Vibrational Spectroscopy at Very High Pressures. Eclipsed Decacarbonyldimanganese and Decacarbonyldirhenium

By DAVID M. ADAMS,* PETER D. HATTON, ANDREA C. SHAW, and TIONG-KIE TAN
(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH)

Summary Solid state phase transitions have been discovered in $Mn_2(CO)_{10}$, (*ca.* 8 kbar), and $Re_2(CO)_{10}$, (*ca.* 5 kbar) and the Raman spectra are consistent with a change in molecular geometry from staggered to eclipsed.

THE metal–metal bonded carbonyls $M_2(CO)_{10}$, (M = Mn, Re), crystallise with the two sets of equatorial carbonyl groups in the staggered configuration, the symmetry of each molecule being close to D_{4d}.[1,2] We have found that at high hydrostatic pressures the vibrational spectra of both solids show dramatic reversible changes, Figure. For M = Mn the transition pressure is near 8 kbar [1 kbar = 0·1 GPa = 10^8 N m^{-2}] whilst for M = Re it is near 5 kbar. The experiments were carried out in a diamond anvil high-pressure cell using techniques described in full elsewhere.[3] A metal gasket was placed between the diamond anvils. The solid under investigation was within a pressure-transmitting fluid which filled the gasket hole (initially 0·4 mm diameter, 0·1 mm deep); pressures on the solid samples were therefore hydrostatic and were estimated using the ruby R-line method. I.r. spectra were also obtained for the region 400—1800 cm^{-1} but the ν(CO) modes could not be investigated as diamond is black in that region.

The spectra show that two changes have occurred. Firstly, the major differences in the region of the libratory and translatory lattice modes show that a phase change has occurred and that the molecules have been packed in a new way. Secondly, the major changes in all regions associated with molecular internal modes witness to a modification of molecular structure.

The high pressure spectra can be accounted for on the basis of a transition to the D_{4h} eclipsed form. Considering only the ν(CO) modes, the selection rules for the two forms are related as shown in the Table. In the normal crystalline form ($C2/c = C^6_{2h}$, $Z = 4$) the degeneracy of the E_2 and E_3 ν(CO) modes is lifted by the site field. Together with correlation coupling between the two molecules in the primitive unit cell, this leads to a doublet ($A_g + B_g$) appearing in the Raman spectrum for each of these two E modes. Detailed assignments have been made of both Raman[4] and i.r.[5] spectra from single-crystal experiments.

TABLE

$D_{4d} \xleftarrow{\times 2}$	C_{4v}, M(CO)$_5$ $\xrightarrow{\times 2}$	D_{4h}
$A_1{}^a + B_2$	A_1 (axial)	$A_{1g}{}^a + A_{2u}$
$A_1{}^a + B_2$	A_1 (equatorial)	$A_{1g}{}^a + A_{2u}$
$E_2{}^a$	B_1	$B_{1g}{}^a + B_{2u}$
$E_1 + E_3{}^a$	E	$E_g{}^a + E_u$

[a] Raman-active.

For the eclipsed isomer (D_{4h}), only *one* of the four Raman-active molecular ν(CO) modes is degenerate. In particular, in a D_{4d} to D_{4h} transformation it is the E_2 doublet, centred initially at 2020 cm,$^{-1}$ which should collapse to a single band; this is precisely what is observed. Three further bands are found in the high-pressure phase ν(CO) spectrum below 2000 cm^{-1}; these are attributed to the A_{1g}(axial) and E_g modes, the latter being split by site and correlation coupling, as in the ambient phase.

If the phase transition involved repacking the molecules with retention of the initial (D_{4d}) structure, it would be necessary to find a site symmetry which lifted the E_3 degeneracy but not that of the E_2 mode; no sub-group of D_{4d} has this property. We conclude that the high-pressure forms of these two carbonyls have eclipsed geometry.

At the phase transition in $Re_2(CO)_{10}$, the axial ν(CO) mode drops by 8 cm^{-1}. Concurrently, the band initially at 476 cm^{-1}, and known to arise from a totally symmetric ν(Re–C) mode, shifts upwards by 17 cm^{-1}. This implies that in becoming eclipsed the back bonding from rhenium to the axial carbonyl groups is sharply increased. The phase transition in $Mn_2(CO)_{10}$ causes no discontinuity in ν(Mn–Mn). We note, *en passant*, a claim that $Re_2(CO)_{10}$ has the eclipsed structure in the gas phase,[6] in contrast with $Mn_2(CO)_{10}$ which has staggered geometry under the same conditions.[7]

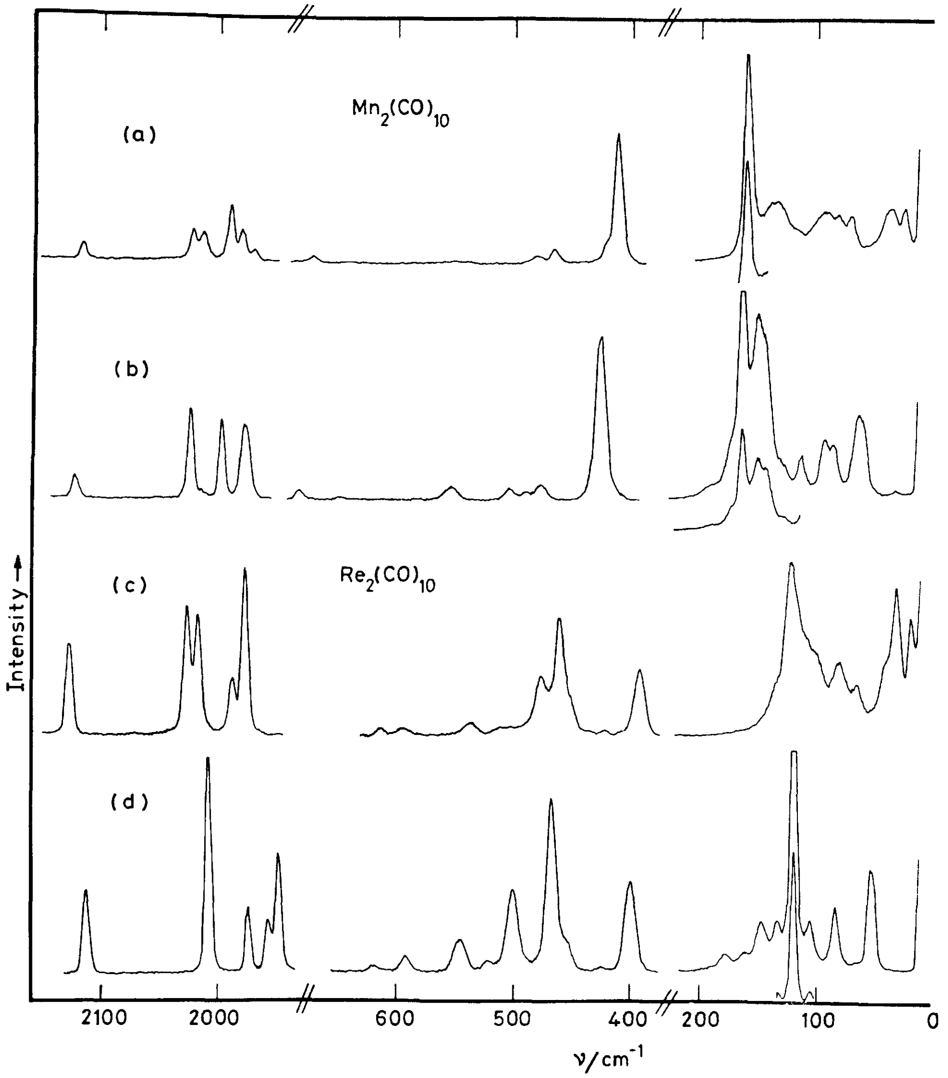

FIGURE. Raman spectra of $Mn_2(CO)_{10}$ at (a) ambient pressure, (b) 16 kbar, and of $Re_2(CO)_{10}$ at (c) ambient pressure, (d) 16 kbar, in a diamond anvil cell.

Both carbonyls show two further phase transitions, visible as Becke lines, below 150 kbar. Phases III and IV of $Re_2(CO)_{10}$ are light yellow in colour. Above about 70 kbar the behaviour of $Re_2(CO)_{10}$ is dependent upon its state of purity. All samples show some apparently irreversible darkening to yield an orange-brown or red material, but the intensity of the darkening appears to depend upon the purity of the sample, being least with freshly sublimed $Re_2(CO)_{10}$. We are currently investigating these effects.

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