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The Gas Phase Structure of Transition Metal Dihydrides

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Abstract

ESR and infrared spectroscopic measurements on matrix isolated MnH_2 and CrH_2 have recently suggested that these simple molecules may be bent. This result would be the opposite of that found experimentally for the transition metal dihalides MX_2 , known to be linear. Here the geometrical structure of MnH_2 has been investigated by molecular electronic structure theory. A large contracted gaussian basis set [$\text{Mn}(14\text{s}11\text{p}6\text{p}/9\text{s}8\text{p}3\text{d})$, $\text{H}(5\text{s}1\text{p}/3\text{s}1\text{p})$] was used in conjunction with self-consistent-field and configuration interaction methods. These suggest that the ${}^6\text{A}_1$ ground state of MnH_2 is linear. Further studies of the ${}^3\text{A}_1$ state (one of several low-lying states) of TiH_2 also favor linearity, although this potential energy surface is extremely flat with respect to bending. Thus it appears probable that most MH_2 molecules, like the related MX_2 family, are linear.

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Introduction

The electronic and molecular structures of the transition metal halides is an established area of research where an increasing amount of experimental data has revealed some interesting variations,¹⁻⁴ thus stimulating theoretical studies on several of these molecules.⁵⁻¹⁰ Considerably less is known about the transition metal hydrides and most experimental studies have been restricted to the monohydrides MH .^{11,12} However the electronic structures and potential energy curves of these hydrides are of interest due to the insight they may give into chemisorption, surface chemistry, and catalysis,¹³ and several quantum mechanical studies have been reported for such systems (mainly for diatomic hydrides).¹⁴⁻²²

These MH_n investigations show that for the transition metal hydrides there is often a tendency to maintain as high a multiplicity as possible, with the $3d^n$ configuration of the metal atom surviving essentially unchanged during the formation of the molecule. In other words, the interaction between the metal 3d orbitals and the hydrogen 1s orbitals found to be very weak, probably because the partially occupied d orbitals are localized within the transition metal atom and are to a significant degree screened by the 4s orbital.

The main question we address in the present work is the prediction of the molecular structure of the dihydrides. If the $3d_M-1s_H$ interaction is weak for all the elements of the first transition metal series (Sc-Cu) then a linear geometry is expected for every HMH molecule. This is based on a bonding scheme involving the interaction of the 1s orbitals of the hydrogen atoms with the two 4s-4p hybrid orbitals available from the transition metal (see Figure 1 and discussion below). That is, in fact, what was found for

NiH_2 ²¹ by Guse, Blint, and Kunz. They state that the ground state of HNiH is derived from the $3d^8 4s^2$ configuration on nickel and not from the $3d^9 4s^1$ configuration, because the $3d_{\text{Ni}}-1s_{\text{H}}$ interaction is too weak. Further, they reported a relatively high resistance of this molecule to C_{2v} bending.

Recent cryospectroscopic experiments have suggested that the previously unknown molecules MnH_2 ²³ and CrH_2 ²⁴ trapped in argon at 4°K are bent, with bond angles of $\sim 120^\circ$ proposed for both of them. Although it is well known that the geometries of matrix isolated molecules may differ from their gas phase structures,²⁵ a bent structure for the lightest elements of the transition metal series could also be rationalized on the basis of a stronger $3d_{\text{M}}-1s_{\text{H}}$ interaction. For example, there seems to be a consensus developing that TiF_2 is bent.^{8,26}

Here we present the most sophisticated and complete theoretical work to date of an MH_2 species. However, rather than carrying out self-consistent-field calculations on each of the transition metal dihydrides, a more qualitative approach was adopted. We decided to choose the molecule MnH_2 and construct an ab initio Walsh diagram from which it might be possible to predict the geometries of the entire series of transition metal dihydrides. MnH_2 is a good choice for the present study since it was the subject of a Weltner's recent spectroscopic study,²³ lies halfway through the series, and is the first molecule for which each of the five transition-metal d-like orbitals becomes occupied. We later checked the validity of such a diagram by an explicit examination of TiH_2 , the MH_2 molecule most likely to be bent.

Theoretical Approach

All calculations were performed on the Harris Slash Four minicomputer.²⁷ Open shell restricted self-consistent-field (SCF) calculations were carried out using Pitzer's method.^{28,29} We started from a large cartesian gaussian basis set labeled M(14s,11p,6d/10s,8p,3d), H(5s,1p/3s,1p) previously used by one of us in the study of the transition metal tetrahydrides.²² For computational reasons (CI limit of 63 contracted gaussian functions) this contracted basis set had to be slightly reduced to a (9s,8p,3d/3s,1p) set for the configuration interaction (CI) studies.

CI calculations were carried out using the Berkeley system of programs.³⁰ The following restrictions were adopted in these CI calculations, performed in C_{2v} symmetry:

Molecule	State	Number of deleted highest virtual orbitals	Frozen core orbitals	Number of configurations
MnH ₂	⁶ A ₁	9	1s,2s,2p,3s,3p	6089
TiH ₂	³ A ₁	6	1s,2s,2p,3s	11375

With these restrictions, all singly and doubly excited Hartree-Fock interacting³¹ configurations relative to the SCF configuration were included. Davidson's formula³² was applied to estimate the importance of higher than double excitations, specifically unlinked clusters.

Results and Discussion

A. MnH₂.

The electronic configuration of the 6A_1 ground state of MnH₂ is relatively unambiguous. It corresponds to the following molecular orbital occupations:

This configuration preserves the high spin configuration of the manganese atom and allows two bonding interactions to occur between the available atomic orbitals of the fragments M, H₁ and H₂.

Careful optimization of the Mn-H bond length was first investigated through SCF calculations for three values of the bond angle ($\alpha = 120^\circ$, 150° and 180°). Then, using interpolated values for the bond distance, three other angles were considered ($\alpha = 135^\circ$, 165° , and 179°).

Table I gives the SCF total energies together with the corresponding Mn-H bond distances. The curve $E_{\text{SCF}} = f(\alpha)$ is seen to be relatively flat since only 3.4 kcal/mole are required to bend the molecule from 180° to 150° . For this reason it was considered mandatory to further test this result by carrying out CI calculations for the three bond angles 120, 150 and 179° .

The CI results reported in Table I support the contention that an SCF treatment of this problem is meaningful. However the SCF energy difference of (between 150° and 180°) 3.4 kcal is slightly reduced at the CI level to 3.0 kcal. Furthermore, the CI coefficient of the SCF reference configuration is ~ 0.96 , confirming the qualitative description

obtained at the Hartree-Fock level.

Our optimized bond length of 1.754 Å may be compared, in Table II, to some Mn-H bond distances previously reported in the literature. Although this Mn-H distance (1.754 Å) is comparable to that known for diatomic MnH, it is notably greater than the 1.601 Å found³³ for the prototype organ-metallic Mn-H bond, that in HMn(CO)₅. It is further surprising that the theoretical Mn-H distance for the highly unstable²² MnH₄ molecule is even shorter.

Table III gives the orbital energies as a function of the molecular bond angle α . As noted in the previous study of the electronic structure of MnH,¹⁵ the half occupied 3d-like orbitals lie lower in energy than the two bonding molecular orbitals 6a₁ and 3b₂. This seemingly paradoxical situation is due to the fact that the radial extent of the manganese 3d orbitals is about the same as that of the 3s and 3p orbitals, while the 4s and the 4p orbitals have a much larger radial extent. The hydrogen atoms must somehow overcome this extensive charge cloud in order to come close enough to have a significant overlap with the d-electrons. It is then energetically favorable for the hydrogen atoms to bond to the 4s and 4p orbitals, even if these outer orbitals are higher in energy.

However due to the partial removal of the initial Mn 4s² population through some charge transfer $\text{Mn}^{+\delta} \rightarrow \text{H}^{-\delta/2}$ (see Table I), some 3d_{Mn}-1s_H interaction is allowed to occur, and this noticeably affects the slope of the α -sensitive molecular orbitals of MnH₂, as shown in Figure 1. For example, the energy of the 6a₁ molecular orbital (which essentially describes the interaction between the symmetric combination of the H 1s atomic orbitals and the 4s orbital of manganese) would be independent of the α angle in

the absence of any 3d character in this molecular orbital. Table III shows that this is not the case and that this doubly occupied bonding orbital favors a linear geometry. Figure 1 also explains why the slope of the other bonding orbital, the $3b_2$, is relatively independent of the molecular bond angle. The 4p character of $3b_2$ would favor a linear geometry while its 3d component would favor some bending of the molecule. Table III further shows that the slopes of the mildly antibonding $8a_1$ and $4b_2$ (both half occupied) molecular orbitals roughly cancel each other, so that the molecular structure is governed by the geometrical preference of the $6a_1$ molecular-orbital. We shall discuss now the geometry of the other transition metal hydrides on the basis of a variable amount of $3d_M-1s_H$ interaction.

B. NiH₂.

For NiH₂ (and for the heavier elements of the transition metal series in general) a weaker $3d_M-1s_H$ interaction is expected, because the 3d orbitals are known to sink in energy and to contract rapidly. As a consequence the $8a_1$ and $4b_2$ molecular orbitals must be always pure atomic 3d orbitals, with energies relatively insensitive to the bond angle. Further the $3b_2$ molecular orbital would be dominated by the interaction of $[1s(H)_1-1s(H)_2]$ with the metal 4p orbital and would therefore favor a linear geometry. Finally the higher resistance to bond bending displayed by NiH₂ compared to MnH₂ (see Figure 2) may be traced to the fact that in the case of nickel, both molecular bonding orbitals $6a_1$ and $3b_2$ favor a linear structure.

C. TiH₂.

For TiH₂ (and for other light elements of the transition metal series) a stronger $3d_M-1s_H$ interaction is now expected, such that the following

relative slopes are expected for the molecular orbitals

$$4b_2 \text{ (linear)} > 8a_1 \text{ (bent)} > 6a_1 \text{ (linear)} > 3b_2 \text{ (bent)} . \quad (3)$$

A major problem for this d^2 case is to predict the electronic configuration of the ground state. Assuming a triplet ground state for TiH_2 and a C_{2v} symmetry, the most plausible electronic states arise from the ten following configurations

$$\begin{array}{llll} (8a_1)^1 (7a_1)^1 & (7a_1)^1 (4b_2)^1 & (4b_2)^1 (3b_1)^1 & (3b_1)^1 (1a_2)^1 \\ (8a_1)^1 (4b_2)^1 & (7a_1)^1 (3b_1)^1 & (4b_2)^1 (1a_2)^1 & \\ (8a_1)^1 (3b_1)^1 & (7a_1)^1 (1a_2)^1 & & \\ (8a_1)^1 (1a_2)^1 & & & \end{array}$$

leading to 3 3B_2 states, 3 3A_2 states, 3 3B_1 states and a unique 3A_1 state.

We chose to study the 3A_1 state for the following reasons:

1. This state is expected to be correctly described at the SCF level of theory since there is no other 3A_1 state energetically nearby expected to interact strongly. This was checked by performing a single CI calculation (see Table IV) in which the SCF reference was found to be dominant, having a coefficient of 0.96.

2. If one of the low-lying electronic states of TiH_2 is bent, then this $7a_1 8a_1$ configuration is one of the best candidates. This is obvious from Figure 3, which shows that the occupation of the $8a_1$ orbital together with the emptying of the $4b_2$ orbital are the best conditions for finding a bent structure. An even better choice would be the $1a_2 8a_1$ 3A_2 state, but

there are two other low-lying states of the same symmetry, precluding a simple SCF study.

For three different values of the bond angle $\alpha = 140, 160, \text{ and } 179$, the Ti-H bond length was optimized through SCF calculations. The results are given in Table IV. The notable increase in the bond length as the bond angle opens from 140 to 179 has to be traced to the mildly antibonding character of the half occupied $8a_1$ orbital and demonstrates the presence of some $3d_M-1s_H$ interaction.

The geometry is predicted to be a linear one. Since very good conditions to find out a bent structure were fulfilled by this 3A_1 state of TiH_2 , it is by no means inconceivable that all of the transition metal dihydrides MH_2 are linear. However, the curve $E = f(\alpha)$ is computed to be extremely flat (see Figure 2), and TiH_2 may indeed be observed in matrices as a bent species since a dipole-induced dipole interaction may be strong enough to counter-balance the small energy required for the bending of the molecule.²⁵ Further, similar effects could readily explain the recent experimental results on MnH_2 ²³ and CrH_2 .²⁴

Concluding Remarks

We present here a theoretical analysis of the electronic structure of the 3d transition-metal dihydrides, supported by extensive ab initio calculations on MnH_2 and TiH_2 . Although the 3d contribution to the bonding increases as we go from the right to the left in the periodic table, the $3d_M-1s_H$ interaction is still too weak to overcome the $4sp-1s_H$ mixing which dominates the bonding scheme and determines the linear geometry. However, the lightest 4d and 5d transition metal dihydrides may be good candidates for a bent structure on the basis of a perhaps stronger d_M-s_H interaction. The spectroscopic observation of trapped MnH_2 and CrH_2 as bent species may be a consequence of a dipole-induced dipole interaction between rare gas atoms and these molecules. Finally it is interesting that the hydrogen atom Mulliken charges within MnH_2 are the same (~ -0.3) as those deduced empirically by Jolly and co-workers for the organometallic hydride $\text{H}_2\text{Fe}(\text{CO})_4$.

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Table I. Energies (in hartrees) and Mulliken populations for MnH_2 .
Note that 1 hartree = 27.21 eV and 1 eV = 1.60219×10^{-19} J.

α	Mn-H (in Å)	SCF energy	CI energy	Population	
				Mn	H
120	1.764	-1150.909622	{ -1151.0238 -1151.0326 ^a	24.330	1.335
	1.766	-1150.909624			
	1.768	-1150.909623			
135	1.762	-1150.919588	--	24.335	1.332
150	1.756	-1150.926472	{ -1151.0395 -1151.0477 ^a	24.352	1.324
	1.758	-1150.926473			
	1.760	-1150.926470			
165	1.756	-1150.930561	--	24.380	1.310
179	1.754	-1150.931928	{ -1151.0443 -1151.0522 ^a	24.398	1.301
	1.752	-1150.931935			
180	1.754	-1150.931937	--	24.399	1.300
	1.756	-1150.931935			

^aNonvariational energy obtained using Davidson's formula³² for unlinked cluster contributions.

Table II. Mn-H bond length (in Å) in some hydrides.

Molecule	Mn-H	H population	Reference
MnH	1.789 (1.722) ^a	1.5	15
MnH ₂	1.754	1.3	this work
MnH ₄	1.577	1.2	22
HMn(CO) ₅	(1.601) ^a	1.3 ^a	33,34

^a Experimental values.

Table III. Orbital energies for MnH_2

Orbital	Occupation	$\alpha = \text{HMnH}$						
		120°	135°	150°	165°	179°	180°	
$D_{\infty h}$	C_{2v}							
$3\sigma_u$	$3b_2$	2	-0.364	-0.367	-0.367	-0.366	-0.366	-0.365
$4\sigma_g$	$6a_1$	2	-0.418	-0.426	-0.433	-0.438	-0.440	-0.440
$5\sigma_g$	$8a_1$	1	-0.621	-0.613	-0.604	-0.599	-0.597	-0.597
$1\pi_g$	$4b_2$	1	-0.609	-0.620	-0.633	-0.642	-0.645	-0.645
$1\pi_g$	$1a_2$	1	-0.644	-0.644	-0.644	-0.645	-0.645	-0.645
$1\delta_g$	$7a_1$	1	-0.650	-0.652	-0.653	-0.655	-0.655	-0.655
$1\delta_g$	$3b_1$	1	-0.651	-0.652	-0.654	-0.655	-0.655	-0.655

2-16

Table IV. Energies (in hartrees) for the 3A_1 State of TiH_2 .

α	Ti-H (in Å)	SCF energy	CI energy
140	1.846	-849.504433	
	1.861	-849.504475	
	1.876	-849.504379	
	1.858 ^a	-849.504517 ^a	
160	1.796	-849.503734	
	1.856	-849.505620	
	1.916	-849.505139	
	1.876 ^a	-849.505710	-849.7384
179	1.860	-849.505717	
	1.880	-849.505827	
	1.900	-849.505687	
	1.879 ^a	-849.505859 ^a	

^aInterpolated values.

Figure Captions

Figure 1. Bond angle sensitive molecular orbitals for MH_2 .

Figure 2. Potential energy curves for the bending of HMH molecules. The NiH_2 results are from reference 21.

Figure 3. Walsh-like diagram for transition metal dihydrides based on MnH_2 ab initio orbital energies.

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