

A COMPARATIVE STUDY OF THE BONDING IN $\text{Ti}(\text{CH}_3)_4$ AND THE MODEL SYSTEM TiH_4

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Summary

Ab initio LCAO and one-centre expansion (OCE) methods are used for comparing the electron densities in TiH_4 and $\text{Ti}(\text{CH}_3)_4$. The OCE description of the Ti atom in TiH_4 is found to be realistic. The Ti–H and Ti–C bonds are qualitatively similar, the latter having a slightly more positive Ti atom. The hydridic nature of the hydrogen is discussed.

1. Introduction

The transition metal hydrides have recently attracted a great deal of interest [1,2,26]. The views on the nature of their M–H bonds have begun to converge towards a predominantly covalent but to some extent “hydridic” description. Similarly, Ti–C bonds are both of great practical interest and a theoretical challenge.

There is also a more general reason for the present work. The purpose of the Dirac–Fock one-centre expansion (DF-OCE) calculations of Desclaux and Pyykkö (parts I, V, VI: refs. 3, 4, 5) has been to study the effect of relativity on molecular structure using the hydrides MH_n as model systems. A third of the periodic table has already been covered by these calculations. We now compare the OCE and regular LCAO methods to see whether the former gives a realistic description of the bonding. Secondly, we compare TiH_4 and $\text{Ti}(\text{CH}_3)_4$ in order to see whether more general chemical conclusions can be drawn from a calculation on a hydride.

We are not aware of any experimental studies on TiH_4 . The instable $\text{Ti}(\text{CH}_3)_4$ has been prepared [6,7]. Its Ti–C bond length should be close to that measured for $\text{Ti}(\text{Bz})_4$ [8].

2. The calculations

The ab initio LCAO calculations were carried out using the programme MOLECULE [9]. The Gaussian type basis sets were as follows: Ti: (12s, 6p, 4d)

[10], C: (8s, 4p) [11] and H: (4s) [12]. All three basis sets were contracted to the double-zeta level. The "4p" functions with orbital exponents $\alpha = 0.2$ and 0.08 were added to the Ti basis set. For TiH₄, calculations were carried out both with and without these 4p functions, whereas they were included in all calculations for Ti(CH₃)₄.

The relativistic, Dirac–Fock OCE wave function, analysed in the present work, was taken from ref. 4. Its angular basis set comprised the functions 4s, 4p, 3d and 4f for the valence Γ_6 , Γ_7 and Γ_8 (a_1 and t_2) MOs. The radial basis set was "infinitely large", i.e. the radial functions were obtained numerically.

3. Results

3.1. Charge densities

The calculated OCE and LCAO charge densities for TiH₄ and the LCAO values for Ti(CH₃)₄ are compared along three directions in Fig. 1. The three-dimensional densities, multiplied by r^2 , are given:

$$D = \rho(r)r^2 \quad (1)$$

Here r is the distance from the Ti nucleus. The OCE and LCAO values for TiH₄ are sufficiently close to each other for the OCE results to be regarded as realistic. An exception is the region near the hydrogen nucleus in Fig. 1(a), where an OCE with 4s, 4p, 3d and 4f functions is unable to describe the sharp cusp. This is a well-known deficiency of the OCE method.

3.2. Comparison between OCE and LCAO

In ref. 4 we found that within the OCE approximation the t_2 MOs of the model systems TiH₄, ZrH₄ and HfH₄ contained roughly 50% of $(n - 1)d$ and 50% of np character, $n = 4, 5$ and 6, respectively. This leads to cancellation of the relativistic SCF expansion of the $(n - 1)d$ shell by the relativistic contraction of the np shell, which was used to explain the chemical similarity between Zr and Hf. (For a summary of relativistic quantum chemistry, see ref. 13.)

The spherically averaged radial distributions of these shells in TiH₄ are analysed in Fig. 2. The 3d curve clearly demonstrates the importance of the d AO–hydrogen interactions in making this bond. It is also seen that most of the 4p and all of the 4f population reside on the hydrogens. The dependence of the OCE 3d and 4p populations on the Ti–H bond lengths is shown in Fig. 3. It is seen that the more diffuse 4p AO increases its population for large R. We advanced in ref. 5 the "catalytic hypothesis" that this availability of several energetically accessible AOs having different radii might be connected with the catalytic properties of elements like Ti.

In the OCE method, the valence functions, 4s, 4p, 3d and 4f, have a dual character. They form the hybrid orbitals of Ti and also describe the hydrogen AOs. The dependence of the 3d and 4p populations on $R(\text{Ti–H})$, shown in Fig. 3, is conserved in the LCAO wave functions, although the 4p gross population is now only about 10% (see section 3.4 and Table 1.)

In Ti(CH₃)₄, the hybridization is still very similar, i.e. the 3d and 4p contributions to the valence orbitals are about the same as those found in TiH₄ by the

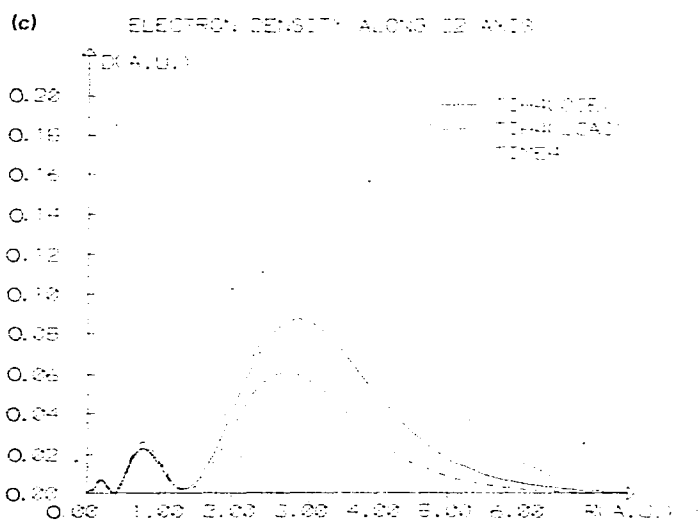
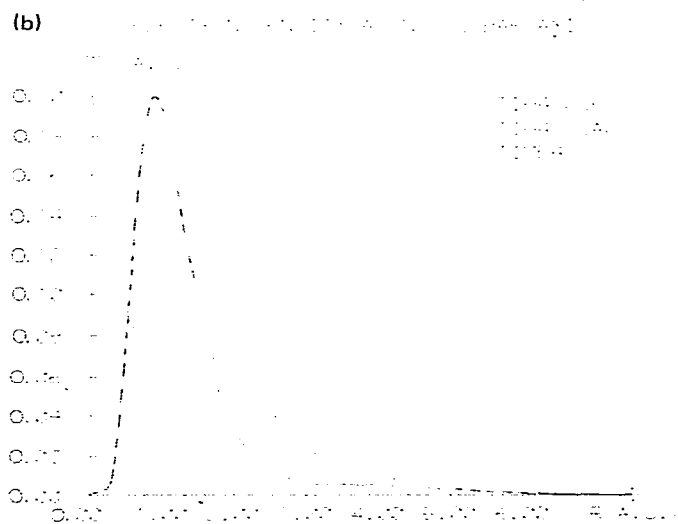
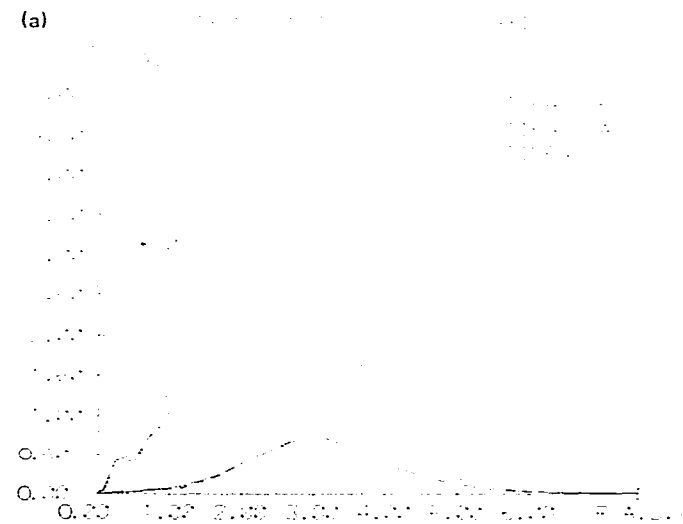


Fig. 1. The electron densities, eq. 1, for TiH_4 at $R(\text{Ti-H}) = 3.044$ a.u. and $\text{Ti}(\text{CH}_3)_4$ at $R(\text{Ti-C}) = 3.90$ a.u. (a) along a Ti-H or Ti-C bond; (b) opposite to a bond; (c) half-way between two bonds.

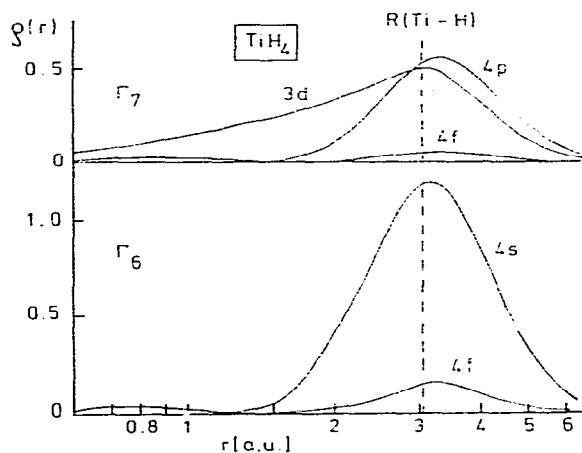


Fig. 2. The radial electron densities of the various AO components of the Γ_6 and Γ_7 OCE MOs of TiH_4 at $R = 3.044$ a.u. The area under each curve is proportional to its population.

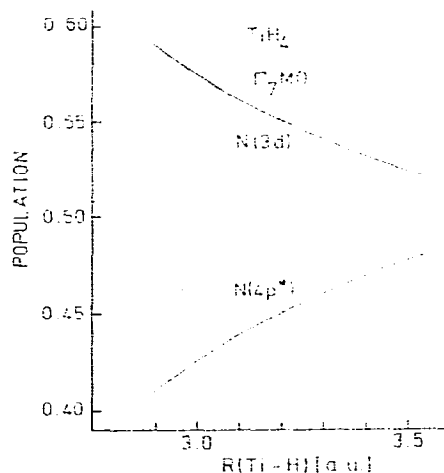


Fig. 3. The dependence of the $3d$ and $4p$ OCE populations for TiH_4 on the Ti-H distance.

LCAO method. The $4s$, $4p$ and $3d$ populations obtained by Stevenson and Lipscomb [24] for TiH_3F , 0.70, 0.75 and 1.37, respectively, also show comparable Ti hybridization.

3.3. Bond lengths

The calculated bond lengths for TiH_4 are shown in Fig. 4. Including the $4p$ AOs in the LCAO calculations makes the Ti-H bond longer, just as in the OCE case [4]. Again the LCAO (with $4p$ AOs) and the OCE results are in reasonable agreement, increasing the credibility of the latter method. As stated in ref. 4, the calculated Ti-H bond lengths are comparable to the experimental values in aluminotitanium hydrides [14]. In ref. 5 we found that these M-H bond lengths ($M = \text{Ti}, \text{Zr}, \text{Hf}, \text{Th}, \text{Cr}, \text{Mo}, \text{W}$) can be interpreted using a

TABLE 1
GROSS POPULATIONS FOR Ti AOs AS A FUNCTION OF THE BOND LENGTH

Case	R (a.u.)	AO		
		4s	4p	3d
$\text{Ti}(\text{CH}_3)_4$	3.60	0.391	0.291	1.665
	3.75	0.431	0.336	1.547
	3.90	0.479	0.362	1.514
	4.05	0.535	0.392	1.454
	4.20	0.601	0.419	1.399
TiH_4	2.90	0.748	0.403	1.760
	3.044	0.764	0.452	1.679
	3.20	0.788	0.494	1.602
	3.45	0.839	0.546	1.495
	3.70	0.899	0.587	1.406

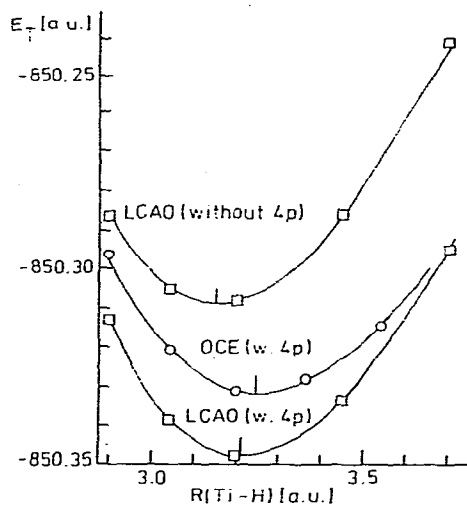


Fig. 4. The calculated total energies of TiH_4 as a function of the Ti-H distance. The curves are Morse potentials fitted to the calculated points. The OCE curve has been lowered to be on the same absolute scale as the two LCAO curves.

“hydridic” hydrogen covalent radius of about 58 pm, consistent with the Pauling halogen radii. Pauling [15] recently considered “the nature of the bonds formed by the transition metals with hydrogen, carbon and phosphorus”. By excluding halogens, he was able to use the usual hydrogen covalent radius of 30 pm. From this he concluded that the M-H bond is a regular covalent bond, comparable with M-C and M-P bonds.

The Ti-C bond length in $\text{Ti}(\text{CH}_3)_4$, found by fitting a Morse potential to the LCAO energies, is 210 pm. It is only slightly below the experimental value, 213(3) pm, in $\text{Ti}(\text{Bz})_4$ [8]. The sum of the covalent radii of ref. 5 for carbon and titanium, 97 and 114 pm, respectively, is 211 pm.

3.4. Comparison between TiH_4 and $\text{Ti}(\text{CH}_3)_4$

The radial charge densities in Fig. 1 show that the Ti-H bond is similar in the OCE and LCAO descriptions. The differences between the Ti-H and Ti-C bonds are also seen to be quite small. Mulliken gross populations of the titanium atoms are 20.39 and 20.88 in $\text{Ti}(\text{CH}_3)_4$ and TiH_4 , respectively. The total titanium 3d populations in $\text{Ti}(\text{CH}_3)_4$ and TiH_4 are 1.514 and 1.602 and the 4p populations 0.362 and 0.494, respectively, thus indicating a strong 4p contribution to the molecular orbitals. The 4p population in $\text{Ti}(\text{CH}_3)_4$ may be somewhat too small due to lack of optimization of the 4p orbital exponents in that case.

The orbital energies are compared in Table 2. The agreement between the OCE and LCAO results for TiH_4 is as good as may be expected when account is taken of the fact that the hydrogen atoms are rather poorly described by the OCE wave function. The Ti-C orbital energies are rather similar to those of Ti-H, as already noted in ref. 5. They may be compared with the experimental ionization energy of 10.8 eV in the photoelectron spectrum of TiMeCl_3 . This

line was assigned to the Ti—C orbital of a_1 symmetry [16]. The present calculations support that assignment. Similar valence orbital energies were found for TiH_4 by Aarstad [27].

The Ti—H force constants for the totally symmetric stretching mode are 0.484 a.u. and 0.592 a.u. from the OCE and LCAO calculations, respectively. They correspond to vibrational frequencies 1790 and 1870 cm^{-1} . These values are not incompatible with the observed Ti—H stretching modes which range from 1230 to 1450 cm^{-1} [17]. The calculated force constant for symmetric Ti—C stretching is found to be 0.634 a.u., leading to a vibrational frequency of 630 cm^{-1} . This could be checked by a Raman measurement. The asymmetric stretching mode of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4$ is reported to fall in the range 470–530 cm^{-1} [18].

4. On the nature of the hydrogen—transition metal bond

There is no conclusive experimental evidence on the character of the M—H bond in transition metal hydrides, although the hydrogen atoms are believed to be more or less “hydridic” [1]. The following arguments have been presented in this connection:

(i) Two sets of covalent radii have been recently presented for the M—H bonds. Pauling [15] excluded all strongly electronegative ligands. He then obtained relatively large metal radii and was able to use the regular H, C and P covalent radii. Pyykkö and Desclaux [5] used the usual Cl, Br and I radii in metal halide molecules as a starting point. This resulted in smaller metal radii and “large” H and C radii of 58 and 97 pm, respectively. As both sets are internally consistent, one cannot actually draw conclusions about the nature of the bond from these, purely operational, radii.

(ii) Some early transition metal complexes are reported to reduce carbonyl compounds, and this is interpreted as a possible evidence for the “hydridic” character of hydrogen in them, although other mechanisms are also conceivable [19]. The reducing power increases on going to the left in the transition metal series.

(iii) Hydrogens directly bound to transition metal atoms usually show a strong high-field NMR chemical shift of 20–30 ppm. Although these shifts were first interpreted as diamagnetic, due to the charge surrounding the proton [20], it is more probable that they are actually caused by electronic excitations involving the metal orbitals [21]. Thus no direct information on the bond character is obtained from this source.

TABLE 2

THE CALCULATED ORBITAL ENERGIES, $-\epsilon$ (eV), FOR THE MOLECULES TiH_4 AND $\text{Ti}(\text{CH}_3)_4$. $R(\text{Ti—H})$ in TiH_4 is 3.044 a.u. and $R(\text{Ti—C})$ in $\text{Ti}(\text{CH}_3)_4$ 3.90 a.u.

MO	TiH_4 (OCE) ^a	TiH_4 (LCAO)	$\text{Ti}(\text{CH}_3)_4$ (LCAO)
α_1	12.21	13.18	11.22
t_2	11.00	12.45	10.78

^a Relativistic TiH_4 ($4s + 4p + 3d + 4f$) results from ref. 4.

(iv) Shul'ga et al. [22] have recently presented PES evidence on MH_4L_4 ($M = Mo$ or W ; $L = PPh_2, PMePh_2, PBuPh_2, PEt_2Ph, P(OPr-i)_3$ or $1/2 dppe$), suggesting that in them Mo would be approximately neutral while W would actually be negative. In addition to the hydrogens, these compounds have electropositive substituted-phosphine ligands. The negative charge on W , if any, may well be provided by them. The nature of the $M-H$ bond remains open.

(v) The only unequivocal evidence for the character of the $M-H$ bond seem to be ab initio calculations. Stevenson and Lipscomb [24] find for the H in TiH_3F a negative charge of -0.30 . The $Ti-H$ overlap population of 0.52 indicates appreciable covalent character also. The present values for TiH_4 are -0.28 and 0.52 , respectively, at $R(Ti-H) = 3.20$ a.u. Although the nature of the bonding in the metallic hydrides is certainly different, band structure calculations [23] indicate positively charged metal atoms and negatively charged hydrogens in them also. As the character of the $M-C$ bond is quite similar to that of the $M-H$ bond, it is also noteworthy that the gross charge on CH_3 in $Ni(C_2H_4)(CH_3)_2$ is -0.51 [25]. Our value for the CH_3 in $Ti(CH_3)_4$ at $R(Ti-C) = 3.90$ a.u. is -0.40 .

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