can be explained by at least three factors which cannot be separated. (1) Hyperconjugation effects in the amine adducts should be smaller. There are two vacant p orbitals in monomeric $(CH_3)_2Be$, only one in monomeric $(CH_3)_2BeN(CH_3)_3$, and none in $(CH_3)_2Be(N(CH_3)_2CH_2)_2$. (2) There is a change in hybridization from sp in $(CH_3)_2Be$ and sp^2 in $(CH_3)_2BeN(CH_3)_3$ to sp^3 in $(CH_3)_2Be(N(CH_3)_2CH_2)_2$. (3) There is also an inductive effect due to coordinated nitrogen which will affect the Be–C bond strength.

Acknowledgment.—We are indebted to the National Science Foundation for support of this work under Grant GP-8595.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA

The Infrared Spectrum and Vibrational Assignments for Pentacarbonylmanganese Hydride[1]

BY WALTER F. EDGELL, JACK W. FISHER, GORO ASATO, AND WILLIAM M. RISEN, JR.[2,3]

Received August 2, 1968

The infrared spectrum of pure $HMn(CO)_5$ in the region 4000–300 cm^{-1} has been obtained in the vapor phase. The observed spectrum has been analyzed to distinguish the fundamental frequencies, the rotational–vibrational band structure, and overtone and combination frequencies. An assignment of the observed vapor-phase frequencies to the fundamental modes of vibration has been made based on C_{4v} symmetry, which the $-Mn(CO)_5$ moiety is known to possess in the solid state. The positions of middle-frequency bands of $DMn(CO)_5$ are reported and used to test the C_{4v} assignment with the Teller–Redlich isotope product rule. It is shown that it is not necessary to assume lower than C_{4v} symmetry for $HMn(CO)_5$, as has been done in all previous considerations of the entire infrared spectrum of $HMn(CO)_5$.

Introduction

Since the initial report[4] of its preparation, the nature of the compound $HMn(CO)_5$ has been the subject of a number of studies. Investigation of the vapor-phase infrared spectrum led Cotton, Down, and Wilkinson[5] and Wilson[6] to the conclusion that the molecular symmetry is definitely lower than C_{4v}, although no vibrational assignments were made. Subsequently, however, La Placa, Hamilton, and Ibers[7] showed that $HMn(CO)_5$ crystallizes such that the $Mn(CO)_5$ moiety does have C_{4v} local symmetry in the solid state and suggested that it is unlikely that it would assume lower symmetry in the vapor phase. This structure determination prompted Huggins and Kaesz[8] to report a prior interpretation[8b] of the C–O stretching region (1900–2200 cm^{-1}) of the solution spectrum of $HMn(CO)_5$ based upon C_{4v} symmetry. Kaesz and coworkers[9] subsequently reported the study of several isotopic analogs of $HMn(CO)_5$ in the same spectral region (1900–2200 cm^{-1}). In addition, Davison and Faller[10] have reported the observation of the 1700–2200-cm^{-1} region of the Raman spectrum of $HMn(CO)_5$ and one band outside of this region.

However, these studies do not solve the problem of the apparent disparity between the X-ray results[7] and previous infrared data,[5,6] which include measurements at frequencies lower than those of the 5-μ region (1900–2200 cm^{-1}). This problem arises only partly from the spectral complexity of the 5-μ region. Its more difficult aspect concerns understanding the middle- and low-frequency modes which compose eleven ($4\ A_1 + 7\ E$) of the fifteen ($7\ A_1 + 8\ E$) infrared-active vibrational frequencies. Since the spectra of both $HMn(CO)_5$ and its deuterated analog, $DMn(CO)_5$, are identical in the 5-μ region, it is only with the remainder of the spectrum that a C_{4v} assignment can be tested by the Teller–Redlich isotope product rule.

In order to resolve this disparity, we have reinvestigated the infrared spectrum of gaseous samples of $HMn(CO)_5$ which are known to be pure, so that no bands due to impurities are taken as indications that it has lower than its true symmetry.

We report here the high-resolution spectrum of highly pure, gaseous $HMn(CO)_5$ in the region 4000–300 cm^{-1}, we propose a vibrational assignment of the infrared-active modes of $HMn(CO)_5$, based upon C_{4v} symmetry, and we test this assignment by the isotope product rule using the reinvestigated high-resolution spectrum, in the middle-frequency region (800–300 cm^{-1}), of the deuterated analog $DMn(CO)_5$.

---

[1] Abstracted from the Ph.D. Thesis of W. M. Risen, Jr., Purdue University, 1967.

[2] Monsanto Predoctoral fellow, 1965–1966.

[3] Department of Chemistry, Brown University, Providence, R. I. 02912

[4] W. Hieber and G. Wagner, *Z. Naturforsch.*, **12b**, 47 (1957); **13b**, 339 (1958).

[5] F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

[6] W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958).

[7] S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

[8] (a) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964); (b) D. K. Huggins, Ph.D. Thesis, UCLA, 1963.

[9] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

[10] A. Davison and J. W. Faller, *Inorg. Chem.*, **6**, 845 (1967).

Experimental Section

The preparation of $HMn(CO)_5$ was carried out as described earlier by Edgell and Risen,[11] the purity being verified by mass spectral analysis. The infrared spectrum of $HMn(CO)_5$ was measured in the spectral region 4000–300 cm^{-1}. The spectra in the region 4000–550 cm^{-1} were measured with a Perkin-Elmer Model 421 spectrophotometer. The spectrum in the region 800–300 cm^{-1} was investigated using a Beckman IR-11 far-infrared spectrophotometer. All spectra were calibrated against known frequency standards[12,13] and the band positions are accurate to better than 1 cm^{-1} throughout and to better than 0.5 cm^{-1} in the 5-μ region.

The infrared spectrum of HMn(CO) at 0.5 mm in the 5-μ region is shown in Figure 1. The dashed line is a construct discussed below. The spectrum in the middle-frequency region (800–300 cm^{-1}) is shown in Figure 2.

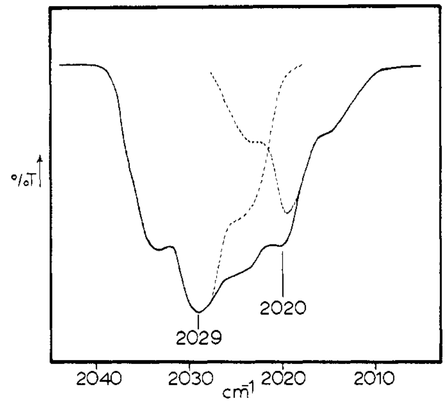


Figure 1.—The $HMn(CO)_5$ spectrum observed at 0.05 mm in a 10-cm KBr cell and the 5-μ region. Dashed lines indicate constructs of the overlapping bands.

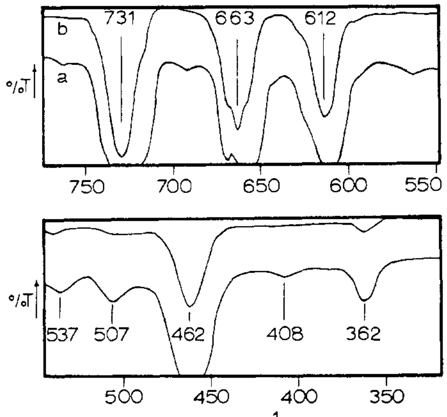


Figure 2.—The observed $HMn(CO)_5$ spectrum in the 800–300-cm^{-1} region, at (a) 19 mm and (b) 4 mm, with a 10-cm path length.

The frequencies of the absorption maxima not shown in the figures, as well as those shown, together with a qualitative indication of the attendant intensity of each, are given in Table I.

The Observed Spectrum

We report in Table I the 67 observed maxima and shoulders in the 4000–300-cm^{-1} infrared spectrum. It is of course to be expected that in the spectrum of a gaseous sample extensive vibrational–rotational band structure will be evident. It is also to be expected in the case of a molecule having several important vibrations close together in frequency that there will be significant band overlapping. Both of these factors are so significant in the present case that it is necessary to consider carefully the observed spectrum in order to determine which of the many maxima actually correspond to centers of vibrational bands, fundamental, combination, or overtone. The results of such analyses are given in Table I, but several details demand comment. One group of bands, in the region 2010–2040 cm^{-1}, is, as shown in Figure 1, very much more intense than any other in the 5-μ spectral region. Peaks occur at 2015, 2020, 2024, 2029, and 2033 cm^{-1}. This structure can, as suggested earlier by Edgell, *et al.*,[14] be seen to arise from two overlapping vibration–rotation bands, each with PQR structure. The dashed line in Figure 1 is a construct of two such bands, having their Q branch centers at 2029 and 2020 cm^{-1}.

Both Cotton, *et al.*,[5] and Wilson[6] reported observing a strong band at 1900 cm^{-1}. In Wilson's paper, in which spectra are shown in figures, there is apparently a typographical misprinting of a 1990-cm^{-1} band illustrated. There is no band at 1900 cm^{-1}.

The 300–800-Cm^{-1} Region.—There are six bands in the 300–800-cm^{-1} region which are clearly individual bands, occurring at 362, 408, 462, 507, 537, and 562 cm^{-1}. The very strong 731-cm^{-1} band is seen in Figure 2 to have a shoulder at 718 cm^{-1}, which is apparently not rotational structure to the 731 cm^{-1} band, and is considered to be a band in itself. There are, in addition, very weak bands to either side of the 731-cm^{-1} band, at 761 and 690 cm^{-1}. It is difficult to understand these absorptions as R and P branches of the 731-cm^{-1} band because of the very unusual intensity relationships between them. They are considered to be combination bands.

The spectrum contains a band centered at 663 cm^{-1}, with shoulders at 669 and 657 cm^{-1}. These are the R and P components of the 663-cm^{-1} band. The R branch is better defined than the 657-cm^{-1} P branch which appears only as a shoulder. This is assumed to result from asymmetry of the Q branch and is not unexpected, a similar effect having been observed in the case of the bands centered at 2125 cm^{-1}.

There is a very strong band at 612 cm^{-1}. Like the 731-cm^{-1} band, it has a very weak band on both sides of it, at 627 and 598 cm^{-1}. Again, their intensity relationship to the 612-cm^{-1} band precludes them from being its P and R components. The 612-cm^{-1} band is a fundamental.

The Region 800–300 Cm^{-1} of the $DMn(CO)_5$ Spectrum.—In this region, we find $DMn(CO)_5$ bands at 668, 663, 541, 517, 456, 408, and 328 cm^{-1}, as listed in Table II. Because of the difficulty in preparing $DMn(CO)_5$ free of $HMn(CO)_5$, there has been disagreement among the several investigators[5,6] as to just which

---

[11] W. F. Edgell and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 5451 (1966).

[12] IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth and Co. Ltd., London, 1961.

[13] L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Natl. Bur. Std.*, **66A**, 223 (1962).

[14] W. F. Edgell, G. Asato, W. Wilson, and C. Angell, *J. Am. Chem. Soc.*, **81**, 2022 (1959).

TABLE I

THE VAPOR-PHASE $HMn(CO)_5$ SPECTRUM AND SPECTRAL ASSIGNMENTS

Obsd freq, cm^{-1}	Intens	Symmetry	Assignment
2584	w	A_1	$\nu_1 + \nu_5$
2518	m–w sh	E	$\nu_3 + \nu_{16}$
2502	m	E	$\nu_{15} + \nu_5$
2479	m–w, sh	A_1	$\nu_2 + \nu_5$
2447	m, br	A_1	$\nu_3 + \nu_4$
2437	m, br	E	$\nu_{15} + \nu_6$
2390	m–w	A_1	$\nu_{15} + \nu_{20}$
2230	w	E	$\nu_1 + \nu_{21}$
2225	w	E	$\nu_1 + \nu_{22}$
2155	w	E	$\nu_9 + \nu_{22}$
2148	w	A_1	$\nu_{15} + \nu_{21}$
2130	m, sh		R (ν_1)
2125	m	A_1	ν_1
2116	m, sh		P (ν_1)
2101	m	E	$\nu_{15} + \nu_7$
2096	m, sh	A_1	$\nu_2 + \nu_7$
2091	w, sh		P ($\nu_2 + \nu_7$)
2063	w, sh		R (ν_9)
2054	m, sh	B_1	Q (ν_9)
2048	m, sh		P (ν_9)
2033	vvs		R (ν_{15})
2029	vvs	E	ν_{15}
2024	vvs		P (ν_{15}), R (ν_2)
2020	vvs	A_1	ν_2
2015	s, sh		P (ν_2)
1999	s		R (1994)
1994	s	A^1	Q ($C^{13}O$)
1989	s, sh		P, R
1978	m	A_1	Q ($C^{13}O$) of ν_2
1971	m–w, sh		P (1978 cm^{-1})
1948	m–w, sh		R ($\nu_2 - \nu_7$)
1943	m–w, sh	A_1	Q ($\nu_2 - \nu_7$)
1937	m		($\nu_9 - \nu_{21}$), P ($\nu_2 - \nu_7$)
1914	vvw	E	$\nu_2 + \nu_{22}$
1789	m, sh		R (ν_3)
1784	m	A_1	ν_3
1779	m–w, sh		P (ν_3)
1269	w	E	$\nu_4 + \nu_{17}$
1200	vvw	E	$\nu_4 + \nu_{18}$
1174	vvw	E	$\nu_4 + \nu_{19}$
1105	w	A_1	$\nu_{16} + \nu_{20}$
1075	vw, br	A_1	$\nu_4 + \nu_6$
1021	m–w	E	$\nu_4 + \nu_{20}$
990	w	E	$\nu_5 + \nu_{18}$
983	vvw, sh		
917	w	A_1	$2\nu_5$
900	vvw, sh	A_1	$\nu_{20} + \nu_{18}$
882	vvw, sh	A_1	$\nu_{20} + \nu_{19}$
859	m–w	A_1	$\nu_5 + \nu_6$
837	vvw	A_1	$\nu_{16} + \nu_{20}$
828	vvw	E	$\nu_5 + \nu_{20}$
761	vw	E	$\nu_4 + \nu_{22}$
731	vs	E	ν_{16}
718	m, sh	A_1	$2\nu_{19}$
690	w	E	$\nu_7 + \nu_{17}$
669	s, sh		R (ν_4)
663	vs	A_1	ν_4
657	s, sh		P (ν_4)
627	vvw	A_1	$\nu_{19} + \nu_{21}$
612	vs	E	ν_{17}
598	vw	E	$\nu_{19} + \nu_{22}$
562	w	E	$\nu_5 + \nu_{22}$
537	w	E	ν_{18}
507	w	E	ν_{19}
462	vs	A_1	ν_5
408	w	A_1	ν_6
362	m–w	E	ν_{20}
(120)		E	ν_{21}
(106)		E	ν_{22}
(77)		A_1	ν_7

TABLE II

OBSERVED BANDS IN THE 800–300-CM^{-1} REGION FOR $DMn(CO)_5$ AT 19 MM IN A 10-CM CELL

ν, cm^{-1}	Intens	ν, cm^{-1}	Intens
668	vs	507	w
663	vs	456	vs
541	w	408	w
517	w–m	328	w–m

maxima observed belong to $DMn(CO)_5$ itself and which belong to small amounts of $HMn(CO)_5$ impurity. In particular, there is the question as to whether the 731- and 612-cm^{-1} bands observed in lower intensity in $DMn(CO)_5$ spectra than in $HMn(CO)_5$ spectra are simply due to $HMn(CO)_5$ impurity or whether one or both belong to $DMn(CO)_5$. Wilson[6] has concluded in his study that the bands both belong only to $HMn(CO)_5$. Cotton, *et al.*,[6] observed the decreases in intensities of the "730-cm^{-1}" and the "606-cm^{-1}" bands, relative to the "453 ± 2 cm^{-1} band," on going from pure $HMn(CO)_5$ to $DMn(CO)_5$ contaminated with 5% of the hydride. Based upon the assumption that the "453 ± 2 cm^{-1} band" is "independent of isotopic substitution," they found that "the intensity of the band at 726 cm^{-1} observed in (their) deuteride sample did not decrease relative to the 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...." They concluded that both the hydride and the deuteride have bands at *ca.* 730 cm^{-1} but that only the hydride has a band at *ca.* 610 cm^{-1}. We have reinvestigated this point and report the following. The "453 ± 2 cm^{-1}" band occurs at 456 cm^{-1} in $DMn(CO)_5$ and at 462 cm^{-1} in $HMn(CO)_5$. In our samples, the 612- and 731-cm^{-1} band intensities each decrease at the same rate when the mole fraction of $DMn(CO)_5$ increases. We conclude, therefore, that $DMn(CO)_5$ has bands at neither 612 nor 731 cm^{-1}.

Assignment of the $HMn(CO)_5$ Spectrum

The X-ray diffraction study of La Placa, *et al.*,[7] demonstrated that the $Mn(CO)_5$ portion of manganese carbonyl hydride in the solid state belongs to the point group C_{4v} and strongly indicated that the hydrogen occupies a definite position in the coordination sphere of manganese on the C_4 axis. The vibrational representation for $HMn(CO)_5$ in C_{4v} is: $\Gamma_{vib} = 7\ A_1 + A_2 + 4\ B_1 + 2\ B_2 + 8\ E$. Of these modes, only the A_1 and E modes are symmetry allowed in the infrared spectrum.

Symmetry coordinates show that the C–O stretching motions form the basis for three infrared-active vibrational modes, $2\ A_1 + E$. The Mn–H stretching motion forms the basis for a coordinate of A_1 symmetry, and a combination of H–Mn–CO bending motions contributes an E mode. Seven modes involving Mn–CO stretching and Mn–C–O bending motions are described by symmetry coordinates of the A_1 and E types, $3\ A_1 + 4\ E$, and are expected in the middle-frequency region of the infrared spectrum. In the low-frequency region we expect $A_1 + 2\ E$ modes, whose coordinates are based principally on OC–Mn–CO deformation motions.

On the basis of symmetry coordinates, three vibrational modes primarily involving C–O stretching motions are expected to be observed in the 5-μ region, $E + 2\ A_1$ modes. As discussed above, the very strong absorption in the 2000–2050-cm^{-1} region is composed primarily of two overlapping very strong bands, each with PQR structure, with the Q branches at 2029 and 2020 cm^{-1}. The doubly degenerate "planar" C–O stretching vibration is expected to be the most intense of these bands, and accordingly the 2029-cm^{-1} absorption is assigned as this E mode. Aside from this band, the most intense are the 2020-cm^{-1} band and the band centered at 2125 cm^{-1}. We assign these bands as the A_1 modes. The totally symmetric "planar" C–O stretching mode is expected to be of lowest intensity of the allowed bands in this region, but, in fact, its intensity is greater than zero by virtue of the slight noncoplanarity of the "planar" CO groups and the admixture in the normal mode of the axial A_1 C–O stretching vibration. This A_1 "planar" C–O stretching mode is also expected to come at the highest frequency of the C–O stretching modes since the planar MC–CO and OC–CO interaction force constants are known from previous studies in this laboratory to be positive. Therefore, the highest frequency, lowest intensity 5-μ fundamental band at 2125 cm^{-1} is assigned to the A_1 vibration predominantly "planar" C–O stretching in character. The third band, at 2020 cm^{-1}, is thus assigned to the A_1 mode, predominantly an axial C–O stretching motion.

The band with Q branch at 2054 cm^{-1} is not very intense, and its intensity is difficult to gauge since it appears only as a shoulder on the high-frequency side of the strong absorption assigned to the overlapping E and A_1 modes. No bands are expected to occur at less than 50 cm^{-1} for $HMn(CO)_5$. Thus, this band is not understandable as a combination band with either the 2020- or 2029-cm^{-1} band. We assign the 2054-cm^{-1} band to the symmetry-forbidden B_1 ν(CO) mode. This band has been observed in the Raman spectrum of liquid $HMn(CO)_5$ at 2041 cm^{-1} and assigned to this infrared-forbidden but Raman-allowed B_1 mode.[10] A shift of 13 cm^{-1} accompanying the change in state is certainly reasonable. Since the observed band is very weak, only a slight breakdown in the C_{4v} selection rules is required to cause its presence.

The several maxima occuring in the 1920–1950-cm^{-1} region are understood as resulting from the overlap of a vibrational–rotational structured band with a Q branch at 1943 cm^{-1} and a band at *ca.* 1934 cm^{-1}. In order to assign these bands, we refer to the work of Edgell and Cengel[15] on the $Mn(CO)_5X$ compounds. They observed that there are three strong far-infrared bands characteristic of the $Mn(CO)_5$ moiety in these compounds: an A_1 mode at 58–63 cm^{-1} and two E modes at 100–106 and 120–126 cm^{-1} in the series. These modes are OC–Mn–CO deformation modes. On this basis it is reasonable to expect frequencies in roughly these positions in the $HMn(CO)_5$ spectrum. The 1943- and 1934-cm^{-1} bands are then assigned as difference bands, which must of course be exactly the difference between fundamental frequencies. The 1943-cm^{-1} band is assigned as $(\nu_2 - \nu_7)$ and fixes ν_7 as 77 cm^{-1}. This difference band is of A_1 species since both ν_2 and ν_7 are also A_1 modes. The 1934-cm^{-1} band is assigned as $(\nu_9 - \nu_{21})$ and is an E mode since $B_1XE = E$. This fixes ν_{21} at 120 cm^{-1}. The third low-frequency mode is predicted by the assignment of the weak 1914-cm^{-1} absorption as $(\nu_2 - \nu_{22})$, of E symmetry, and requires that ν_{22} be 106 cm^{-1}.

The observed spectrum of $DMn(CO)_5$ in the 1900–2250-cm^{-1} region we confirm to be, as reported previously, identical with that of $HMn(CO)_5$. This is due to the rather unusual occurrence of essentially zero coupling between the ν(CO) mode and the ν(Mn–H) mode of vibration.

The band centered at 1784 cm^{-1} was observed by Edgell, *et al.*,[14] to shift to 1287 cm^{-1} and by Cotton, *et al.*,[5] to shift to 1290 cm^{-1} upon deuteration. It has been assigned to the Mn–H stretching vibration; this is a sound assignment.

In the 300–800-cm^{-1} portion of the $HMn(CO)_5$ spectrum we expect four E and three A_1 modes composed primarily of combinations of Mn–C stretching and Mn–C–O bending motions. In addition, the X–Mn–C doubly degenerate bending mode of $XMn(CO)_5$ compounds is expected in the middle-frequency region where X = H or D although it occurs at much lower frequencies for heavier X atoms.

The middle-frequency spectrum of $HMn(CO)_5$ contains four very strong bands at 731, 663, 612, and 462 cm^{-1}, and, as discussed above, the strong $DMn(CO)_5$ bands occur at 668, 663, and 456 cm^{-1}. It is helpful in assigning the middle-frequency bands to refer to the work on the $Mn(CO)_5X$ (X = Cl, Br, I) compounds. By reference of the $HMn(CO)_5$ and $DMn(CO)_5$ spectra to these assignments, we may compare their band positions to those in molecules in which the coupling between modes involving the X ligand with those of the $Mn(CO)_5$ moiety *per se* is small. Figure 3 shows that several important aspects of the $Mn(CO)_5X$ middle-frequency spectra correlate well with the $DMn(CO)_5$ spectrum. The extent of correlation with the $HMn(CO)_5$ spectrum is less.

We conclude from this that in $HMn(CO)_5$ there is extensive coupling of motions involving the H atom with those of the $Mn(CO)_5$ moiety. Although this makes assignment of $HMn(CO)_5$ bands more difficult, its apparent absence in $DMn(CO)_5$ permits several $DMn(CO)_5$ bands to be assigned to their proper symmetry

---

(15) W. F. Edgell and J. Cengel, unpublished work; also J. A. Cengel, Ph.D. Thesis, Purdue University, 1965.

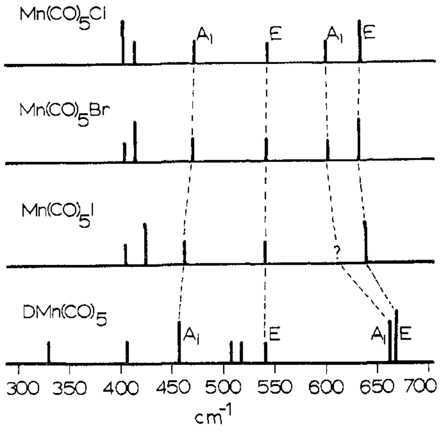


Figure 3.—Middle-frequency fundamental bands of $Mn(CO)_5X$ (X = Cl, Br, I, D).

classes by direct comparison with the $Mn(CO)_5X$ spectra. This comparison identifies the 456-cm^{-1} band as an A_1 mode, and the 541-cm^{-1} band as an E mode. In addition, the correlation indicates that one of the 663- and 668-cm^{-1} bands is an A_1 mode and one is an E mode.

By comparison of the $HMn(CO)_5$ and $DMn(CO)_5$ spectra, as in Figure 4, several of the $HMn(CO)_5$ band assignments become clear. The strong 462-cm^{-1} hydride band is assigned to the A_1 mode analogous to the 456-cm^{-1} deuteride mode. This mode is primarily an axial Mn–C stretching mode but is of course mixed with other A_1 modes. The 537-cm^{-1} hydride mode is the E mode analogous to the 541-cm^{-1} deuteride mode and is due largely to Mn–C–O bending motions of the axial and in-plane CO groups.

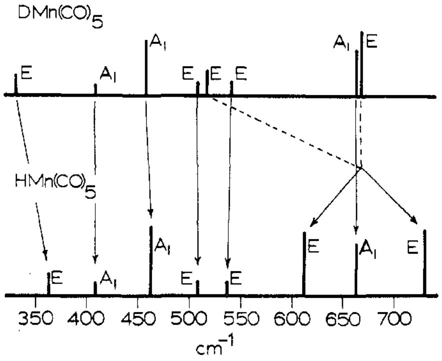


Figure 4.—Correlation of the middle-frequency spectra of $HMn(CO)_5$ and $DMn(CO)_5$.

In both the deuteride and hydride spectra there is a band at 663 cm^{-1}. There is expected to be one A_1 mode in this region involving Mn–C–O bending motions of the planar CO groups. The 663-cm^{-1} band is assigned to this A_1 mode in both the hydride and the deuteride on the following bases. The correlation between $Mn(CO)_5X$ and $Mn(CO)_5D$ spectra indicates that the lower frequency of the 600–700-cm^{-1} bands is the A_1 mode. In addition, with the assignments of the 1784- and 1287-cm^{-1} and the 462- and 456-cm^{-1} bands as A_1 modes, the A_1 isotopic shift product constitutes very nearly the maximum allowable values as required by the Teller–Redlich product rule.

Several very strong bands, then, remain to be assigned in these spectra, the $HMn(CO)_5$ 731- and 612-cm^{-1} bands and the 668-cm^{-1} $DMn(CO)_5$ band. The $Mn(CO)_5X$ correlation indicates that the 668-cm^{-1} band is an E mode involving Mn–C–O bending motions of the planar CO groups. The key to the understanding of the two hydride bands is provided by the discussion of Edgell, *et al.*[14] A relatively weak deuteride band of E symmetry is shifted up, when D is replaced by H, to become nearly coincident with the 668-cm^{-1} band. Now there is a deuteride band at 517 cm^{-1}, absent in the hydride spectrum, which we assign as an E mode. A reasonable frequency ratio of *ca.* 1.3 is required to make an analogous hydride band coincident with the 668-cm^{-1} band, also of E symmetry. Two vibrational motions of a molecule of the same symmetry which would independently give rise to the same vibrational frequency can effectively couple to give two vibrational motions which are strongly mixtures of those motions. When this occurs, the two resultant modes usually appear at frequencies somewhat displaced from that which either would have independently, and very often there is extensive "intensity borrowing" such that both bands are more intense than the weaker of the original bands. That is just what happens in this case. The 517-cm^{-1} $DMn(CO)_5$ band shifts upon H substitution to give an "uncoupled" vibration at *ca.* 668 cm^{-1} but couples with the other 668-cm^{-1} "uncoupled" vibration to give rise, in the hydride, to the 731- and 612-cm^{-1} bands. The 731- and 612-cm^{-1} hydride bands are thus also E modes.

TABLE III

CHARACTERIZATION OF INFRARED-ACTIVE FUNDAMENTAL MODES OF $HMn(CO)_5$

Freq, cm^{-1}	i from v_i	Symmetry	Description[a]
2125	1	A_1	C–O planar str
2020	2	A_1	C–O axial str
1784	3	A_1	Mn–H str
663	4	A_1	Mn–C–O out-of-plane bend
462	5	A_1	Mn–CO axial str
408	6	A_1	Mn–CO planar str
(77)	7	A_1	OC–Mn–CO out-of-plane bend
2029	15	E	C–O planar str
731	16	E	C–Mn–H and Mn–C–O bends
612	17	E	C–Mn–H and Mn–C–O bends
537	18	E	Mn–C–O axial and in-plane bends
507	19	E	Mn–C planar str
362	20	E	Mn–C–O and Mn–H bends
(120)	21	E	OC–Mn–CO axial bends
(106)	22	E	OC–Mn–CO planar bend

[a] The Mn–CO stretching and Mn–C–O bending motions are known to be mixed extensively in the actual middle-frequency modes. None of these middle-frequency modes is comprised simply of the motions briefly described.

The band at 507 cm^{-1} in both $DMn(CO)_5$ and $HMn(CO)_5$ is assigned to an E mode on the basis of the $Mn(CO)_5X$ spectra. An E mode which is a combination occurs at *ca.* 400 cm^{-1}. The 362-cm^{-1} hydride and 328-cm^{-1} deuteride bands are assigned to an E mode strongly involving this motion and the C–Mn–H bending motion. We interpret the 408-cm^{-1} band as the expected A_1 mode in both $HMn(CO)_5$ and $DMn(CO)_5$. The assignments of the middle-frequency bands are given in Table I.

In making the assignments of several conbination bands in the high-frequency region, it was recognized that there are three strong fundamentals expected in the low-frequency region. Since three of these combination bands are difference bands, we found that the low-frequency bands are at 120, 106, and 77 cm^{-1}. The analogous bands in $Mn(CO)_5X$ (X = Cl, Br, I) occur as follows: E (120–126 cm^{-1}), E (100–106 cm^{-1}), and A_1 (58–63 cm^{-1}).

Discussion

In order to test the present assignment, the Teller–Redlich isotope products can be compared with the theoretical requirements. These requirements are found by taking into account not only the changes in vibrational reduced masses which occur upon substitution of D for H but also the concomitant changes in total mass and moments of inertia. Assuming that the geometry of the $Mn(CO)_5$ moiety is the same in the vapor as in the solid and taking the Mn–H distance as 1.3 Å (a number in some dispute but to which only I_x and I_y are only very slightly sensitive), one finds the required products, including the relevant translations and rotations, to be

$$(A_1)\quad \prod_{i=1}^{7} \frac{\nu_i^{H}}{\nu_i^{D}} = 1.411;\quad (E)\quad \prod_{i=1}^{8} \frac{\nu_i^{H}}{\nu_i^{D}} = 1.402$$

The products calculated from the present assignments are

$$(A_1)\quad \Pi = 1.403 \qquad (E)\quad \Pi = 1.418$$

While the value for the A_1 modes fulfills the requirement well, the value for the E modes is slightly above expectation. It is quite likely that the explanation of this variation involves a Fermi resonance effect to be expected on the basis of the rather great vibrational anharmonicities of motions involving H and D and the presence in the middle-frequency region of the combination band of E symmetry species.

We conclude that the spectrum of $HMn(CO)_5$ is understandable on the basis of C_{4v} symmetry, which the molecule is known to have in the solid state, and that it is not necessary to assume lower symmetry, such as C_s or C_{2v}, to explain the entire spectrum.

Acknowledgment.—The support of this work, in part, by the Advanced Research Projects Agency, through the Purdue I.D.L. program, is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ILLINOIS INSTITUTE OF TECHNOLOGY, TECHNOLOGY CENTER, CHICAGO, ILLINOIS 60616

Infrared, Raman, and Proton Magnetic Resonance Spectra of Dicyclopentadienylmercury and Related Compounds[1,2]

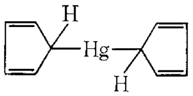
BY E. MASLOWSKY, JR.,[3a] AND KAZUO NAKAMOTO

Received October 31, 1968[3b]

The infrared and Raman spectra of $(C_5H_5)_2Hg$ and $(C_5H_5)HgX$ types of compounds (X = halogen) have been compared with those of C_5H_6. It has been concluded that the Hg atoms of these compounds are σ bonded to the C_5H_5 rings. In $(C_5H_5)_2Hg$, the C–Hg–C bond is linear and the antisymmetric and symmetric Hg–C stretching vibrations are assigned at 348 and 321 cm^{-1}, respectively. However, the relative orientation of the C_5H_5 rings could not be determined, since there was no appreciable vibrational coupling between the vibrations of the two C_5H_5 rings.

Introduction

Originally, dicyclopentadienylmercury was formulated as containing the mercury atom bonded to the carbon atoms of the cyclopentadienyl rings by means of σ bonds.[4] The π-bonded structure such as that found in ferrocene was rejected since the infrared spectrum of this compound is much more complex than that of ferrocene. However, its pmr spectrum at room temperature consists of a single sharp peak (τ 4.2), which is indicative of the π-bonded structure. To reconcile these conflicting results, Piper and Wilkinson[5] proposed that, while the mercury atom is indeed σ bonded to the ring, the point of attachment changes at such a rate that the protons on the ring appear equivalent in the pmr spectrum (valence tautomerism). Recently, Nesmeyanov, *et al.*,[6] questioned the σ-bonded structure; in addition to the pmr evidence mentioned above, they



---

[1] This work was supported, in part, by research grants from the Petroleum Research Fund (2096-A3,5 and 3318-C3,5).

[2] To be submitted by E. M. to the faculty of Illinois Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] (a) Supported by an NDEA fellowship during this investigation. (b) Revised March 25, 1969.

[4] G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956).

[5] T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

[6] A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Y. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **159**, 847 (1964)