167. *Infrared Spectra of Manganese Carbonyl Hydride and Deuteride.*

By F. A. Cotton, J. L. Down, and G. Wilkinson.

Infrared spectra of gaseous $HMn(CO)_5$ and $DMn(CO)_5$ in the range 3000—400 cm.$^{-1}$ are reported and discussed. The molecule appears to have very low symmetry, as Wilson also concluded, but the present interpretation of isotopic shifts differs significantly from Wilson's interpretation, notably in the assignment of the band at 1783 cm.$^{-1}$ in $HMn(CO)_5$ and the Mn–H stretching frequency.

The nuclear resonance spectrum of the hydride at 40 Mc./sec. shows a single peak at −13·0 parts per million due to a highly shielded proton such as those in other metal carbonyl hydrides.

Hieber and Wagner [1] have recently described the preparation of manganese pentacarbonyl hydride and some chemical and physical properties. In particular they found it to be scarcely acidic [in contrast to $HCo(CO)_4$ and $H_2Fe(CO)_4$] and their physical data suggest that the $Mn(CO)_5^-$ skeleton probably has a structure quite similar to that of iron pentacarbonyl.

The infrared spectra of gaseous manganese pentacarbonyl hydride and deuteride in the frequency range 3000—400 cm.$^{-1}$ have been studied. Although it was originally intended to examine also the region from 400 to 275 cm.$^{-1}$, the appearance of a paper by Wilson,[2] who has studied this region as well as the range which we have examined, has made this unnecessary. For the most part, Wilson's results for the hydride are in agreement with ours; however, his results for the deuteride were not given in detail and it appears from his discussions of the comparison of the spectra of the hydride and deuteride that there are errors in his data for the latter and thus also in his interpretation of the isotopic shifts.

Spectrum of Manganese Pentacarbonyl Hydride.—Present observations are listed in Table 1, together with those of Wilson for comparison. The agreement between the two sets of data is excellent. Wilson has bracketed together various groups of peaks in the 2150—1950 cm.$^{-1}$ range to indicate what he considers to be P, Q, and R, or P and R components of vibrational transitions. Our data are not inconsistent with such groupings but cannot be said to require them; they could conceivably be grouped in other ways. However, in any event, the complexity of the spectrum in this region makes it fairly certain that the molecular symmetry is very low, and definitely lower than C_{4v} such as the spectra [2] suggest for $XMn(CO)_5$ when X is halogen, or the pseudo C_{4v} when X is methyl. Wilson reached the same conclusions.

[1] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13b**, 339.
[2] Wilson, *ibid.*, p. 349.

It is not unreasonable to assume that the $Mn(CO)_5$ unit will adopt the same arrangement as $Fe(CO)_5$ and that the subsequent attachment of the proton will not seriously alter this geometry. Such an approach can be justified by analogy with the series $H_2Fe(CO)_4$, $HCo(CO)_4$, $Ni(CO)_4$, all of which have a tetrahedral $M(CO)_4{}^{n-}$ ($n = 2, 1, 0$) skeleton, and, in two of which, protons are affixed with little distortion. Two structures have been suggested for iron pentacarbonyl—the square pyramidal and the trigonal bipyramid. Although an infrared study [3] has suggested that the former is correct, Lippincott's studies [4] and other infrared and Raman spectral evidence [5] to be described shortly favour the latter model, which was originally proposed by Ewens and Lister [6] on the basis of electron-diffraction studies. If iron pentacarbonyl and hence also the $Mn(CO)_5$ unit have a square pyramidal structure, the proton might be introduced into the skeleton in several ways. It has already been concluded that it is unlikely to lie along the fourfold axis but it could, for instance, lie along a line from the manganese atom through a triangular face or through an edge of the pyramid. No such structure could have a symmetry higher than C_s and would thus have five infrared-active carbonyl stretching fundamentals.

TABLE 1. *The infrared spectra of* $HMn(CO)_5$ *and* $DMn(CO)_5$.

HMn(CO)₅		DMn(CO)₅	HMn(CO)₅		DMn(CO)₅
Wilson	Authors		Wilson	Authors	
4142 (w)			2000 ⎫	2000 ⎫	2000 ⎫
4069 (w)			1994 ⎬(vs)	1995 ⎬(vs)	1994 ⎬(vs)
4021 (w)			1900 ⎭	~1900 (sh) ⎭	~1900 (sh) ⎭
2594 (w)	2588 (w)	2583 (w)	1978 (m)	1979 (m)	1976 (m)
2527 (w, sh)	(a)		1938 (m)	1940 (m, b)	1936 (m, b)
2514 (w)	2506 (w)	2509 (w)			1829 (vw)
2490 (w)	2482 (w)	2478 (w)			1801 (w)
2459 (w) ⎱	~2441 (w, vb)	⎧2451 (w)	1785 (m)	1783 (m)	1783 (vw)
2445 (w) ⎰		⎩2437 (w)			1614 (w)
2400 (w)	2393 (w)	2392 (w)	1269 (w)	1271 (w)	1290 (m)
2375 (w)	(b)	2350 (vw)			1236 (w)
2231 (w)	2232 (w)	2230 (w)	1183 (w)	1179 (w, b)	1205 (w)
2221 (w)	2226 (w)	2224 (w)	1106 (w)	1103 (w)	1190 (w)
2199 (w)					1074 (w)
2148 (w)	2151 (w)	2150 (w)	1021 (w)	1020 (w)	1019 (w)
2128·5 ⎫	2130 ⎫	2130 ⎫	989 (w)	984 (w)	989 (w)
2124·0 ⎬(m)	2125 ⎬(m)	2124 ⎬(m)	915 (w)	916 (w)	891 (w)
2118·5 ⎭	2120 ⎭	2118 ⎭	859 (w)	855 (w)	855 (w)
2100·5 ⎫			760 (w)	760 (w, sh)	794 (w, sh)
2095·5 ⎬(m)	2101 ⎱(m)	2103 ⎱(m)	730 (vs)	730 (vs)	726 (m)
2090·0 ⎭	2097 ⎰	2096 ⎰	688 (w)	~685 (vvw)	
2064 (w)	2069 (w)	2067 (w)	669 (vs, sh)	668 (sh)	670 (vs)
2052 ⎱(m, sh)	2051 (m)	2052 (m, sh)	663 (vs)	658 (vs)	650 (vs)
2046·5 ⎰	2045 (m)	2047 (m)	612 (vs)	610 (vs)	606 (mw)
2033·5 ⎱(vvs)	2036 (vvs)	2034 (vvs)	558 (w)		
2028 ⎰	2029 (vvs)	2029 (vvs)	535 (w)	532 (vw)	536 (w)
2025·5 ⎫	2023 ⎱	2025 ⎫	506 (w)	503 (vw)	511 (mw)
2020·5 ⎬(vvs)	2016 ⎰(vvs)	2020 (sh) ⎬(vvs)	484 (s) (c)	454 (s)	452 (s)
2015 ⎭		2015 ⎭			

(a) The shoulder reported by Wilson is present in our spectrum but too poorly resolved for its frequency to be measured accurately.

(b) This region obscured by CO_2 absorption.

(c) The band listed by Wilson at 484 cm.$^{-1}$ does not appear in our spectra or in Fig. 1 of his paper. The latter does, however, show a strong peak at 21·7 μ (462 cm.$^{-1}$). We assume, therefore, that the figure 484 listed in his table is a typographical error.

For the more probable trigonal bipyramidal structure the proton might lie on lines from the manganese atom to the centre of a face, or to the centre of a slant edge (in both cases the symmetry is C_s), or on a line to the centre of an equatorial edge: the symmetry

[3] O'Dwyer, *J. Mol. Spectroscopy*, 1958, **2**, 144.
[4] Fately and Lippincott, *Spectrochim. Acta*, 1957, **10**, 8.
[5] (a) Stammreich, personal communication, to be published shortly; (b) Cotton, Danti, Fessenden, and Waugh, *J. Chem. Phys.*, in the press.
[6] Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.

would then be C_{2v}. In all these cases, however, there would be five infrared-active carbonyl stretching modes.

Hence, while we can probably rule out a C_{4v} structure, as Wilson has noted, it is impossible from analysis of C–O stretching frequencies to decide among a number of other less symmetric structures. The remainder of the spectrum provides no definite structural information since few other band assignments can be made with any certainty.

The Spectrum of Manganese Pentacarbonyl Deuteride.—Since $DMn(CO)_5$, like other carbonyl deuterides, exchanges with traces of water, care is required to obtain an authentic spectrum, and, at the same time, to interpret the results. The spectra (Table 1) indicate that the samples contained some hydride (perhaps 5—15% in various samples).

The most important point of divergence of our results and conclusions from those of Wilson concerns the band at 1783 cm.$^{-1}$ in the hydride. Our spectra indicate that this band shifts on deuteration to 1290 cm.$^{-1}$, the ratio of frequencies being 1·38. There is no indication that any band of higher frequency shifts on deuteration. Hence we may conclude that the 1783 cm.$^{-1}$ band is due to a vibrational mode involving hydrogen. If the hydrogen is bound closely to the metal atom, as seems probable,[7-9] then this mode is most reasonably assigned as an Mn–H stretching vibration. In the only other carbonyl hydride studied, cobalt tetracarbonyl hydride,[7,10] the highest frequency observed to shift on deuteration, and thus assigned to a mode involving appreciable motion of the hydrogen atom, is that at 703 cm.$^{-1}$; it may be noted, however, that the manganese carbonyl hydride is considerably more stable thermally and chemically than is the cobalt compound, and the metal–hydrogen bond may reasonably be assumed to be stronger.

According to Wilson, the band at 361 cm.$^{-1}$ in the spectrum of the hydride is shifted to 326 cm.$^{-1}$ in that of the deuteride, the ratio of frequencies being 1·11; two more shifts in the middle-frequency region are from 730 to 674 (1·08) and from 612 to 518 (1·18). We find, however, that some rather unusual intensity changes accompany the latter. The region 400—750 cm.$^{-1}$ was carefully studied, the best sample of the deuteride [≤5% of the hydride] being used, and the relative intensities reported in Table 2 were calculated from plots of $(\log I_0/I)/lp$ against wavenumber (cm.$^{-1}$), where l, the cell length, was 10 cm., and p, the sample pressure, was 20 mm. for both hydride and deuteride. The band at 453 ± 2 cm.$^{-1}$ appears to be independent of isotopic substitution and has therefore been used as the reference of intensities in Table 2.

TABLE 2. *Relative intensities of principal peaks in the range* 400—750 *cm.*$^{-1}$.

HMn(CO)₅		DMn(CO)₅		HMn(CO)₅		DMn(CO)₅	
cm.$^{-1}$	Rel. intensity	cm.$^{-1}$	Rel. intensity	cm.$^{-1}$	Rel. intensity	cm.$^{-1}$	Rel. intensity
454	1	452	1	$\{^{658}_{668}\}$	1·22	$\{^{\sim650}_{\sim670}\}$	2·55
—	—	511	0·14	730	1·61	726	0·43
610	1·33	606	0·17				

The following explanation of the frequency shifts and concomitant intensity changes is proposed. In manganese pentacarbonyl deuteride there is a weak band at $\sim$511 cm.$^{-1}$ and a strong one at $\sim$670 cm.$^{-1}$ of the same symmetry species (say X) and there are bands at 650—660, $\sim$670, and $\sim$726 cm.$^{-1}$, all of symmetry species other than X. The weak band at 511 cm.$^{-1}$ in the deuteride is shifted up in the hydride so that it becomes degenerate or nearly so with the strong band of species X at about 670 cm.$^{-1}$. Strong, first-order coupling between the two causes the appearance of two bands of comparable intensities at $\sim$730 and 610 cm.$^{-1}$. The peak observed at $\sim$606 cm.$^{-1}$ in the spectrum of the deuteride is thus considered to be due solely to the hydride in our sample. Since the intensity of the band at $\sim$726 cm.$^{-1}$ observed in our deuteride sample did not decrease relative to the

[7] Cotton and Wilkinson, *Chem. and Ind.*, 1956, 1305.
[8] Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 4425.
[9] Bishop, Down, Richards, and Wilkinson, unpublished work.
[10] Edgell, Magee, and Gallup, *J. Amer. Chem. Soc.*, 1956, **78**, 4185.

730 cm.$^{-1}$ band in the hydride as much as did the ~606 cm.$^{-1}$ band relative to the ~610 cm.$^{-1}$ band in the hydride, we believe that both hydride and deuteride have a band of medium to weak intensity and of symmetry species other than X at ~726 cm.$^{-1}$. The ratio (RD/RH) of the total intensity of the shifted bands in the deuteride to that of their counterparts in the hydride is difficult to estimate accurately owing to overlapping with isotope-independent bands, but is 0·6—0·8, which is qualitatively to be expected. We are thus in superficial agreement with Wilson as to his reported 730—674 cm.$^{-1}$ and 612—518 cm.$^{-1}$ shifts, but believe that the relations are more complicated than his discussion implies when the intensity changes are considered.

Whether the molecular symmetry of manganese pentacarbonyl hydride is C_{2v} or C_s, it appears that there must still be other bands of the same symmetry species as the 361 cm.$^{-1}$ band which are appreciably shifted upon deuterium substitution. The internal co-ordinates of the hydrogen atom must contribute to three symmetry co-ordinates, which, in the case of C_{2v} symmetry, would all be of different symmetry classes. For each of these there should be a set of bands whose shift ratios when multiplied together give a product a little less than 1·41, according to the Teller–Redlich theorem (and allowing for the effects of translations and anharmonicities). The 1785—1290 shift can, by itself, be one of these sets (ratio ~1·38) and the two shifts 730—670 and 610—511 with a product of ratios of ~1·30 can account for most of a second. The shift 361—326 (ratio 1·11) reported by Wilson would seem therefore to be a contributor to the product of shift ratios in a third set, since both $1·30 \times 1·11 = 1·43$ and $1·38 \times 1·11 = 1·53$ exceed 1·41. Presumably, one or more shifts of bands belonging to the same symmetry species as the 361 cm.$^{-1}$ band remain to be found, and one may be due to a mode which involves very considerable motion of the hydrogen atom. Such a band or bands probably lie below 300 cm.$^{-1}$. In the case where manganese pentacarbonyl hydride has C_s symmetry the argument is changed in detail but the same conclusion is drawn.

Proton Resonance Spectrum.—The nuclear resonance spectrum at 40 Mc./sec. of manganese pentacarbonyl hydride consists of one line at 519·5 c./sec. (13·0 parts per million) on the high-field side referred to water at 22°. Thus it can be concluded that the proton in the hydride is in an environment qualitatively similar to that of the protons in HCo(CO)$_4$ and H$_2$Fe(CO)$_4$ for which shifts of $15·5 \pm 2·0$ [11] and $15·6 \pm 0·5$ parts per million,[7] respectively, have been observed.

EXPERIMENTAL

Preparation of Samples.—Manganese carbonyl, Mn$_2$(CO)$_{10}$, was treated with aqueous potassium hydroxide in a nitrogen atmosphere to form a solution of KMn(CO)$_5$. On addition of a slight excess of dilute sulphuric acid the hydride was liberated. It was slowly swept out of the reaction vessel and through a column of calcium chloride with a stream of nitrogen and collected in a trap cooled with solid carbon dioxide. It was then further purified by several trap-to-trap distillations on a vacuum line.

In order to prepare the deuteride, the hydride (prepared as described above) was distilled into a solution of sodium deuteroxide in deuterium oxide and the solution set aside for 12 hr. The deuterium oxide was then pumped off, fresh deuterium oxide (99·5% D$_2$O) condensed on the solid sodium compound, and the solution stored for several hours. Acidification was with a solution of deuterium chloride in deuterium oxide, prepared by hydrolysis of boron trichloride in deuterium oxide. The deuteride was then swept out with dry nitrogen and subjected to several trap-to-trap distillations to give a product of m. p. ~−21°. Care was taken to dry all apparatus with which manganese pentacarbonyl deuteride came into contact.

Infrared Spectra.—Gaseous samples were examined in 10-cm. cells equipped with potassium bromide windows. Gas pressures were generally of the order of 20—28 mm. except when the intense carbonyl peaks were examined, for which they had to be considerably reduced. The entire spectrum of each compound was studied by using a Perkin-Elmer model 21 double-beam spectrometer with sodium chloride and potassium bromide prisms. The CO stretching region

[11] Gutowsky, quoted by Sternberg *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

was studied with a modified Grubb-Parsons double-beam spectrometer with a lithium fluoride prism.

Special precautions were taken to eliminate water vapour from the cell and auxiliary apparatus when studying the deuteride. The cell was repeatedly treated with deuterium oxide vapour (several times overnight), followed by evacuation, before being filled with the deuteride. In certain cases, as noted in the Discussion, pressures in the cell were measured fairly accurately for comparing intensities of bands in the spectra of the two compounds.

Proton Resonance Spectrum.—The spectrum of the hydride containing a trace of 1 : 2-dimethoxyethane was recorded by using a Varian Associates Model V-4300B high-resolution spectrometer and the conventional techniques. The ether proton line, used as an internal standard, was then referred to water at $22° \pm 1°$. Measurements were made at 40 Mc./sec.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
    IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
        LONDON, S.W.7.
DEPARTMENT OF CHEMISTRY,
    MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
        CAMBRIDGE 39, MASS.