensor in the antisymmetric C_{3v} local mode, as well as the symmetric mode. The symmetry lowering effect of the hydrogen bridges ($T_d \longrightarrow D_{2d}$) would also be difficult to quantify.

The experimental results are given in Table 3, along with more precisely calibrated values for the i.r.-active modes than those currently available.[3] All five i.r.-active modes are seen, but only three of the eight Raman. Since totally symmetric D_{2d} modes are i.r. inactive, the 2 029—2 029.9 Raman–i.r. near coincidence must be accidental if D_{2d} symmetry is retained in solution. Unfortunately, the Raman spectra are not of high enough resolution to permit proper separation of the 2 023–2 029 pair for more accurate determination of frequency. Indeed the only clear evidence for the composite nature of this observed feature comes from manipulation of the very low resolution multiplex spectra. Following the arguments of Kettle *et al.*[3] we tentatively assign the 2 023–2 029 Raman doublet as the $b_1 + a_1$ pair arising from the e mode of T_d symmetry. From powder spectra, these were assigned to substantially lower frequency but also high-intensity bands in the solid state (2 001 + 2 010 cm^{-1}) by Kettle *et al.*[3] According to our results, they are (in solution) accidentally very close to the strongly i.r.-active ($e + b_2$) pair arising from the f_2 mode of T_d (itself of the same local C_{3v} e-mode origin). This would probably lead to substantial mixing and intensity redistribution in the (low symmetry) solid.

[$Ru_5C(CO)_{15}$].—The preliminary results obtained for this compound at low resolution suggest a very similar pattern of bands. Thus there is a high-frequency highly polarised band at *ca.* 2 110 cm^{-1}, and a broader, largely depolarised band, probably complex, at *ca.* 2 020 cm^{-1}.

Conclusions

The solution Raman data obtained for these low-solubility 'parent' compounds should pave the way for an increasing use of Raman spectroscopy in the chemistry of cluster carbonyl derivatives.

Appendix

Raman Activity and the Form of the Normal Vibrations for Cluster Molecules.—Cluster molecules, particularly those of high symmetry, possess some unusual vibrational properties. Since these appear not to have been described qualitatively (although a correctly formulated normal co-ordinate analysis contains them intrinsically) it seems worth attempting.

We consider in particular the $[M_3(CO)_{12}]$ molecules examined here. In this case the three $>M(CO)_4$ moieties have full local C_{2v} symmetry in the equilibrium geometry. This situation is formally identical to that in a molecular crystal, where largely autonomous molecular (or moiety) vibrations couple in symmetry-determined ways to give unit-cell (or global molecular) modes.[9] The only mechanism by which the local modes may lose their autonomy (that is, fail to conform to local symmetry requirements) is for that local symmetry to be perturbed by rotation or translation within a potential well. In a molecular crystal, that is another way of describing coupling with external or ' lattice ' modes; in an unbridged cluster the corresponding coupling is with skeletal modes of the metal cage, or with librations of a complete sub-molecule. In $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ these modes are in the region of 200 cm^{-1} or lower, so that it is unlikely that, for example, the carbonyl stretching vibrations at *ca.* 2 000 cm^{-1} will suffer this kind of perturbation. Note that no constraint is put upon the frequency separation of different global combinations, which can occur without upsetting the form of the vibration.

The correlations for local C_{2v} symmetry with global D_{3h} symmetry are as shown below (note that b_1 and b_2 labels are interchangeable for C_{2v}).

C_{2v}	D_{3h}
a_1	$a_1' + e'$
a_2	$a_1'' + e''$
b_1	$a_2'' + e''$
b_2	$a_2' + e'$

The carbonyl stretching local modes are $2a_1 + b_1$ (axial antisymmetric), $+b_2$ (radial antisymmetric). Thus the two a_1 modes, allowed to couple under local symmetry, will be extensively mixed to in-phase and out-of-phase radial/axial vibrations. The extent of that mixing will however remain closely similar for both the a_1' and e' global combinations. Where global modes have the same formal symmetry, but derive from local modes of different symmetry (*e.g.* e' modes derived from a_1 or b_2 under C_{2v}) the mixing will be negligible unless they attempt to fall very close; thus the radial antisymmetric stretch remains as such in its global e' combination. Kettle and co-workers[1] had already noted this behaviour, without discussing its origin.

Continuing to the M–C–O deformations, we find local modes classify as $2a_1 + 2a_2 + 2b_1 + 2b_2$. Here the second different origin combinations appear (e'' from a_2 and b_1 of C_{2v}), and coupling in this case is *via* librations. Thus the cage vibrations are limited to $a_1' + e'$; the moiety librations cover every D_{3h} species save the totally symmetric. There is one difference between translatory and libratory coupling; the former is to an extent forced by legitimate movement of the central atom within an autonomous local vibration, whereas this cannot occur for librations. The practical difference between these cases is probably small for relatively heavy central atoms like Ru and Os. Such slight movements do however constitute the formal mechanism by which global vibrations are kept in the proper phase locally.

A complete treatment would also consider thermal population of the low lying levels, akin to coriolis coupling in a freely rotating molecule.

Detailed Application to $[M_3(CO)_{12}]$.—*Carbonyl stretching modes.* The mode correlations in this case are shown below.

$$\begin{array}{lll}
C_{2v} & D_{3h} & \\
a_1 \longrightarrow & a_1' + e' & \text{(in-phase)} \\
a_1 \longrightarrow & a_1' + e' & \text{(out-of-phase)} \\
b_2 \longrightarrow & a_2' + e' & \text{(radial antisymmetric)} \\
b_1 \longrightarrow & a_2'' + e'' & \text{(axial antisymmetric)}
\end{array}$$

The only case for which the form of the Raman tensor is not entirely symmetry determined is the a_1. Using D_{3h} axes and the conventional Raman tensor notation,[9] we may see how the local mode (for the moiety best showing its symmetry with D_{3h} axes) correlates into the appropriate global modes. Thus applying the appropriate axis transformations T to the Raman tensor R as $R' = TRT^{t}$, followed by summing according to the linear combinations $\tau_{a_1'} = 3^{-\frac{1}{2}}(\tau_1 + \tau_2 + \tau_3)$, $\tau_{e'_a} = 6^{-\frac{1}{2}}(2\tau_1 - \tau_2 - \tau_3)$, and $\tau_{e'_b} = 2^{-\frac{1}{2}}(\tau_2 - \tau_3)$, gives the result shown below (leaving out overall scaling factors). Then

$$\underset{a_1\ (C_{2v})}{\begin{bmatrix} a & & \\ & b & \\ & & c \end{bmatrix}} \longrightarrow \underset{a_1'\ (D_{3h})}{\begin{bmatrix} (a+b) & & \\ & (a+b) & \\ & & 2c \end{bmatrix}} +$$

$$\underset{e'\ (D_{3h})}{\begin{bmatrix} (a-b) & & \\ & (b-a) & \\ & & 0 \end{bmatrix}\begin{bmatrix} & 0 & (a-b) \\ (a-b) & & 0 \\ & & 0 \end{bmatrix}}$$

to predict global Raman activity, we need to know the local values a, b, and c for both a_1 modes, and to predict local activity for the two antisymmetric modes.

For the high-frequency in-phase a_1 mode, we have observed $\rho = 0$ within experimental sensitivity for both Ru and Os. This implies $2c = a + b$, and most likely that $a = b = c$, so the e' combination is not expected to show Raman activity at the same sensitivity. For the out-of-phase mode, it remains plausible that a and b, the two in-plane components, should be equal, and this again leads to zero or near zero activity for the e' component. For the two antisymmetric modes, we see that the axial mode, with the bonds opposite each other, may well show zero polarisability change [*cf.* trigonal bipyramidal $M(CO)_5$, where this is a rigorous symmetry requirement]. The radial mode however, is likely to show net activity.

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