The microwave spectrum and Mn–H bond length for $HMn(CO)_5$

Stephen G. Kukolich and Shane M. Sickafoose

Department of Chemistry, The University of Arizona, Tucson, AZ 85721, USA

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The microwave rotational spectrum for the symmetric top, manganese pentacarbonylhydride, was measured in the 5-11 GHz range using a pulsed-beam, Fourier transform microwave spectrometer. For HMn(CO)₅ we obtained A=B=907.9841(2) MHz and eqQ(Mn) = -44.22(2) MHz. For DMn(CO)₅, A=B=902.7682(3) MHz and eqQ(Mn) = -45.24(4) MHz. Only K=0 and K=4 transitions were observed, confirming the expected C_{4v} symmetry. With other structural parameters constrained to previously reported values, $r_0(Mn-H) = 1.64(4)$ Å. The C_{ax}-Mn-C_{eq} angle derived from the data is approximately 97°, if Mn-C-O angles are constrained to 180°.

1. Introduction

Transition metal hydrides are involved in many important reactions, as stoichiometric reactants, or as key intermediates in hydrogenation or hydroformulation reactions [1,2]. Since the transfer of the hydrogen atom to the organic reagent is an important feature of these reactions, much attention has been focused on the M-H bond. Structural data on this complex was obtained from an electron diffraction study [3] and from crystal structures obtained from neutron diffraction [4] and X-ray diffraction work [5]. The synthesis of this complex was reported in 1931 [6]. The present measurements on HMn(CO)₅ and recent work [7] on HRe(CO)₅ are believed to be the first microwave studies for transition metal hydrides.

2. Experimental

The preparation of $HMn(CO)_5$ from $Mn_2(CO)_{10}$ using sodium amalgam is described by King [8]. An alternative synthesis using "superhydride" was given by Gladysz et al. [9]. Both of these procedures involve tetrahydrofuran, which is difficult to separate from the product and gave nearby interfering peaks in both microwave and IR spectra. A cleaner preparation for spectroscopic purposes was developed following the general procedure described by King [8]. The oxygen was removed from 60 ml of triglyme by bubbling nitrogen through it for 0.5 h and then 2 g of $Mn_2(CO)_{10}$ was added. About 3 g of clean NaK_{2.8} was then added using a small glass pipette. This mixture was then stirred for 15 h to produce $KMn(CO)_5$ and $NaMn(CO)_5$ in the triglyme solvent. Degassed 85% phosphoric acid was then added dropwise under partial vacuum to produce the HMn(CO), which distilled into a 78 K trap. The vapor pressure of the triglyme is sufficiently low that very little would distill onto the trap, and any that did can be removed in the subsequent distillation. The collected product was then distilled twice through P₂O₅ columns (using Fluka No. 79610) under vacuum. This produced a pure, clear product which would gradually become light yellow above the melting point, due to loss of hydrogen. The deuterated sample was prepared as described above, but using D_3PO_4 (Aldrich No. 17, 675-3).

The microwave transitions were measured in the 5-11 GHz range using a Flygare-Balle type pulsed beam Fourier transform spectrometer [10]. A 1% mixture of the HMn(CO)₅ in first-run neon at 0.7 atm pressure was pulsed into the cavity using a solenoid valve. A c-dipole oblate symmetric top spectrum was observed with well-resolved splittings of a few MHz due to the ⁵⁵Mn quadrupole coupling. Most of the observed transitions were $\Delta J=1$, K=0, except

for four K=4 transitions each, for $J=4\rightarrow 5$ and $5\rightarrow 6$. Higher frequency transitions were weaker, with partially resolved quadrupole hyperfine structure, so were not included in the fits.

3. Results and data analysis

The manganese nuclear quadrupole coupling was analyzed in the coupled representation F=I+J, where F is the total angular momentum, I is the Mn nuclear spin (magnitude=5/2) and J is the rotational angular momentum. The Hamiltonian matrix, including rotational energy and quadrupole coupling matrix elements, was diagonalized in blocks for each possible F value. The quadrupole matrix elements were given earlier [11,12]. For K=0 transitions the adjustable parameters for the least-squares fit were the rotational constant *B*, the ⁵⁵Mn quadrupole coupling strength eqQ, centrifugal distortion constant D_J and the ⁵⁵Mn spin-rotation interaction component C_{aa} . When fitting the K=4 transitions, *B* and D_J were fixed at values obtained for K=0, and eqQ, the centrifugal distortion constant D_{JK} and the spin-rotation constant C_{cc} were adjusted for the best fit.

The measured and calculated, best fit transition frequencies for $HMn(CO)_5$ and $DMn(CO)_5$ are listed in tables 1-3. For $HMn(CO)_5$, the K=0 fit included 28 transitions and the standard deviation for the fit is 2.5 kHz. The observed transitions were weaker, due to isotopic purity and more line-broadening was present for the $DMn(CO)_5$ transitions

Table 1

Measured and calculated K=0 transition frequencies for HMn(CO)₅. The calculated frequencies were obtained using a least-squares fit to the measured frequencies. The "best fit" parameters are listed in table 4. The total angular momentum is F=I+J. The standard deviation for the fit is 2.5 kHz. The values are given in MHz

J	J′	2 <i>F</i>	2 <i>F'</i>	Measured	Calculated	Measured — calculated
 2	3	9	9	5440.303	5440.300	0.003
2	3	3	5	5444.443	5444.443	0.000
2	3	5	7	5446.628	5446.628	0.000
2	3	1	1	5447.877	5447.879	-0.002
2	3	9	11	5448.434	5448.435	-0.001
2	3	7	9	5448.854	5448.851	0.003
2	3	. 3	3	5449.583	5449.586	-0.003
2	3	5	5	5450.740	5450.736	0.004
3	4	3	5	7262.138	7262.137	0.001
3	4	5	7	7262.476	7262.476	0.001
3	4	1	3	7262.887	7262.889	-0.002
3	4	7	9	7263.506	7263.505	0.001
3	4	11	13	7264.199	7264.198	0.001
3	4	9	11	7264.463	7264.461	0.002
3	4	7	7	7266.586	7266.584	0.002
3	4	3	3	7266.859	7266.860	-0.001
3	4	5	5	7267.282	7267.280	0.002
4	5	5	7	9078.834	9078.840	-0.006
4	5	7	9	9079.073	9079.076	-0.003
4	5	3	5	9079.254	9079.256	-0.002
4	5	9	11	9079.685	9079.688	-0.002
4	5	13	15	9080.038	9080.040	-0.002
4	5	11	13	9080.221	9080.221	0.000
5	6	7	9	10895.122	10895.119	0.003
5	6	9	11	10895.298	10895.294	0.004
5	6	11	13	10895.702	10895.703	-0.001
5	6	15	17	10895.912	10895.913	-0.001
 5	6	13	15	10896.044	10896.044	0.000

Table 2

J	J'	2 F	2 <i>F'</i>	Measured	Calculated	Measured – calculated	
 2	3	3	5	5413.062	5413.069	-0.008	
2	3	5	7	5415.302	5415.303	-0.001	
2	3	9	11	5417.153	5417.151	0.003	
2	3	3	3	5418.335	5418.333	0.001	
2	3	5	5	5419.509	5419.509	-0.001	
3	4	11	11	7214.434	7214.430	0.004	
3	4	3	5	7220.374	7220.373	0.001	
3	4	5	7	7220.721	7220.719	0.002	
3	4	1	3	7221.140	7221.144	-0.004	
3	4	7	9	7221,771	7221.771	0.000	
3	4	11	13	7222.481	7222.478	0.003	
3	4	9	11	7222.751	7222.748	0.003	
3	4	7	7	7224.928	7224.925	0.003	
3	4	3	3	7225.207	7225.208	-0.001	
3	4	5	5	7225.635	7225.637	-0.002	
4	5	5	7	9026.655	9026.664	-0.009	
4	5	7	9	9026.903	9026.905	-0.002	
4	5	3	5	9027.098	9027.090	0.008	
4	5	9	11	9027.532	9027.529	0.002	
4	5	13	15	9027.891	9027.888	0.002	
4	5	11	13	9028.069	9028.074	-0.005	
5	6	11	13	10833.118	10833.118	0.000	
5	6	15	17	10833.324	10833.331	-0.007	
5	6	13	15	10833.473	10833.466	0.007	

Measured and calculated K=0 transition frequencies for DMn(CO)₅. The values are listed in MHz and the standard deviation for the fit is 4.6 kHz

Table 3

Measured and calculated K=4 transition frequencies for HMn(CO)₅. The parameters determined in this fit are $D_{JK}=0.054(9)$ kHz, $C_{cc}=2.1(15)$ kHz and eQq=-44.17(3) MHz. Other parameters were fixed at the values listed in table 4. The standard deviation for the fit is 2.2 kHz and values are listed in MHz

J	K	2 <i>F</i>	<i>J</i> ′	Κ'	2 <i>F'</i>	Measured	Calculated	Measured – calculated
4	4	9	5	4	11	9076.045	9076.043	0.002
4	4	11	5	4	13	9076.494	9076.497	-0.003
4	4	13	5	4	15	9082.878	9082.877	0.001
4	4	3	5	4	5	9086.398	9086.400	-0.002
5	4	11	6	4	13	10893.498	10893.499	-0.001
5	4	13	6	4	15	10894.128	10894.129	-0.001
5	4	7	6	4	9	10896.807	10896.804	0.003
5	4	15	6	4	17	10897.654	10897.653	0.001

shown in table 2 and the standard deviation for the fit was 4.6 kHz for 24 transitions. There are 8 transitions with K=4 for HMn(CO)₅ listed in table 3 and the standard deviation is 2.2 kHz. A term was included for change in eqQ with $\langle J^2 \rangle$ for K=0 transitions, but the uncertainty was only slightly smaller

than the value and the fit was not significantly improved. A slightly different value for eqQ was obtained, however, for K=4 transitions, due to centrifugal distortion effects on the quadrupole coupling. The molecular parameter values are listed in table 4.

The magnitude of the ⁵⁵Mn quadrupole coupling

Table 4

Molecular parameters obtained from least-squares fits to the observed transition frequencies listed in tables 1–3. The listed uncertainties are 2σ . The eqQ and C values are for ⁵⁵Mn

Isotopomer	HMn(CO) ₅	DMn(CO) ₅	
	907.9841(2)	902.7682(3)	
$D_{I}(kHz)$	0.093(4)	0.084(8)	
D_{IK} (kHz)	0.054(9)	-	
eqQ(K=0) (MHz)	-44.22(2)	-45.24(4)	
eqQ(K=4) (MHz)	-44.17(3)	-	
C_{a} (kHz)	5.1(4)	4.4(9)	
$C_{\rm ec}$ (kHz)	2.1(15)	-	

Table 5

Results of the least-squares fits to determining the structural parameters r(Mn-H) and $C_{ax}-Mn-C_{eq}$, and the fixed bond lengths used in the calculations. All angles Mn-C-O were fixed at 180°. ED refers to the electron diffraction data and ND to the neutron diffraction data

Paran	neters	Using ED data	Using ND data	
adjust	able r(Mn-H) (Å)	1.613		
$\angle C_{ax}$ -Mn- C_{eq}		6.8°	8.9°	
fixed	$r(C-O_{ax})$	1.142	1.143	
$r(C-O_{m})$		1.142	1.132	
	$r(Mn-C_{ax})$	1.854	1.822	
	$r(Mn-C_{eq})$	1.856	1.853	

is increased 2.3% in the deuterated isotopomer relative to the hydrogen isotopomer. We believe that this is due to the shorter vibrationally averaged Mn-D bond length, resulting from anharmonic contributions to the potential energy as a function of Mn-H bond length. A similar effect was observed and discussed for HRe(CO)₅ [7]. The centrifugal distortion constants are quite small, indicating that the Mn(CO)₅ moiety is fairly rigid. Centrifugal stretching of the Mn-H bond would not make a very large contribution to these distortion constants.

We observed gas-phase vibrational transitions for H-Mn and D-Mn stretching modes at 1784.4 and 1288.6 cm⁻¹ in agreement with previous work [13,14]. If we make a simple pseudodiatomic molecule approximation for this stretching vibration, we find that $\omega^2 \mu$ where μ is the reduced mass, increases by 2.4% on deuterium substitution. This result is similar in magnitude to the isotope effect for eqQ and both are due to the anharmonic contributions to the Mn-H potential.

4. Mn-H bond length

The measured rotational constants can be used to determine the Mn-H bond length, if we fix the Mn-C and C-O bond lengths at values determined by the previous electron diffraction [3] or neutron diffraction [4] work. The electron diffraction values are $r(C-O) = 1.142 \text{ Å}, r(Mn-C_{ax}) = 1.854 \text{ Å and } r(Mn-C$ C_{eq} = 1.856 Å. Using these parameters, and the measured rotational constants, we find r(Mn-H)=1.613 Å and $\angle C_{ax}$ -Mn- C_{eq} =96.8°. The neutron diffraction values are $r(C-O)_{ax} = 1.143$ Å, r(C- $O_{eq} = 1.132$ Å, $r(Mn-C_{ax}) = 1.822$ Å, and $r(Mn-C_{ax}) = 1.822$ C_{eo} = 1.853 Å. Using these parameters we find $r(Mn-H) = 1.669 \text{ Å and } \angle C_{ax}-Mn-C_{eq} = 98.9^{\circ}$. In both cases we assume a linear geometry for Mn-C-O. This assumption would not affect the values obtained for Mn–H bond lengths, as long as $\angle C_{ax}$ -Mn– C_{eq} is a variable parameter. Changes in A or B due to varying $\angle Mn-C_{eq}-O$ away from 180° would be compensated by changes in $\angle C_{ax}$ -Mn- C_{eq} . The bond length calculations are summarized in table 5. We have averaged the results obtained using electron diffraction parameters with the values obtained using neutron data to obtain $r_0(Mn-H) = 1.64(4)$ Å. This value is in very good agreement with previous electron diffraction and neutron diffraction results.

The magnitude of quadrupole coupling strength of eqQ = -44.22 MHz is smaller than the value of 68.00 MHz observed for cyclopentadienyl manganese tricarbonyl [11], indicating a more symmetrical charge distribution around the Mn nucleus for the hydride complex.

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