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# Isomers of Manganese Tetracarbonyl Hydride: A Density Functional Study of Structure and Vibrational Spectra

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Density functional theory (DFT) calculations have been used to find and characterize various isomers of $HMn(CO)_4$, a coordinatively unsaturated complex. For comparison, its saturated parent compound $HMn(CO)_5$ has been included in the study. Optimized geometries and vibrational spectra were calculated for each species. For the pentacarbonyl, the theoretical geometry allows a critical discussion of various experimental results. Its calculated vibrational spectrum agrees with experiment within an average error of less than 10 $cm^{-1}$ and maximum deviation of $\sim$30 $cm^{-1}$. In a search for isomeric forms of the tetracarbonyl complex, two minima have been found on the potential surface. The most stable form is a $C_s$ structure, with a second isomer of $C_{4v}$ symmetry lying about 3 kcal/mol higher in energy. The existence of these two structures is in agreement with the conclusions of a sophisticated matrix isolation photolysis study by Church et al.[18] The calculated vibrational spectrum supports the interpretation of the CO region of the infrared spectrum, a crucial part of the experimental evidence, in every detail. This refers not only to the dominant $C_s$ form but also to the very difficult experimental proof of the presence of a small amount of the $C_{4v}$ isomer. We suggest, in addition, that the Mn−H stretching frequency, although difficult to observe, could be used for identification: we predict an unexpectedly large frequency shift of $\sim$140 $cm^{-1}$ between the $C_s$ and the $C_{4v}$ isomers. A third isomer, the $C_{2v}$ structure—suggested in some studies as an alternative to $C_s$—was found to be a saddle point, rather than a minimum, in our study. For the heterolytic Mn−CO bond cleavage the calculations predict a dissociation energy of 41.8 kcal/mol.

## Introduction

Coordinatively unsaturated transition metal carbonyl complexes are intriguing systems for the structural chemist. Often, the most fundamental question about their structure, the geometric arrangement of the ligands around the central metal atom, has been the subject of debates. Specifically, for pentacoordinate $d^6$ (or, 16-valence-electron) systems, like the present $HMn(CO)_4$ species, a variety of structures of different symmetry have been proposed.[1] Also, the correct description of the electronic structure of these systems—due to the weak metal−ligand bonds—is a challenge for theory. Apart from the theoretical interest, several systems of this type, like cobalt, rhodium, and iron carbonyls, have considerable practical importance in catalytic processes[2] and as intermediates in dissociative substitution reactions.[3] The unsaturated complex is usually produced from its saturated "parent" by loss of CO in photolysis experiments, and it is reasonable to study the pair of complexes together, as we do here for the title compound and the corresponding pentacarbonyl hydride complex.

The experimental study of unsaturated complexes is quite difficult due to their high reactivity. Only a few methods are capable of examining them in the gas phase[1] or in frozen gas matrix.[4] Quantum chemical calculations may give valuable additional information, but their use is not quite obvious, either. Hartree−Fock (HF) calculations are known to be unreliable for transition metal complexes.[5−9] The basic problem is easy to understand: in a weak metal−ligand bond, the nonbonding orbital lies close to the bonding one and should

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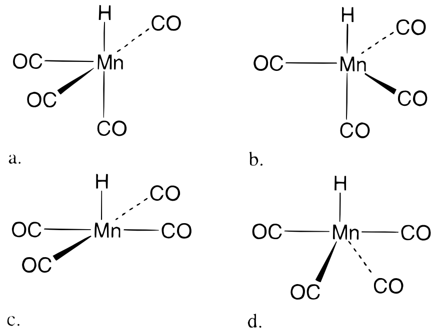

**Figure 1.** Possible isomers of $HMn(CO)_4$: $C_s$ structure (a), $C_{3v}$ structure (b), $C_{4v}$ structure (c), $C_{2v}$ structure (d)

be included in the description of the system. To take into account this "nondynamic" electron correlation, the use of a multideterminant wave function is required. However, calculations of this type are viable for small molecules only. For fairly large systems such as the present one, practically the only alternative is to use density functional (DFT) theory. With all the uncertainties, experience has shown that DFT calculations give reasonable description of the electronic and molecular structure of transition metal compounds.[10,11]

The subject of the present study is the $HMn(CO)_5$/$HMn(CO)_4$ system. Beyond the above general considerations about the theoretical treatment, one has to distinguish in our case between the pentacarbonyl and tetracarbonyl complex. The first one is a coordinatively saturated, 18-valence-electron system. The tetracarbonyl, however, is an unsaturated system with 16 electrons only. This may make the description of the electronic structure even more difficult, as the significance of higher-spin states cannot be precluded. Fortunately, some recent studies[12-14] on transition metal monocarbonyls show reasonable results for various properties (ground state configuration, geometry parameters, bond dissociation energies, vibrational frequencies) of these coordinatively unsaturated compounds as well, indicating the adequacy of the DFT method also in these systems. In preliminary test calculations we checked the possibility of a triplet ground state in the case of the tetracarbonyl complex. With the exception of a $C_{3v}$ structure (see below), assumption of a singlet ground state proved justified. Consequently, a regular closed shell description of the electronic structure was used in all detailed geometry and vibrational frequency calculations.

The tetracarbonyl complex, $HMn(CO)_4$, can be derived from $HMn(CO)_5$ by CO loss (Figure 1). Starting with the tetragonal bipyramidal structure of the pentacarbonyl, four isomers can be derived. If the carbonyl ligand leaves an initially equatorial position, a $C_s$ structure (Figure 1a) is formed. Making the equatorial carbonyl angles equal results in a $C_{3v}$ structure (Figure 1b). If the ligand leaves the axial position, a $C_{4v}$ structure can be obtained (Figure 1c). Appropriate distortion of the latter (along an asymmetric carbonyl internal coordinate) leads to a $C_{2v}$ isomer (Figure 1d).

Experimentally, the CO loss can be achieved by photolysis. Several matrix isolation studies have investigated the photolysis of the manganese pentacarbonyl hydride complex.[15-19] The reaction can lead to two different products. The first reaction[17,18] (predominant at $\lambda = 229$ nm) takes place with a CO loss resulting in the $HMn(CO)_4$ complex, while the other one (at $\lambda = 193$ nm) starts with a homolytic Mn−H bond scission[15,16] leading to the $\bullet Mn(CO)_5$ radical. These sophisticated experiments gave important information about the structure of $HMn(CO)_4$ that we will compare with our results.

Among early theoretical investigations, an approximate MO calculation (of Fenske−Hall type[20]) by Lichtenberger and Brown[21] should be mentioned. High-level quantum chemical studies have been reported by Veillard et al.[22] and Daniel.[23,24] They examined the photolysis of $HMn(CO)_5$ by means of electron correlation calculations applying the contracted CI method and proposed a mechanism for the process. It involves a $d_\pi \rightarrow \pi^*$ ($^1A_1 \rightarrow {}^1E$) transition followed by a radiationless transition to the $^3A_1$ state for the hydride homolysis and a $d_\pi \rightarrow \sigma^*$ ($^1A_1 \rightarrow {}^1E$) transition for the carbonyl loss. Although the authors reported full potential energy curves for the $HMn(CO)_4 + CO$ system, they performed their calculations at the experimental geometry of $HMn(CO)_5$ and applied $C_{4v}$ symmetry constraint. Therefore, these calculations, although of high quality, give no information about the possible existence and relative energies of different structures of $HMn(CO)_4$ nor of the geometry parameters of the $C_{4v}$ structure.

The primary aim of the present study is to find and characterize—by their energies, fully optimized geometries, and vibrational spectra—the various isomers of $HMn(CO)_4$. Before doing that, we report results on the "parent" molecule, the stable and well-described pentacarbonyl compound. This is mainly for comparison and test. Beyond that, however, we shall give a critical discussion of the various experimental results available for $HMn(CO)_5$. Then, for the unstable tetracarbonyl species, we can compare our theoretical results with the experimental matrix isolation results, especially with those by Church et al.[18] The present theoretical results are based on DFT calculations.

## Computational Details

Calculations were carried out using the BLYP gradient corrected density functional (Becke 1988 exchange term[25] and Lee−Yang−Parr[26] correlation term), in Gaussian-94.[27] Some

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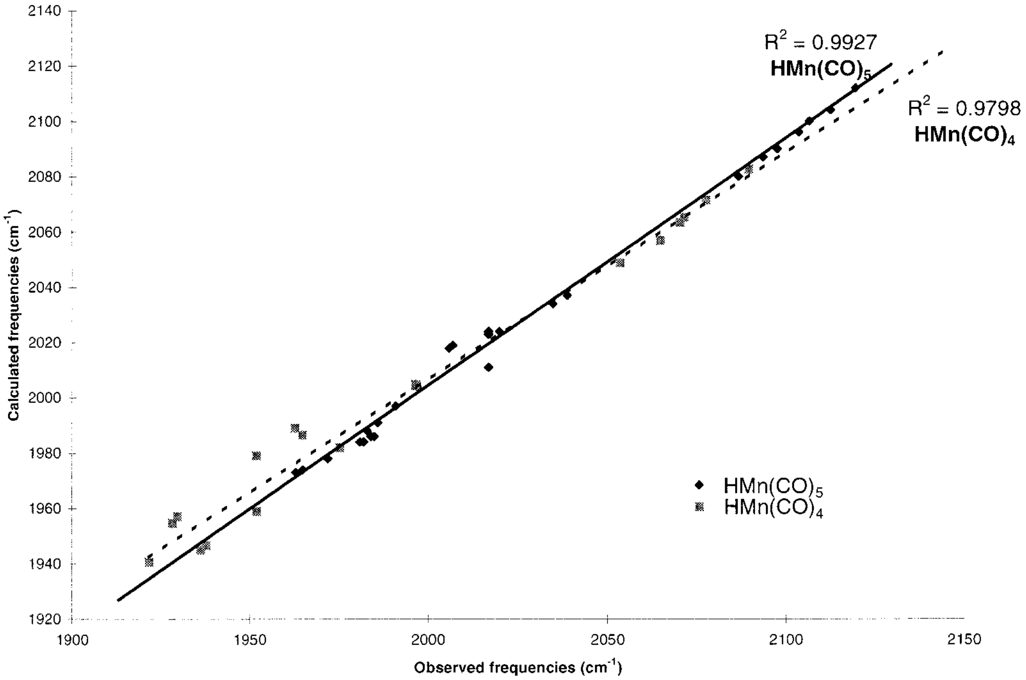

**Figure 2.** Correlation chart of observed and calculated frequencies of HMn(CO)$_5$ and HMn(CO)$_4$. The square of the correlation coefficient is indicated.

HF calculations have also been performed for comparison by using TX90[28] and Turbomol[29] program packages. These results, however, will only be reported qualitatively, due to the considerations in the Introduction.

DFT geometry optimizations were done in redundant internal coordinates, as available in Gaussian-94. For the HF calculations natural internal coordinates were used, defined by the INTC[30] program. The latter was also used when converting Cartesian force constants to internal coordinates in vibrational analysis.

All calculations were carried out applying Ahlrichs' sv and svp[31] basis sets (sv: {31} for H, {311/31} for C and O and {63311/53/41} for Mn. svp: one additional polarization function [p-type for H and Mn and d-type for C and O]). In the tables, only BLYP/svp results are reported. Where results obtained at BLYP/sv level of theory significantly differ from those, this fact will be noted.

## Results and Discussion

**(a) Test Results on Free CO.** We start with simple test results on carbon monoxide itself. For this simple molecule the present low-level calculations give obviously no new information; still, it seemed worthwhile to list some data for comparison, as given in Table 1.

**Table 1. Bond Length (Å), Harmonic Vibrational Frequency (cm$^{-1}$), and Dipole Moment (D) of Free CO**

| | BLYP/sv | BLYP/svp | expt[a] |
|---|---|---|---|
| *R*(C−O) | 1.168 | 1.143 | 1.128 |
| freq | 1980 | 2143 | 2170 |
| dipole moment | 0.130 | 0.309 | 0.109 |

[a] From ref 38.

The bond length tends to be significantly overestimated. An excellent result is obtained for the vibrational frequency. The essential role of polarization functions, however, is to be noted, as the smaller basis strongly overestimates the bond length and underestimates the frequency.

The very small dipole moment in CO is a delicate quantity, and it is well-known that HF calculations fail to reproduce even its correct direction. By DFT the sign is correct, but the result is still sensitive to the basis set; disturbingly, the larger basis set gives poorer results.

**(b) Geometry and Vibrational Spectrum of HMn(CO)$_5$.** Results on the geometry are compiled in Table 2. It should be noted that a similar study was reported very recently by Jonas and Thiel,[11] using HF, MP2, DFT/BLYP, and DFT/BP86. The two results are similar. The results, overall, are close to the experimental values. One should notice, however, the uncertainty in the experimental results: quite recently Kukolich and Sickafose reported a microwave spectroscopic (MW) study[32] in order to reinvestigate the molecular structure of the complex. Some parameters were kept fixed on the basis of previous neutron diffraction (ND)[33] and electron diffraction (ED)[34] results. This refinement caused an important effect: the Mn−H bond in the MW result is

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**Table 2. Calculated and Experimental Structural Parameters of $HMn(CO)_5$ (distances in Å, angles in deg)**

| | BLYP/svp | expt[a] | expt[b] | expt[b] |
|---|---|---|---|---|
| MnH | 1.587 | 1.576 | 1.645 | 1.65 |
| $MnC_{eq}$ | 1.864 | 1.856 | 1.853[c] | 1.856[c] |
| $MnC_{ax}$ | 1.865 | 1.854 | 1.822[c] | 1.822 |
| $C-O_{eq}$ | 1.157 | 1.142 | 1.148 | 1.142[c] |
| $C-O_{ax}$ | 1.160 | 1.142 | 1.143[c] | 1.142[c] |
| $\angle C_{ax}MnC_{eq}$ | 97.1 | 94.5 | 97.0 | 97.3 |
| $\angle MnCO_{eq}$ | 177.3 | 169.9 | 176.3 | 177.0 |
| $\angle C_{eq}MnC_{eq}(1)$ | 165.7 | | | |
| $\angle C_{eq}MnC_{eq}(2)$ | 89.1 | | | |

[a] Electron diffraction data, ref 34. [b] MW data, some parameters were kept fixed on the basis of previous experimental values ref 32. [c] Fixed.

0.07 Å (!) longer than its ED value. Our results are much closer to the ED results: the calculated bond distance agrees with the ED value within 0.02−0.01 Å, and the direction is as expected (it is a general observation that DFT calculations tend to slightly overestimate X−H distances). For the metal−carbon bond lengths the BLYP/svp results match the ED result within 0.01 Å, an excellent agreement. More importantly, there is virtually no difference between the equatorial and axial bonds, contrary to the MW analysis. The calculated C−O bond lengths are slightly longer than the experimental value. This is in line with the results on free CO in Table 1. The equatorial−axial splitting is negligible. The change relative to free CO may also be of interest: as a result of the metal−CO bonding, the C−O bonds become weaker, thus longer, in the complex. The lengthening of 0.014−0.017 Å is quite significant for this stiff bond and agrees perfectly with experiment. (The effect is less exposed but present even in the HF results.) In summary, the present results on the geometry of $HMn(CO)_5$ strongly prefer the electron diffraction results[34] to the microwave spectroscopic results.[32]

The harmonic vibrational frequency data of the complex and its deuterated analogue are shown in Table 3. In the carbonyl stretching region, the calculated DFT values show an excellent agreement (with an error of $\sim$10 cm$^{-1}$) with the experimental spectrum; this must be partly fortuitous, as the basis set effect between BLYP/sv and BLYP/svp is still significant (again, the BLYP/sv values lie $\sim$120 cm$^{-1}$ lower than those obtained at BLYP/svp) and we cannot be certain that the basis set is already saturated.

A basic characteristic of the carbonyl stretching region is that one of the two totally symmetric frequencies, $\nu_1$, lies 70−100 cm$^{-1}$ higher than the other three modes, the latter forming a close-lying group. It is then interesting to ask about the nature of this $\nu_1$ mode, and we carried out a vibrational analysis in terms of internal coordinates to this purpose. Perhaps against intuition, the "lonely" band $\nu_1$ is *not* the unique *axial* CO stretching. Rather, $\nu_1$ is the symmetric combination of the *equatorial* CO stretchings. This shows that the latter have a nonnegligible coupling. The axial CO appears as $\nu_2$. Apart from the frequencies, a very important source of information for assignment of a spectrum is given by the relative intensities. As seen in Table 3, intensities are well reproduced in the calculations: in agreement with observation, $\nu_1$ is of weak-medium intensity, $\nu_9$ very weak, while $\nu_{15}$ and $\nu_2$ stand out with very strong intensities. Finally, a comparison with free CO shows that the overall range of the carbonyl stretching modes lies at lower frequencies, indicating a slightly weakened bond, in agreement with the bond length variation discussed above.

The results for the metal−ligand vibrations also show quite amazing agreement with experiment. Not only the band positions but also the spectral intensities are well reproduced. Our results confirm the assignment[11] of the MnC stretching modes $\nu_{19}$ (e symmetry) and $\nu_5$ ($a_1$ symmetry) to one single band in the experimental spectrum (462 cm$^{-1}$);[36] its intensity comes apparently mainly from the e mode.

**(c) Isomers of $HMn(CO)_4$.** The main purpose of this study was to find out in what isomeric forms $HMn(CO)_4$ may exist. Accordingly, we made a complete search for all four forms shown in Figure 1. Looking for stationary points on the potential surface, two minima have been identified, plus a first-order saddle point. The structure of $C_{3v}$ symmetry could not be determined: in this symmetry, the HOMO belongs to the two-dimensional e symmetry species, and due to degeneracy no closed shell solution exists. Rather, the electronic ground state in this case is a triplet. It lies about 15 kcal/mol higher in energy than the other structures to be discussed and will not be considered further. For the three stationary points found, relative energies, the number of negative eigenvalues of the Hessian, and parameters of the optimized geometries are shown in Table 4.

The lowest energy conformer is of $C_s$ symmetry, corresponding to Figure 1a. The second isomer lies about 3 kcal/mol higher and is basically the $C_{4v}$ structure depicted in Figure 1c. This latter qualification needs, however, refinement. This second minimum is strictly $C_{4v}$ according to the HF and BLYP/sv calculations. In the BLYP/svp results, however, the exact symmetry of the minimum is in fact $C_{2v}$, derived from the $C_{4v}$ structure by slight distortion along a $b_1$ mode dominated by the $\delta$CMnC internal coordinate. In the "best" calculation then, the $C_{4v}$ isomer is strictly speaking a saddle point. However, the difference in geometry is very small, and the energy difference is smaller than the zero-point vibrational energy (ZPVE). Consequently, the distortion is physically insignificant, and this structure will be referred to as the $C_{4v}$ minimum. The third stationary point found is a saddle point of $C_{2v}$ symmetry, the structure sketched in Figure 1d.

Our results should now be compared with the experimental matrix isolation studies. $HMn(CO)_4$ was first identified as the photolysis product of $HMn(CO)_5$ in a classic study of this field by Rest and Turner.[17] They presumed first that the tetracarbonyl fragment had $C_{3v}$ structure. Ten years later McHugh and Rest[35]—after more experience with analogous systems—revised the interpretation of the original experiments and suggested $C_{2v}$ symmetry. It was then Church et al.[18] who carried out sophisticated new matrix isolation photolysis experiments and presented evidence for *two* isomers of

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**Table 3. Calculated and Experimental Harmonic Vibrational Frequencies (in cm$^{-1}$) and IR Absorption Intensities[a] of $HMn(CO)_5$ and $DMn(CO)_5$**

| | | | $HMn(CO)_5$ | | | $DMn(CO)_5$ | |
|---|---|---|---|---|---|---|---|
| | | | expt (gas-phase)[b] | expt ($CH_4$ matrix)[c] | BLYP/svp | expt[d] | BLYP/svp |
| $a_1$ | $\nu_1$ | CO | 2125 (m) | 2120(vw) | 2112 (1) | 2125 (m) | 2112 (1) |
| $b_1$ | $\nu_9$ | CO | 2054 | | 2042 (−) | | 2042 (−) |
| e | $\nu_{15}$ | CO | 2029 (vvs) | 2016[e] | 2024 (675) | 2029 (vvs) | 2024 (684) |
| $a_1$ | $\nu_2$ | CO | 2020 (vvs) | 2006 | 2019 (188) | 2016 (vvs) | 2017 (185) |
| $a_1$ | $\nu_3$ | MnH | 1784 (m) | | 1753 (3) | 1287 (m) | 1251 (2) |
| e | $\nu_{16}$ | δCMnH | 731 (vs) | | 735 (76) | 668 (vs) | 678 (87) |
| $a_1$ | $\nu_4$ | δMnCO | 663 (vs) | | 663 (32) | 663 (vs) | 662 (32) |
| e | $\nu_{17}$ | δCMnH | 612 (vs) | | 599 (16) | 541 (w) | 545 (0) |
| $b_2$ | $\nu_{13}$ | δMnCO | | | 561 (−) | | 561 (−) |
| e | $\nu_{18}$ | δMnCO | 537 (w) | | 535 (0) | 517 (w−m) | 505 (1) |
| $b_1$ | $\nu_{10}$ | δMnCO | | | 474 (−) | | 474 (−) |
| e | $\nu_{19}$ | MnC | 462 (vs) | | 463 (9) | 456 (vs) | 459 (6) |
| $a_1$ | $\nu_5$ | MnC | 462 (vs) | | 455 (1) | 456 (vs) | 455 (0) |
| $b_1$ | $\nu_{11}$ | MnC | | | 419 (−) | | 419 (−) |
| $a_1$ | $\nu_6$ | MnC | 408(w) | | 413 (0) | 408 (w) | 413 (0) |
| $a_2$ | $\nu_8$ | δMnCO | | | 371 (−) | | 371 (−) |
| e | $\nu_{20}$ | δMnCO | 362 (m−w) | | 343 (0) | 328 (w−m) | 311 (0) |
| $a_1$ | $\nu_7$ | δCMnC | 106[f] | | 114 (0) | | 114 (0) |
| e | $\nu_{21}$ | δCMnC | 120[f] | | 107 (0) | | 107 (0) |
| $b_2$ | $\nu_{14}$ | δCMnC | | | 101 (−) | | 102 (−) |
| e | $\nu_{22}$ | δCMnC | 77[f] | | 83 (0) | | 83 (0) |
| $b_1$ | $\nu_{12}$ | δCMnC | | | 38 (−) | | 38 (−) |

[a] Relative to the total absorption intensity (=1000; in parentheses). [b] Ref 36; new assignments (concerning the bands at 77, 106, 120, and 462 cm$^{-1}$) have been accepted from ref 10. [c] Ref 18. [d] Ref 39. [e] Mean value of matrix split bands. [f] Obtained from combination bands.

**Table 4. Calculated Relative Energy (in au), Number of Negative Hessian Eigenvalues, and Selected Geometrical Parameters (Å and deg, respectively) of Different Stationary Points of $HMn(CO)_4$ at the BLYP/svp Levels of Theory**

| $C_s$ | BLYP/svp | $C_{4v}$ | BLYP/svp |
|---|---|---|---|
| rel energy[a] | 0 | rel energy | 0.005301 |
| λ[b] | 0 | λ[b] | 1[c] |
| MnH | 1.593 | MnH | 1.525 |
| $MnC_{eq}(1)$[d] | 1.784 | MnC | 1.855 |
| $MnC_{eq}(2)$[d] | 1.857 | | |
| $MnC_{ax}$ | 1.863 | | |
| $CO_{eq}(1)$[d] | 1.165 | CO | 1.161 |
| $CO_{eq}(2)$[d] | 1.159 | | |
| $CO_{ax}$ | 1.162 | | |
| $\angle HMnC_{eq}(1)$[d] | 94.6 | ∠HMnC | 84.7 |
| $\angle HMnC_{eq}(2)$[d] | 78.9 | | |
| $\angle HMnC_{ax}$ | 171.1 | | |
| $\angle C_{eq}(2)MnC_{eq}(2')$[d] | 157.8 | ∠CMnC(1) | 89.5 |
| $\angle C_{eq}(1)MnC_{eq}(2)$[d] | 91.9 | ∠CMnC(2) | 169.4 |

[a] Relative energy with respect to the most stable conformer (zero-point vibrational energy is not taken into account). [b] Number of the negative eigenvalues of the Hessian. [c] See text. [d] (1) and (2) denote the single and two equivalent carbonyl ligands, respectively, in the case of the $C_s$ structure.

$HMn(CO)_4$. They definitely proved that the major product is a $C_s$ structure. Furthermore, they showed that narrow-band photolysis produces from this $C_s$ structure another product, which should be another isomer, "most probably with $C_{4v}$ structure". As we see, it required highly sophisticated experiments and much effort in the interpretation to come to the final conclusion. It is thus really very comforting to see that the theoretical results are in complete accord with this last conclusion, confirming it. Because the experimental evidence relied to a large extent on the infrared spectrum, we shall return to further details below when discussing the calculated spectrum.

A few remarks about the geometrical parameters of the isomers may also be of interest. The $C_s$ structure originates from $HMn(CO)_5$ by removing an equatorial carbonyl ligand. Comparing Tables 2 and 4, it is interesting to see that the equatorial C−Mn−C bond angles change only a few degrees. After removal of one CO ligand, the remaining carbonyls are still roughly at their original positions, thus leaving a vacant coordination site in the equatorial plane. Note that in the experimental study[18] a considerable blue shift was observed in the UV spectrum of the complex on changing the matrix from Ar to $CH_4$. This was considered as an indication of the presence of a vacant site where a molecule of the matrix can be coordinated (the interaction being stronger in the case of $CH_4$). The theoretical result completely supports this picture.

As to details of the structural changes in the $C_s$ isomer relative to the pentacarbonyl, the only site significantly affected is the equatorial CO ligand opposite the vacant coordination place. The Mn−C distance is shorter by 0.08 Å, and even the stiff C−O distance is longer by 0.008 Å. These data show a more effective overlap between the $p_z$ orbital of this ligand and the manganese $d_{xz}$ orbital, resulting in a stronger back-donation from the metal to the antibonding orbital of the ligand.

The second isomer, of $C_{4v}$ symmetry, lies about 3 kcal/mol higher than the $C_s$ minimum. This isomer is obtained from the pentacarbonyl complex if the ligand leaves the axial position. Again, removal of one ligand does not change the general arrangement of the rest. According to the DFT results, the only significant structural change affects the Mn−H distance: it is shortened by 0.06 Å relative to the pentacarbonyl complex. This fact is consistent with expectation, as the absence of the donation of the $d_{z^2}$ electrons to the carbonyl ligand results in a stronger ability to bind the hydride ligand.

As noted above, besides the two minima a saddle point was found. This is the $C_{2v}$ symmetry structure of Figure 1d. Distorting this structure along an internal coordinate of $b_1$ symmetry dominated by a δHMnC causes relaxation to the $C_s$ isomer. The saddle point thus represents a transition state between the $C_s$ structure

**Table 5. Calculated and Experimental Harmonic Vibrational Frequencies (in $cm^{-1}$) and IR Absorption Intensities[a] of the Conformers of $HMn(CO)_4$ at the BLYP/svp Level of Theory**

| | | $C_s$ | | | | | $C_{4v}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | character | BLYP/svp | expt[b] | | | character | BLYP/svp | expt |
| a′ | $\nu_{1}$ | [CO] | 2083 (3) | 2090 | $a_1$ | $\nu_{1}$ | [CO] | 2090 (0) | |
| a′ | $\nu_{2}$ | [CO] | 2005 (199) | *c* | $b_1$ | $\nu_{7}$ | [CO] | 2020 (−) | |
| a″ | $\nu_{16}$ | [CO] | 2004 (447) | 1997 | | | | | |
| a′ | $\nu_{3}$ | [CO] | 1987 (258) | 1965 | e | $\nu_{13}$ | [CO] | 1988 (908) | 1966 |
| a′ | $\nu_{4}$ | [MnH] | 1745 (12) | 1742[d] | $a_1$ | $\nu_{2}$ | [MnH] | 1883 (11) | |
| a″ | $\nu_{17}$ | [δCMnH] | 717 (18) | | | | | | |
| a′ | $\nu_{5}$ | [δMnCO] | 670 (11) | | e | $\nu_{14}$ | [δCMnH] | 763 (22) | |
| a″ | $\nu_{18}$ | [δMnCO] | 603 (6) | | $a_1$ | $\nu_{3}$ | [δMnCO] | 625 (12) | |
| a′ | $\nu_{6}$ | [δMnCO] | 599 (19) | | | | | | |
| a′ | $\nu_{7}$ | [δMnCO] | 552 (8) | | e | $\nu_{15}$ | [MnC] | 600 (26) | |
| a″ | $\nu_{19}$ | [δMnCO] | 536 (1) | | $b_2$ | $\nu_{11}$ | [MnC] | 563 (−) | |
| a′ | $\nu_{8}$ | [MnC] | 498 (1) | | $b_1$ | $\nu_{8}$ | [δMnCO] | 463 (−) | |
| a′ | $\nu_{9}$ | [δMnCO] | 482 (1) | | | | | | |
| a″ | $\nu_{20}$ | [MnC] | 439 (8) | | $a_1$ | $\nu_{4}$ | [δMnCO] | 422 (0) | |
| a′ | $\nu_{10}$ | [MnC] | 439 (1) | | e | $\nu_{16}$ | [MnC] | 456 (20) | |
| a′ | $\nu_{11}$ | [MnC] | 412 (1) | | $b_1$ | $\nu_{9}$ | [δMnCO] | 420 (−) | |
| a″ | $\nu_{21}$ | [δMnCO] | 355 (0) | | $a_2$ | $\nu_{6}$ | [MnC] | 367 (−) | |
| a″ | $\nu_{12}$ | [δMnCO] | 349 (1) | | | | | | |
| a′ | $\nu_{12}$ | [δMnCO] | 300 (3) | | e | $\nu_{17}$ | [δCMnC] | 315 (2) | |
| a′ | $\mathrm{n}_{13}$ | [δCMnC] | 106 (0) | | $a_1$ | $\mathrm{n}_{5}$ | [δCMnC] | 105 (0) | |
| a" | $\mathrm{n}_{13}$ | [δCMnC] | 105 (0) | | $b_2$ | $\mathrm{n}_{12}$ | [δCMnC] | 100 (−) | |
| a′ | $\mathrm{n}_{14}$ | [δCMnC] | 92 (0) | | | | | | |
| a" | $\mathrm{n}_{14}$ | [δCMnC] | 86 (0) | | e | $\mathrm{n}_{18}$ | [δCMnC] | 89 (0) | |
| a′ | $\mathrm{n}_{15}$ | [δCMnC] | 72 (0) | | $b_1$ | $\mathrm{n}_{10}$ | [δCMnC] | 31 (−) | |

[a] Relative to the total absorption intensity (=1000; in parentheses). [b] In $CH_4$ matrix, ref 18. [c] This band was not observed separately due to overlapping with the a″ band. [d] This band position was only reported in Ar matrix, ref 18.

and its inverted form. The barrier height is about 3 kcal/mol. Early considerations[17,18] about the possibility of a $C_{2v}$ isomer (see also below) seem thus unjustified.

**(d) Vibrational Frequencies of $HMn(CO)_4$.** The calculated vibrational frequencies are shown in Table 5. The $C_s$ conformer has 15 a′ and 9 a″ internal normal modes; all of them are IR and Raman active. The vibrational representation of the $C_{4v}$ conformer is $\Gamma_{vib} = 5\ a_1 + a_2 + 4\ b_1 + 2\ b_2 + 6\ e$; the $a_1$ and e modes are IR active, while all but the $a_2$ mode are Raman active. (The lowest frequency $b_1$ mode of the $C_{4v}$ structure in Table 5 refers actually to a $C_{2v}$ structure, as discussed above.)

Analysis of the calculated spectra is important because the experimental proof for the identification of $HMn(CO)_4$ was primarily based on the (matrix) infrared spectrum, mainly in the CO region. It was already observed by Rest and Turner[17] that the product appearing during photolysis of $HMn(CO)_5$ shows three bands in the CO region: two bands of high intensity around 1970−2000 $cm^{-1}$ plus a third, very weak one at significantly higher frequency, close to 2100 $cm^{-1}$. In $C_{4v}$ symmetry there would be only two infrared active vibrations ($a_1$ + e), while $C_s$ or $C_{2v}$ symmetries would both allow four active modes (with symmetries 3 a′ + a″, and $2a_1 + b_1 + b_2$, respectively). Thus, the obvious first conclusion was that the structure was $C_{3v}$, with CO stretchings of symmetry 2 $a_1$ + e. As already mentioned above, this interpretation was revised later,[35] suggesting $C_{2v}$ symmetry, assuming coincidence of two bands. The final conclusion by Church et al.[18] that the structure was $C_s$ rather than $C_{2v}$ was based on their $^{13}C$ spectra. Using model calculations for the CO region, based on estimated empirical force constants and dipole moment derivatives, they concluded that agreement between calculations and experiment is better if a $C_s$ structure is assumed. As can be seen in Table 5, our completely independent ab initio results agree with the experimental results and the interpretation given by Church et al.[18] in every single respect. (See also Figure 3 of ref 18.) First, the most crucial assumption, that about two overlapping bands, is confirmed: for the $C_s$ structure we calculate two bands (a′ and a″) of strong intensity at 2005 and 2004 $cm^{-1}$, which can be identified with the observed absorption at 1997 $cm^{-1}$. The third vibration, calculated at 1987 $cm^{-1}$, explains the second, slightly weaker but still intense absorption at 1964 $cm^{-1}$. The fact that the third observed absorption is at higher frequency and is very weak is also well reproduced. Finally, as compared to the parent pentacarbonyl compound, an overall shift of the CO region to lower frequencies by 30−50 $cm^{-1}$ is also there in the calculations, cf. Tables 3 and 5.

A crucial point about the composition itself of the photolysis product is the proof of the presence of hydrogen. The Mn−H stretching vibration gives weak absorption, and it was first Church et al.[18] who succeeded in identifying it with an absorption at 1742 $cm^{-1}$. Reassuringly, we are again in complete agreement, as shown by the calculated value of 1745 $cm^{-1}$. (Of course, such a close agreement is partly coincidental: the Mn−H stretching frequency was underestimated in the pentacarbonyl by about 30 $cm^{-1}$, so that the true gas-phase frequency may lie somewhat lower.)

The most intriguing part of the experimental study by Church et al.[18] was the suggestion of the existence of a second isomer, one of $C_{4v}$ symmetry. In light of the present theoretical results listed in Table 5, it is interesting to consider what are the chances of identification of the $C_{4v}$ isomer. As we see, the most striking feature in the CO stretching region is that there is only one strong band, calculated at 1988 $cm^{-1}$, and this is stronger than any other one in the $C_s$ form or in the pentacarbonyl. This band, listed as $\nu_{13}$ in Table 5, would then be a good candidate for identification. However, this e symmetry band perfectly coincides with $\nu_3$ (of symmetry a′) in the $C_s$ isomer, the latter being also strong. One should notice, however, that the strong pair of bands at ~2000 cm$^{-1}$ of the $C_s$ form discussed above should disappear in the $C_{4v}$ form. There is then some chance for identification of the second isomer on the basis of relative intensities. This is exactly what Church et al. did (without, of course, having any information on theoretical spectra)! They came to their conclusion about the second isomer by following the changes in the IR spectrum of $HMn(CO)_4$ upon irradiation at 367 nm in a $CH_4$ matrix. This irradiation converts the tetracarbonyl species back to the pentacarbonyl, which is seen very clearly in the increase of the CO stretching bands assigned to $HMn(CO)_5$ and a simultaneous decrease of the $HMn(CO)_4$ bands. Beyond this, "interestingly there is also a small but reproducible change in the relative intensities of these $HMn(CO)_4$ bands".[18] Following these changes in detail, they concluded that there is a new band at 1966 cm$^{-1}$, indicating the presence of a second isomer. Obviously, this was a bold statement, as the original $C_s$ isomer had its lowest CO stretching band at practically the same position, 1965 cm$^{-1}$. As the above discussion shows, the theoretical spectra completely confirm this conclusion.

As isotope enrichment $^{13}$C IR data were also measured[18] in the CO stretching frequency range and played an important role in the analysis, we have calculated the spectra of all the relevant isotopomers as well. The good correlation between the calculated and observed frequencies of the pentacarbonyl and tetracarbonyl hydride, as shown in Figure 3, gives further support for the reliability of the theoretical spectra.

Beyond the CO frequencies, the present results raise an interesting other possibility for identification of the $C_{4v}$ structure. The largest frequency change is in fact found for the Mn−H stretching: its calculated value of 1883 cm$^{-1}$ is about 140 cm$^{-1}$ (!) higher than its counterpart in the $C_s$ isomer (or that in the parent molecule). Unfortunately, in the experimental study[18] "no convincing spectra could be obtained in the Mn−H region". As discussed above, the relatively weak Mn−H stretching was difficult to observe even in the dominant $C_s$ isomer. Still, we think it is possible that the authors did not expect such a large shift. In any future study it may be interesting to search the Mn−H stretching again, including the predicted higher frequency range.

Finally, in light of the theoretical spectra, a few remarks may be worth mentioning about possibilities of identification in the lower frequency part of the spectra, which were not yet studied experimentally. We consider relatively strong bands only. Noticeable is a shift in the $\delta$CMnH mode, from 735 cm$^{-1}$ in the pentacarbonyl to 717 cm$^{-1}$ and 763 cm$^{-1}$ in the $C_s$ and $C_{4v}$ isomer, respectively. In addition, the bands at ~550 and ~440 cm$^{-1}$ in the $C_s$ isomer may be distinguished from the pentacarbonyl spectrum. In the $C_{4v}$ isomer, the band at 625 cm$^{-1}$ seems to be a candidate for identification. Also striking is the intense MnC band at 456 cm$^{-1}$, but this would be difficult to separate from the pentacarbonyl bands at 463 and 455 cm$^{-1}$. Finally, the medium-intensity bands at 300 and 315 cm$^{-1}$ in the $C_s$ and $C_{4v}$ isomer, respectively, are in a region relatively empty in the parent pentacarbonyl; thus they may be useful for identification.

**(e) Dissociation Energy of $HMn(CO)_5$.** The dissociation energy of $HMn(CO)_5$ is calculated to be 41.8 kcal/mol (ZPVE has been taken into account) at the BLYP/svp level of theory. To the best of our knowledge no previous experimental data have been published, but the DFT data are comparable to those published for the carbonyl dissociation energy of $Fe(CO)_5$ (41.5 ± 2 kcal/mol[37]).

## Conclusions

We have investigated in a theoretical study, based on DFT calculations, various isomeric forms of $HMn(CO)_4$ and, for comparison, its parent compound $HMn(CO)_5$. For the latter, the theoretical geometry agrees well with the electron diffraction results, while it indicates that unjustified assumptions were made in the microwave spectroscopic refinement of these results. The calculated vibrational spectrum of the pentacarbonyl compound agrees with experiment within an average error of less than ~10 cm$^{-1}$ and maximum deviation of ~30 cm$^{-1}$.

In a search for isomeric forms of the tetracarbonyl complex, we have identified two minima on the potential surface. The most stable form is a $C_s$ structure, with a second isomer of $C_{4v}$ symmetry lying about 3 kcal/mol higher in energy. The existence of these two structures is in agreement with the conclusions from a sophisticated matrix isolation photolysis study by Church et al.[18] Considering that the experimental conclusions were based mainly on the infrared spectra, specifically the CO stretching region, it is especially reassuring that the calculated vibrational spectrum supports the interpretation given in the experimental study in every respect. This refers not only to the dominant $C_s$ structure but also to the very difficult proof of the appearance of a small amount of the $C_{4v}$ isomer, upon irradiation of the $C_s$ form. We suggest, in addition, that a further important evidence could be given by identifying the Mn−H stretching frequency. This was found only in the $C_s$ isomer, even there with difficulty. For the $C_{4v}$ isomer we predict an unexpectedly large frequency shift of ~140 cm$^{-1}$, putting $\nu_{Mn-H}$ around 1880 cm$^{-1}$.

A third isomer, the $C_{2v}$ structure—which showed up in several studies as an alternative to $C_s$—was found to be a saddle point, rather than a minimum, in our study.

The DFT calculations give a heterolytic Mn−CO bond dissociation energy of 41.8 kcal/mol.

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