Corrections and Additions to Microwave spectra and theoretical calculations for two structural isomers of methylmanganese pentacarbonyl

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(abstract)

High-level calculations for the asymmetric top acyl isomers of methyl manganese pentacarbonyl were done with ab initio and DFT methods. In order to obtain better agreement between the measured and calculated quadrupole coupling parameters calculations, new assignments of quantum numbers to the previously measured transitions were made. The new assignments gave a much better fit to the spectrum. The best agreements were obtained for B3LYP and M11 DFT calculations with def2 basis sets. Experimental molecular parameters from the new analysis are: A = 840.084(5), B = 774.286(2), C = 625.653(1). D_J = 0.00021(2). D_{JK} = 0.0049(2), $1.5\chi_{aa}$ = -47.0(1), $0.25(\chi_{bb} - \chi_{cc})$ = -13.44(3) MHz. These experimental parameters agree best with calculations for the dihapto isomer, rather than the agostic form of this complex. Excellent agreement is obtained for the rotational constants, and much better agreement for the quadrupole coupling parameters.

(abstract will not appear in final form)

I. Introduction

In the original paper on methylmanganese pentacarbonyl,[1] good agreement was obtained between the experimental rotational constants and the calculated values for dihapto acyl-$CH_3C(O)Mn(CO)_4$, but agreement between experimental and calculated quadrupole parameters was poor. Calculated χ_{aa} were positeve whereas the experimental values are negative. This note provides corrections and some additions to the earlier paper[1] Subsequently, many calculations were carried out using different methods and basis sets and the calculated quadrupole coupling parameters between these different calculations were reasonably consistent. In particular, the calculations consistently gave negative values for the ^{55}Mn quadrupole parameters, whereas the reported experimental values were positive. Alternative assignments of the quantum numbers to measured transitions could be found which yielded negative quadrupole parameters and a better fit to the spectrum. Results of the new spectral analysis are given below.

The three lowest energy structures for methylmanganesepentacarbonyl. The symmetric isomer (1a) and the two distinct acyl-Mn isomers; the agostic form (1b) and the dihapto form(1c) are shown in Figure 1.

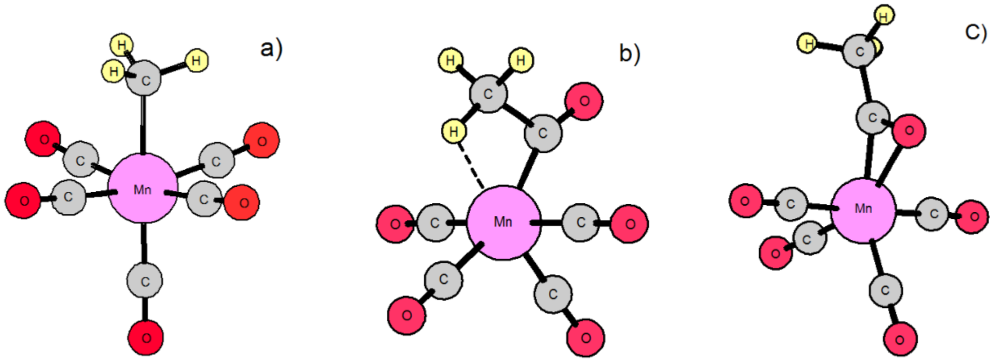

Figure 1. The three structural isomers of methyl manganese pentacarbonyl complex. Structure 1a (symmetric top) is the lowest energy structural isomer. (1b) is the agostic form and (1c) is the dihapto form.

The experimental and calculated parameters for the dihapto and agnostic forms are given in Table 1. Prior computational analysis of the asymmetric top acyl methyl manganese[1] revealed good agreement with experimental rotational constants, but the nuclear quadrupole coupling constants varied significantly between methods and showed poor agreement with experimentally determined nuclear quadrupole coupling constants. To rectify the poor agreement between theory and experiment, new computations were run, some with uncontracted basis sets for Mn.

The microwave measurements were carried out using a pulsed molecular beam Fourier transform microwave spectrometer like the Flygare-Balle microwave spectrometer.[2] Strong *a*-type and weak *c*-type dipole transitions were observed with hyperfine splittings due to coupling of the nuclear spinning angular momentum (I) and the rotational angular momentum (J). The characteristic ^{55}Mn (I = 5/2) hyperfine splittings[3,4] on top of the rotational lines unambiguously confirmed the presence of ^{55}Mn spectral carrier. The observed spectrum is congested due to asymmetry and hyperfine splittings. There is the possibility that both the dihapto and agostic forms contribute to some regions of the spectrum. In total, 172 lines were observed between 4 to 8 GHz region. Quantum number assignment was made possible by matching the experimental spectrum to the simulated spectrum.

II. Analysis of the Spectrum and DFT Calculations

The spectrum was fit using a rigid rotor Hamiltonian. We performed least-squares fits with Watson S-reduced prolate Hamiltonian using the JPL Pickett's SPFIT/SPCAT program[5]. These 7-parameters fit included the rotational constants A, B, and C, the centrifugal distortion constants D_J and D_{JK}, and the quadrupolar parameters $1.5\chi_{aa}$ and $0.25(\chi_{bb} - \chi_{cc})$. χ is used to denote the quadrupole coupling strength, eQq, where e is the electron charge, Q is the electric quadrupole moment of ^{55}Mn, and q is the electric field gradient along the inertial axis, *a*, *b* and *c*. In the units of MHz, χ(MHz) = 234.9647 × Q(barn) × q(a.u.)[6]. The nuclear quadrupole moment of ^{55}Mn atom is relatively large (330 mb)[7] resulting a in relatively large eQq value in this complex.

High-level Gaussian (G16) calculations were done at Wesleyan University and the University of Arizona. The calculations at Arizona were done on the ocelote HPC, 28 processor system using 268 Gb memory[8]. The primary software used in all calculations was the Gaussian-16 suites (G-16). For some calculations, the geometry optimization were followed by single point computations with fixed geometry to obtain EFG values. In some cases, a large combined basis set with polarization was used(Def2QZVPP for Mn and Def2TZVPP for the other elements). The results of the newer calculations for asymmetric top acyl methyl manganese are shown in Table 1 (at end). The experimental parameters which provided the best fit deviation using the new assignments to experimental lines, are in the first column. The DFT results in columns 3, 4 and 5 of Table 1 yielded rotational constants within 2% of experimental values. The ab-initio MP2 rotational constants are not as good. The 1.5 χ_{aa} values are within 2% across the first 6 columns. Wider variations were seen for some of the other functionals tested. The variations of the 0.25(χ_{bb}- χ_{cc}) terms are significantly larger, up to 7 MHz. The MP2 result was closer, within 1.5 MHz.

The new assignments were obtained by starting with the calculated values for the parameters and predicting spectra using spcat.[5] Rotational constants, centrifugal distortion constants, and the nuclear quadrupole hyperfine coupling constants obtained from the best least-squares fit to the spectrum are shown in Table 2. The fit results, root mean square error, and 1σ standard error (67% confidence level) are given in Table 2. Table 3 shows observed frequencies and "best fit" calculated frequencies computed from the best least-squares fit for the dihapto isomer. Quantum number assignments were assigned according to F = J + I angular momentum coupling scheme (F is round up to whole number). The pseudo quantum number K_aK_c is used to label asymmetry splitting. With the newer assignments the 1σ standard deviation dropped from 41 kHz to 17 kHz. Now the nuclear quadrupole coupling constants displayed in table 1 shows a good agreement between different methods for the same structure and with the experimental value. This offers increased optimism that computational and experimental nuclear quadrupole coupling constants can be used to determine the preferred isomer of the asymmetric top acyl methyl We note that calculated quadrupole parameters for the agostic isomer are much different from experimental values. The good agreement of nuclear quadrupole coupling constants between different methods, along with the stark difference in calculated 1.5χ_{aa} values, strongly suggests the lower energy asymmetric form of methyl manganese pentacarbonyl is the dihapto form. In addition, as was also observed in our previous work[1], the calculated rotational constants for the dihapto form show much better agreement with the experimental rotational constants, as compared to the calculated rotational constants for the agostic form.

Table 2. Rotational constants, centrifugal distortion constants, and the nuclear quadrupole hyperfine coupling constants obtained from the best least-squares fit. Spectroscopic constants are in MHz. 1σ standard error = RMS × [number of lines/(number of lines – number of fit constants)]$^{1/2}$

Measured constant	**This work**	**Previous work**
A	840.0843(52)	839.955(42)
B	774.2861(17)	774.203(67)
C	625.6528(13)	625.628(14)
D_J	0.000212(21)	-
D_{JK}	0.00488(18)	-
1.5χ_{aa}	-46.96(11)	44.9(47)
0.25(χ_{bb} - χ_{cc})	-13.44(3)	11.9(12)
Number of lines	40	31
RMS, kHz	16	39
1σ, kHz	17	41

Table 3. Observed and calculated fit frequencies (MHz).

J_{KaKc}→	**$J'_{Ka'Kc'}$**	**F→**	**F′**	**Observed**	**Calculated**	**Obs. – Calc.**

3_{31}	2_{21}	1	1	4948.9594	4948.9646	-0.00516
4_{13}	3_{12}	5	6	5570.2344	5570.2270	0.00736
4_{13}	3_{12}	6	6	5570.5930	5570.5842	0.00881
4_{13}	3_{12}	5	5	5570.8934	5570.8713	0.02213
4^{13}	3_{12}	5	4	5570.8934	5570.8794	0.01400
4_{13}	3_{12}	6	5	5571.2264	5571.2284	-0.00202
4_{31}	3_{21}	5	4	6371.0428	6371.0527	-0.00987
4_{31}	3_{21}	5	5	6371.0428	6371.0521	-0.00931
4_{13}	3_{03}	4	3	6411.9379	6411.9427	0.00476
4_{13}	3_{03}	3	3	6413.7332	6413.7295	0.00372
4_{23}	3_{13}	3	3	6432.5583	6432.5556	0.00275
5_{15}	4_{14}	6	6	6432.8545	6432.8589	-0.00445
4_{23}	3_{13}	5	5	6432.9602	6432.9919	-0.03174
4_{23}	3_{13}	5	4	6433.0220	6432.9943	0.02769
5_{05}	4_{04}	6	6	6433.2539	6433.2336	0.02031
4_{23}	3_{13}	6	5	6433.3471	6433.3404	0.00671
5_{15}	4_{14}	5	4	6433.5597	6433.5583	0.00137
5_{15}	4_{14}	4	3	6433.6426	6433.6782	-0.03562
5_{05}	4_{04}	5	4	6433.9471	6433.9326	0.01447
5_{05}	4_{04}	4	3	6434.0541	6434.0518	0.00231
4_{23}	3_{13}	4	5	6434.1097	6434.1074	0.00233
4_{23}	3_{13}	4	4	6434.1097	6434.1097	-0.00003
5_{05}	4_{04}	6	5	6434.5340	6434.5182	0.01577
5_{15}	4_{14}	3	2	6434.6960	6434.7363	-0.04027
5_{15}	4_{14}	7	6	6435.0143	6434.9955	0.01877
5_{05}	4_{04}	3	2	6435.0928	6435.1091	-0.01634
5_{05}	4_{04}	7	6	6435.3732	6435.3702	0.00301
5_{15}	4_{14}	8	7	6435.4603	6435.4700	-0.00966
4_{41}	3_{31}	7	6	6614.9449	6614.9794	-0.03453
4_{41}	3_{31}	6	5	6615.5978	6615.5763	0.02153

4_{41}	3_{31}	2	1	6615.7941	6615.7832	0.01089
6_{16}	5_{15}	7	6	7685.6269	7685.6524	-0.02554
6_{16}	5_{15}	4	3	7686.0249	7686.0160	0.00890
6_{06}	5_{05}	4	3	7686.0696	7686.0643	0.00529
6_{16}	5_{15}	8	7	7686.2674	7686.2601	0.00730
6_{06}	5_{05}	8	7	7686.3208	7686.3085	0.01229
6_{16}	5_{15}	9	8	7686.5690	7686.5723	-0.00334
6_{06}	5_{05}	9	8	7686.6211	7686.6207	0.00043
6_{16}	5_{15}	6	7	7686.6878	7686.6854	0.00238
6_{06}	5_{05}	6	7	7686.7366	7686.7338	0.00277

III. Results and Discussion

We have now obtained a satisfactory least-squares fit analysis of the hyperfine spectrum of the dihapto isomer of acyl methyl manganese pentacarbonyl. The new results have yielded the nuclear quadrupole coupling constants that are in good agreement with the current quantum chemical calculations comparing with the previous results. The quantum number assignments of ^{55}Mn hyperfine components were not as straightforward as several factors complicated the analysis. One factor was that the hyperfine components fell in the spectral region with somewhat heavy spectral congestion. Some possible origins of the congestion are a) methyl internal rotation splitting and b) the presence of lines from the agostic isomer. The assignment of hyperfine lines was further complicated by the following facts: both *a*-type and *c*-type hyperfine splitting patterns show asymmetrical splitting patterns with respect to the central frequencyand that *a*-type transitions have relatively small asymmetry splitting smaller than the hyperfine splittings. A consequence of this complication is that the strong hyperfine components, especially of the *a*-type transitions, are clustered about the hypothetical central frequencies with few outlier satellite components. As seen Table 3, a cluster of lines about 6435 MHz for $J = 3 \rightarrow 4$ and $4 \rightarrow 5$, $\Delta F = 0, \pm 1$ transitions fit relatively well, but the current fit is missing several outlier satellite hyperfine components.

The diagonal components of the nuclear quadrupole coupling tensor in the principle axis for the asymmetric top acyl methylmanganese pentacarbonyl obtained from the new least-squares fit analysis are in good agreement qualitatively with the calculated values shown in Table 1. The measured diagonal components in the principle axis are $eQq_{aa} = -31.31(7)$, $eQq_{bb} = 42.52(12)$, and $eQq_{cc} = -11.23(12)$ MHz. Also, the sign of the eQq(^{55}Mn) obtained from this work agrees with calculated eQq(^{55}Mn) values computed at various level of calculations as displayed in Table 1. The centrifugal distortion constants, $D_J = 0.21(2)$ and $D_{JK} = 4.9(2)$ kHz, obtained from the least squares fit are relatively small in value. We can infer that the gas-phase structure of this molecule in the ground vibrational and low-J states has a fairly rigid structure.

The present microwave work has improved the value of rotational constants and the diagonal elements of the nuclear quadrupole coupling tensor for the asymmetric top acyl methyl manganese pentacarbonyl. Now, for the dihapto acyl isomer calculated values for both rotational constants and quadrupole coupling strengths agree well with the measurements. Microwave measurements of the nuclear quadrupole coupling constants and rotational constants are of considerable importance because these spectroscopic constants provide a touchstone to test the reliability and accuracy of computational methods.

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Table 1. The experimental and calculated molecular parameters for dihapto (+3 agostic) isomers of CH$_3$Mn(CO)$_5$ in MHz. Basis sets for the calculations are as described in the text. For the experimental results, 40 transitions were included with rms = 16 kHz and a standard deviation of 18 kHz for the experimental fit.

Parameter	1. Experimental	2.B3LYP –dihapto	3. M11-dihapto	4. CCSD - dihapto	5. MP2 - dihapto	6. B3LYP-Agos	7. PBE1PBE -Agos	8. TPSSH-Agos
A	840.084(5)	825.589	831.458	833.095	938.300	819.810	840.899	828.042
B	774.286(2)	770.664	778.362	777.454	838.050	788.101	807.776	797.837
C	625.653(1)	635.694	637.850	641.665	706.278	654.867	669.182	661.694
1.5 χ_{aa}	-46.96(11)	-46.5	-45.50	-40.65	-47.3	-97.1	-94.6	-89.3
0.25(χ_{bb}-χ_{cc})	-13.44(3)	-7.2	-6.667	-7.697	-11.9	-12.9	-13.2	-18.2
Mu-a		2.65	2.14	2.125	5.39	-1.01	-0.98	0.30
Mu-c		-0.62	0.87	0.590	0.68	-2.93	-2.97	-3.12
X_{aa}		-31.0		-27.1	-31.5	-64.7	-63.1	-59.6
χ_{bb}		1.1		-1.85	-8.0	6.6	5.1	-6.6
χ_{cc}		29.9		28.94	39.5	58.1	57.9	66.2
Method/ Basis set		B3LYP/Def2TZVPP	M11/def2QZvpp	CCSD/cc-pvQZ,	MP2/Def2TZVPP	B3LYP/Def2TZVPP	PB1PBE/Def2TZVPP	TPSSH/Def2TZVPP