

Computational Study of H₂ binding to MH₃ (M= Ti, V, and Cr)

James J. Hales^a, Michel L. Trudeau^b, David M. Antonelli^c, Nikolas Kaltsoyannis^{a,*}

^aSchool of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

^bMaterials Science, Hydro-Quebec Research Institute, 1800 Boul. Lionel-Boulet, Varennes, Quebec, J3X 1S1, Canada

^cDepartment of Chemistry, Lancaster University, Lancaster, LA1 4YB, United Kingdom

Abstract

A series of amorphous materials, produced by Antonelli et al., based on hitherto elusive early transition metal hydrides MH₃ (M= Ti, V, and Cr) capable of binding H₂ via the Kubas interaction, has shown great promise for hydrogen storage applications, approaching US DoE system targets in some cases, even when considerations for the system are taken into account. We here apply quantum chemical computational techniques to study these materials. Starting with monomeric MH₃ (M= Ti, V, and Cr) we progress to M₂H₆ and then penta-metallic systems as representations of the H₂ binding sites, analyzing the geometries, energies, H₂ vibrational frequencies and binding modes, finding clear evidence of significant Kubas binding. This enables these materials to bind dihydrogen with a binding energy of between 22 and 53 kJ mol⁻¹. In agreement with experiment, we conclude that while TiH₃ binds H₂ exclusively through the Kubas interaction, VH₃ and CrH₃ additionally physisorb dihydrogen, making these more attractive for practical applications.

Introduction

Hydrogen fuel cells are potential alternatives to the current fossil fuel powered engines that are detrimental to the environment¹⁻⁴. However, the current generation of hydrogen powered vehicles makes use of carbon fibre-based high pressure cylinders that require frequent refuelling^{5,6}; although hydrogen is very energy rich by weight the volume required to fuel a vehicle for long distances is prohibitive. For a driving range exceeding 500 km around 5 kg of H₂ is required; this needs a carbon fibre cylinder with a volume of around 125 L when pressurised to 700 bar⁷, adding additional constraints to vehicle design. Hence a more commercially attractive and efficient solution to storing the gas is required to encourage higher rates of adoption of hydrogen powered vehicles.

Materials-based solutions have been proposed to store hydrogen in large quantities⁸⁻¹⁰. In general, these materials can be categorised into three groups depending on the type of interaction they have with dihydrogen. One group, which includes many MOFs, binds hydrogen through physisorption^{11,12}; the interaction is weak, with a binding energy of around 10 kJ mol⁻¹, which can give promising kinetic properties but requires cryogenic temperatures, 77 K, to store significant amounts of the gas, which generates other problems. By contrast, metal hydrides^{13,14} show much stronger binding interaction with H₂ (> 50 kJ mol⁻¹) which leads to greater storage capacities but at the expense of difficulties in extracting the dihydrogen for use. Both physisorption and chemisorption materials have problems with heat management as the gas either readily boils off or is difficult to release. An ideal solution should in principle arise from material–dihydrogen binding with energies between these extremes¹⁵⁻¹⁷, and a third category of proposed hydrogen storage solutions does indeed meet this requirement. These materials exploit the Kubas interaction¹⁸, in

which the H₂ σ orbital donates electronic density into a metal d orbital and concurrently a second metal d orbital donates electronic density into the H₂ σ^* orbital; analogous to the bonding between d block metal centres and alkenes in the Dewar-Chatt-Duncanson model¹⁹. This orbital interaction produces metal-H₂ complexes characterised by a weakening and extension of the H–H bond.

In recent years there has been an increasing interest in developing materials that exploit the Kubas interaction including, from our labs, those based on hydrazines²⁰, hydrazides²¹, doped mesoporous silica molecular sieves^{22,23}, and early transition metal alkyl hydride gels²⁴⁻²⁷. The latter have shown considerable promise as novel hydrogen storage materials; TiH₃, VH₃, and CrH₃ have hydrogen storage capacities of 3.49, 5.80, and 5.08 wt% under pressure at room temperature, with the potential to be much greater. Raman spectroscopy indicates that these materials bind H₂ *via* the Kubas interaction, although they have surprisingly low adsorption enthalpies as measured by *in situ* calorimetry considering that the hydrogen binding properties persist at room temperature. Hence to probe further the hydrogen binding properties of these materials we here look towards computational methods, which we have previously found to be very informative in understanding Kubas-based systems²⁷⁻³⁰. We have calculated dihydrogen binding to MH₃ monomers and dimers (M = Ti, V, Cr), as well as to more extended pentameric structures. We find extensive Kubas binding in all metal hydrides, with maximum loading levels and H-H stretching frequencies in good agreement with experiment.

Methodology

Dispersion-corrected generalised gradient approximation density functional theory (DFT) has been employed throughout this study, combining the PBE functional^{31,32} with Grimme's D3 dispersion corrections³³ and the 6-311++G** basis set³⁴⁻³⁷. This approach has been shown by others^{38,39} to provide reasonable geometry, IR and electronic data in benchmarking against *ab initio* techniques.⁴⁰⁻⁴³ Both Gaussian 09 revision D.01⁴⁴ and Gaussian 16 revision A.03⁴⁵ have been used to perform the calculations presented herein; we have found that both codes produce the same outputs in test cases.

Spin unrestricted DFT was used throughout. Ti(III), V(III), and Cr(III) centres were treated with 1, 2, and 3 unpaired electrons (upe) respectively; base structures (*i.e.* the metal hydrides without added H₂) with multiple metal centres were considered to have the highest possible number of unpaired metal-based valence electrons.

No constraints were imposed during geometry optimisations, which were performed with the default settings except (i) the integration grid was increased from default to UltraFine (ii) geometry convergence criteria were tightened to a maximum force on an atom of 2×10^{-6} a.u., the root mean squared average (RMS) force to 10^{-6} a.u. on all the atoms, the maximum displacement of an atom to 6×10^{-6} a.u., and the RMS of the displacement to 4×10^{-6} a.u. for each of the monomeric and dimeric systems along with the pentameric base structures. Systems with H₂ bound to the pentamers and those marked in the supplementary information were converged to at least the Gaussian default criteria, with maximum force of 4.5×10^{-4} a.u., RMS force to 3×10^{-4} a.u. on all the atoms, the maximum displacement to 1.8×10^{-3} a.u., and the RMS of the displacement to 1.2×10^{-3} a.u. Harmonic vibrational frequency analysis was performed on all optimised systems to confirm the

calculation has reached a true minimum structure with no imaginary frequencies, and to provide thermal energy corrections to the hydrogen binding energies (HBEs) to yield Gibbs energies.

Throughout this work we have used molecular representations of the H₂ binding sites. These can be broken down into the representation of the MH₃ base structure and the base structure plus bound H₂. The average HBE is calculated by taking the energy of the system loaded with dihydrogen and subtracting the energies of the base structure and the individual H₂ molecules; this is then divided by the number of dihydrogen molecules present n to give the average HBE:

$$HBE = \frac{1}{n} [E(\text{Loaded System}) - E(\text{Base Structure}) - nE(\text{Dihydrogen})]$$

The distance $d_{\text{M-H}_2}$ is defined as the mean of the distances from the closest metal centre to each atom in the H₂ unit.

The maximum H₂ loading on the base structures was determined through the following method: H₂ was added to the base structures incrementally until further additions had no strong interaction with the base structure. For the MH₃ monomers and dimers this point was determined by the orientation of the additional H₂; these were considered to be non Kubas binding when there are differences in the two M-H(H₂) distances greater than 0.4 Å. For the pentamers a different approach was used; the maximum loading was determined to be the point at which an added H₂ was found to be closer to another H₂ than to the base structure. This latter approach is that adopted in our recent study of H₂ binding to the Mn-based storage material KMH-1²⁷.

Results and Discussion

H₂ binding to monomers of MH₃ (M = Ti, V, Cr)

The initial step towards understanding the dihydrogen binding occurring in these MH₃ systems was to probe the interaction between H₂ and monomeric MH₃ (M = Ti, V, Cr). The latter are all non-planar, although VH₃ has an H-V-H angle of 119° and so is approaching a trigonal planar geometry. Table 1 contains the hydrogen binding energies and key geometric data for the MH₃ systems with a single H₂ present, as well as the maximum loading level achieved for each metal hydride.

Table 1. Hydrogen Binding Energies (kJ mol⁻¹), H₂ Geometric data (Å) and Stretching Frequencies (cm⁻¹) for MH₃ (M= Ti, V, Cr)

| Metal | Number of H ₂ bound | Average HBE, ΔE | Average HBG, ΔG | Average d _{H-H} H ₂ | Average d _{M-H2} | Stretching Frequencies |
|-------|--------------------------------|-------------------------|-------------------------|---|---------------------------|------------------------|
| Ti | 1 | -36.3 | 5.9 | 0.834 | 1.917 | 3044 |
| | 5 | -41.1 | 2.1 | 0.817 | 1.939 | Table 2 |
| V | 1 | -51.8 | -9.2 | 0.810 | 1.839 | 3414 |
| | 4 | -55.0 | -11.2 | 0.829 | 1.850 | Table 2 |
| Cr | 1 | -24.1 | 13.8 | 0.786 | 1.973 | 3761 |
| | 3(4) | -48.0 | -5.1 | 0.867 | 1.823 | Table 2 |

At the SCF energy level (ΔE) each of the systems binds a single dihydrogen in a thermodynamically favourable manner, with the strongest interaction seen for V. All are within the expected range for Kubas binding (20-50 kJ mol⁻¹). The Gibbs energies of the binding (HBG) for a single H₂ is favourable only for V, and is much weaker than at the SCF level, with the other systems producing energies suggesting no binding would occur. Indeed, the Gibbs energies are all between 37.9 and 42.6 kJ mol⁻¹ less favourable than the SCF energies, unsurprising given the entropic penalty of bringing together two molecules to form one.

The bond length in an isolated H₂ molecule is calculated to be 0.752 Å. All the H-H distances in Table 1 are significantly longer than this; a hallmark of the Kubas interaction.

The largest extension (0.082 Å) is seen for a single H₂ bound to TiH₃, clearly within the range proposed by Kubas (0.05-0.25 Å). However, this lengthening does not correlate well ($R^2 = 0.19$) with the HBEs as V, the metal which generates the strongest H₂ binding, leads to an H-H bond extension of only 0.058 Å. The geometric feature which best correlates ($R^2 = 1.00$) with the binding energies is the distance from the metal centre to the H₂ unit; V holds H₂ the closest followed by Ti then Cr. The stretching frequency of the bound H₂ correlates inversely and perfectly ($R^2 = 1.00$) with $d_{\text{H-H}}$ H₂ for the singly loaded systems.

H₂ binding induces only minor changes in the geometries of the MH₃ structures; in all cases when H₂ is added the symmetry reduces from C_{3v} to C_s. For the Ti system, figure 1A, there is a less than 1% extension in the Ti-H bonds. The 2-1-4 and 3-1-4 H-Ti-H angles are slightly contracted, by 2.5%, and the other H-Ti-H angle, 2-1-3, is expanded by 1.1%. The V system, figure 1B, shows slightly different behaviour; the V-H bonds are contracted by <1% and the 2-1-3 and 4-1-3 H-V-H angles are contracted, by 3.2%, whereas 2-1-4 is expanded by 2.2%. The Cr system, figure 1C, shows the most significant change as the Cr-H bond length, 1-3 is extended by 1% and the other bond lengths extend by <1%; the H-Cr-H angle, 2-1-4, increases by 6.3% and the other two are contracted by 2.8%.

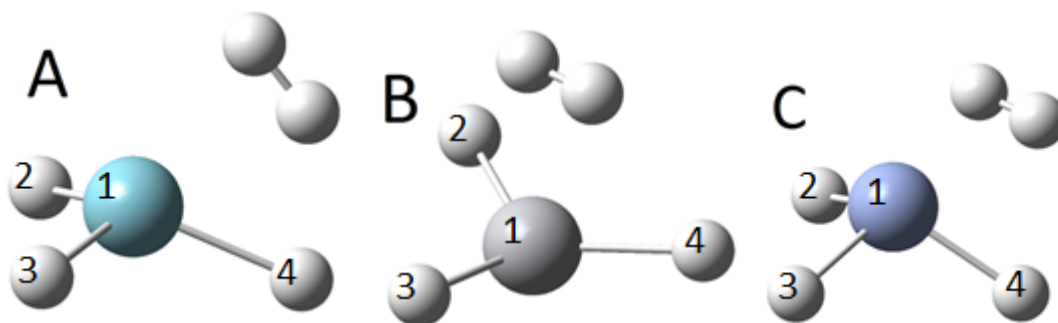


Figure 1. Ball and stick representations of a single H₂ binding to the MH₃ monomers. A = TiH₃, B = VH₃ and C = CrH₃.

In order to verify the presence of the Kubas interaction, we have analysed the molecular structure of the H₂ bound systems. The Kohn-Sham molecular orbitals that contribute to the bonding between H₂ and VH₃ are shown in figure 2; the pertinent orbitals for Ti and Cr can be found in the supplementary information figures S1 and S2. There are two orbitals, HOMO-1 and HOMO-3, that show back bonding in which a metal d-orbital interacts with the H₂ σ* orbital and a third molecular orbital, HOMO-5, which shows the donation from the H₂ σ orbital into another metal d-orbital.

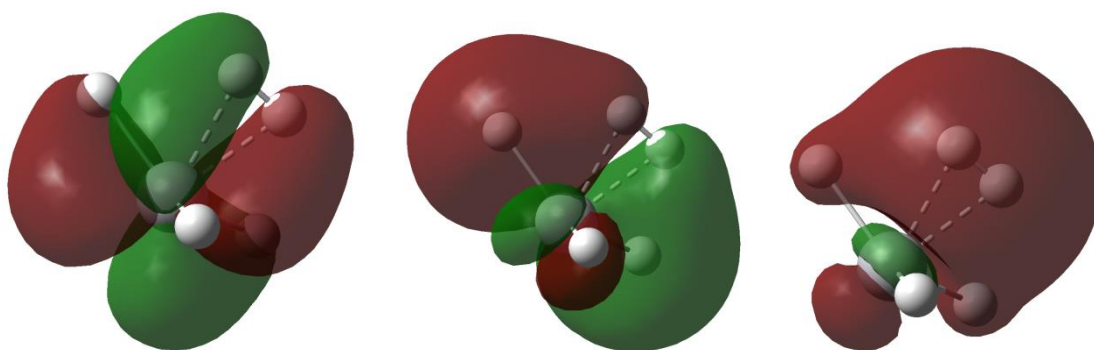


Figure 2. The orbitals involved in the binding of H₂ to VH₃. Left: HOMO-1, Centre: HOMO-3, and Right: HOMO-5. Isovalue = 0.02 a.u.

Ball and stick representations of the maximally loaded MH₃ systems are shown in figure 3. At the maximum loading level, the VH₃ and CrH₃ units are now planar, C_{2v}, with two co-planar H₂ units and the remaining H₂ in “axial” positions. TiH₃ remains non-planar, C_s; at its maximum loading the hydrides are in plane with each other, and the H₂ units are arranged all around the central TiH₃ structure. The maximum H₂ loading decreases from five for TiH₃ to four for VH₃ and three/four on CrH₃. The geometry of CrH₃ changes very significantly as the H₂ loading is increased; most notably, at the maximum loading, two of the hydrides come together to an H-H distance of 0.917 Å, which is within the range that can be considered as dihydrogen complexation, and so we view the final structure as having

three added H₂ with another H₂ coming from the base structure itself. The average HBE at the SCF level is greater for all three systems when at a maximum loading than for their singly loaded counterparts, with the greatest change seen for the Cr system. The increase in HBE is such that even at the Gibbs level both the V and Cr systems show weakly favourable binding, although ΔG for TiH₃/5H₂ is still very slightly positive (probably because complexation involves the greatest reduction in the number of molecules in this system); the change from SCF to Gibbs level is, again, around 40 kJ mol⁻¹.

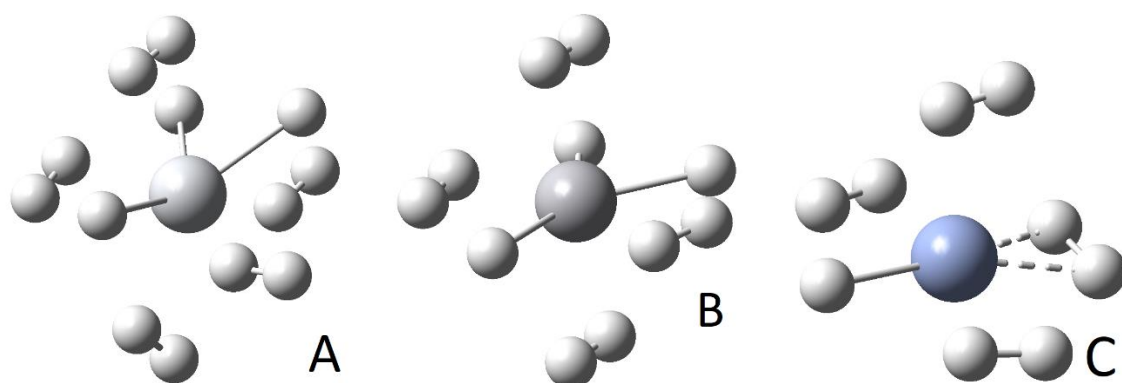


Figure 3. Ball and stick representations of the maximum loading on the MH₃ monomers. A = TiH₃, B = VH₃ and C = CrH₃. The dashed lines in C indicate the change in the base structure to form a dihydrogen unit.

As with the single H₂ case, the average extension of the H₂ bond distances (Table 1) in the maximally loaded systems does not correlate ($R^2 = 0.05$) with stronger binding, as for maximum loading the Cr system has the greatest average $d_{\text{H-H}}$ increase but is not the most strongly binding. There is no longer a strong correlation between the average HBE and the average distance from the metal centre to each H₂ ($R^2 = 0.53$) although a modest inverse correlation ($R^2 = 0.69$) is now seen between $d_{\text{H-H}}$ and $d_{\text{M-H}_2}$ that is not present in the singly loaded cases.

The bond lengths and associated stretching frequencies for each H₂ on MH₃ at the maximum loading level are given in table 2. The correlation between these two metrics is essentially perfect in all cases. For the V system there are two pairs of H₂; the H₂ co-planar with the base structure are the most extended with the lowest stretching frequencies. The two H₂ in the Cr system which have the same bond length are both ones introduced to the base structure, and do not come from changes in the geometry of the base structure upon H₂ loading.

Table 2. Individual H-H Bond Distances (Å) and Stretching Frequencies (cm⁻¹) for the Maximum Loadings of H₂ on MH₃ (M=Ti, V, and Cr). *R*² data are for the correlation of these two variables.

| | d _{H-H} H ₂ | Stretching Frequency | <i>R</i> ² | | d _{H-H} H ₂ | Stretching Frequency | <i>R</i> ² | | d _{H-H} H ₂ | Stretching Frequency | <i>R</i> ² |
|----|------------------------------------|-------------------------|-----------------------|---|------------------------------------|-------------------------|-----------------------|----|---------------------------------|-------------------------|-----------------------|
| | 0.834 | 3077 | | | 0.861 | 2782 | | | 0.917 | 2291 | |
| | 0.831 | 3122 | | | 0.861 | 2797 | | | 0.889 | 2530 | |
| Ti | 0.813 | 3335 | 0.99 | V | 0.797 | 3586 | 1.00 | Cr | 0.889 | 2547 | 1.00 |
| | 0.810 | 3387 | | | 0.797 | 3604 | | | 0.774 | 3936 | |
| | 0.799 | 3570 | | | | | | | | | |

While the monomeric model shows that in principle MH₃ can form complexes with H₂, the experimental data²⁴⁻²⁶ suggest that these compounds are extended, networked hydrides. It is therefore of interest to explore what happens when these binding sites are part of larger systems, and the next step in our study was to probe the effect of a second metal centre on the binding characteristics. This approach to find more realistic binding sites for H₂ on transition metal hydrides has been used in our recent study of MnH₂ and its hydrogen storage properties²⁷.

H₂ binding to M₂H₆ (M = Ti, V, Cr)

The dimeric base structures are shown in figure 4. They are quite similar to one another with three terminal hydrides and three bridging hydrides. The Ti structure has no mirror plane as the two terminal hydrides that share a metal centre are offset from the Ti-Ti axis. The other two structures have mirror planes through the terminal hydrides and the metals. In the Cr system the terminal hydrides that share a metal are much closer together than for the other two systems.

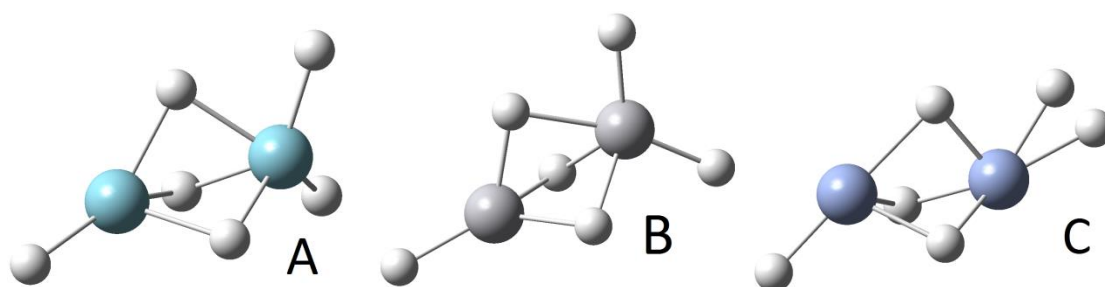


Figure 4. Ball and stick representations of the base structure representations of the MH_3 dimers. A = Ti_2H_6 , B = V_2H_6 and C = Cr_2H_3 .

Table 3 contains the hydrogen binding energies and key geometric data for the M_2H_6 systems with a single H_2 present, as well as the maximum loading level achieved for each metal hydride dimer. At the single H_2 loading level the binding energies are larger than those seen on the monomeric systems. For the M_2H_6 systems Cr is the strongest binding at a single loading with V being the weakest; different from that seen for MH_3 . Interestingly, in Cr_2H_6 a dihydrogen unit is formed from the base structure when a second H_2 is introduced, figure 5. This is similar to the maximum loading case for CrH_3 , although now only one additional H_2 is needed to induce this change. As before, the Gibbs energies are much lower, by around 50 kJ mol^{-1} , than the SCF (ΔE) energies although in all cases the HBG are negative, unlike for the smaller model.

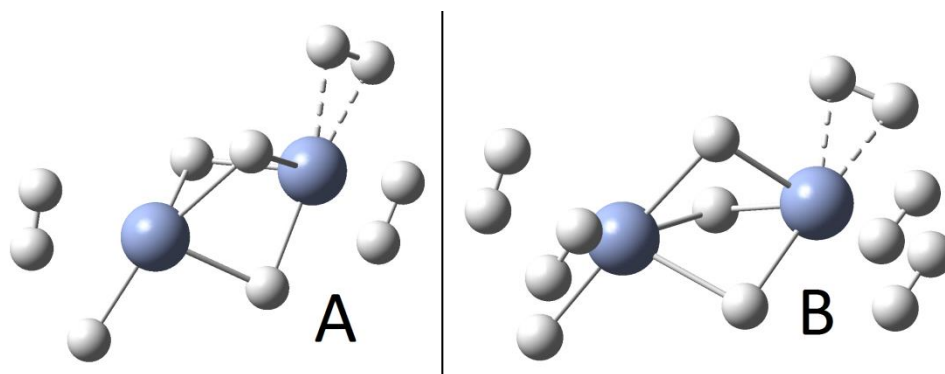


Figure 5. Ball and stick representations of the CrH_3 dimers at various H_2 loading levels. A = $\text{Cr}_2\text{H}_3 \cdot 2\text{H}_2$, B = $\text{Cr}_2\text{H}_3 \cdot 4\text{H}_2$. The dashed lines indicate the change in the base structure to form a dihydrogen unit.

Table 3. Hydrogen Binding Energies (kJ mol^{-1}), H_2 Geometric data (\AA) and Stretching Frequencies (cm^{-1}) for M_2H_6 (M = Ti, V, Cr)

| Metal | Number of H_2 | Average HBE, ΔE | Average HBG, ΔG | Average $d_{\text{H-H}}$ H_2 | Average $d_{\text{M-H}_2}$ | Stretching Frequencies |
|-------|------------------------|-------------------------|-------------------------|---------------------------------------|----------------------------|------------------------|
| Ti | 1 | -83.7 | -34.6 | 0.822 | 1.928 | 3229 |
| | 6 | -51.7 | -7.1 | 0.822 | 1.946 | Table 4. |
| V | 1 | -71.0 | -21.7 | 0.872 | 1.776 | 2671 |
| | 5 | -57.5 | -13.0 | 0.818 | 1.865 | Table 4. |
| Cr | 1(2) | -97.9 | -50.2 | 0.892 (0.903, 0.881) | 1.725 | 2405, 2595 |
| | 4(5) | -50.6 | -9.4 | 0.825 | 1.871 | Table 4. |

As before, the complexed H_2 bonds are significantly extended, especially for the V and Cr systems where the extension is more than 0.1 \AA with a single H_2 present. The two geometry metrics given in table 3 correlate perfectly ($R^2 = 1.00$) *i.e.* as the H_2 move further from the metal centre they are less extended. Neither metric correlates with HBE; for $d_{\text{H-H}}$ $R^2 = 0.09$ and for $d_{\text{M-H}_2}$ $R^2 = 0.07$. The H_2 stretching frequencies correlate perfectly with the lengthening of the bonds ($R^2 = 1.00$).

The amount of H_2 was increased to the maximum loading which maintains the orientation required for Kubas orbital interaction; however for Cr, as noted above, an additional H_2 is formed from the base structure upon addition of H_2 , figure 5. As the amount of bound H_2 is increased the HBE falls significantly; this is by contrast to the monomeric

systems but consistent with earlier studies,²⁷ with all the metals giving final average HBEs between 50 and 60 kJ mol⁻¹. The strength of binding follows the order V > Cr > Ti, with V now binding most strongly, by contrast to when only a single H₂ is added; at the Gibbs level the trend is maintained.

The bond lengths and associated stretching frequencies of each H₂ on M₂H₆ at the maximum loading level are given in table 4. The H₂ bonds are extended in each system suggesting complexation through the Kubas interaction. For each M₂H₆ the stretching frequency of H₂ is correlated with the distance between H₂ and its closest metal centre, and the H-H bond length is inversely correlated with both of them; *R*² values can be found in table 4. Unexpectedly, the average extension in H₂ bond length and average distance from the closest metal centre to each H₂ are not correlated for the dimer at the maximum loading level (*R*² = 0.03). The relationship between average bond length and average HBE is now almost linear for d_{H-H} (*R*² = 0.93), as expected the more energetically favoured interactions are linked with longer H-H bonds. There is very little correlation between the average HBE and average d_{M-H₂} (*R*² = 0.19).

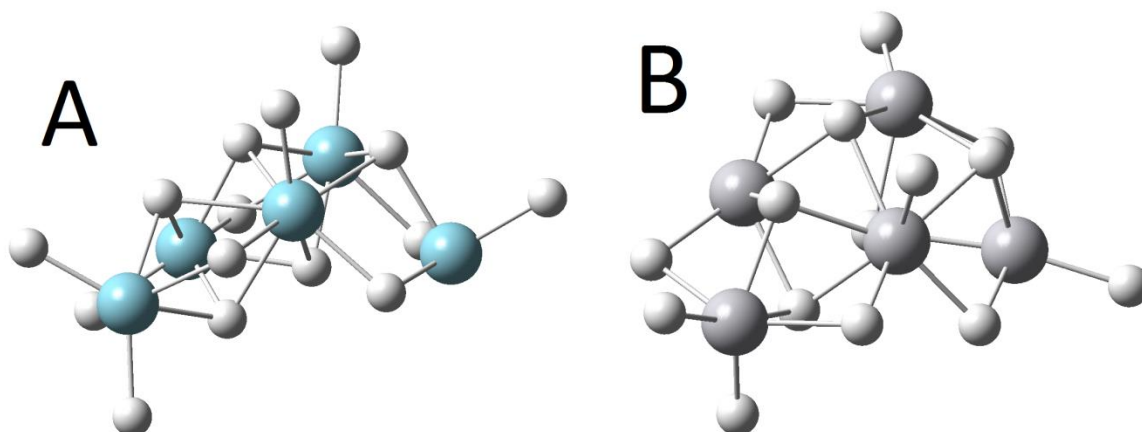
Table 4. Individual H-H bond distances (Å) and stretching frequencies (cm⁻¹) for the maximum loadings of H₂ on M₂H₆ (M=Ti, V, and Cr). *R*² values for correlation between d_{H-H} and d_{M-H₂}, d_{H-H} and stretching frequency, and d_{M-H₂} and stretching frequency are given in this order. Ti: 0.78, 1.00, and 0.80. V: 1.00, 1.00, and 1.00. Cr: 0.91, 1.00, and 0.94.

| | d _{H-H} H ₂ | d _{M-H₂} | Stretching Frequency | | d _{H-H} H ₂ | d _{M-H₂} | Stretching Frequency | | d _{H-H} H ₂ | d _{M-H₂} | Stretching Frequency |
|------|------------------------------------|------------------------------|-------------------------|------|------------------------------------|------------------------------|-------------------------|------|------------------------------------|------------------------------|-------------------------|
| Ti | 0.852 | 1.912 | 2855 | V | 0.832 | 1.827 | 3123 | Cr | 0.875 | 1.732 | 2643 |
| | 0.833 | 1.910 | 3087 | | 0.826 | 1.839 | 3204 | | 0.865 | 1.752 | 2734 |
| | 0.824 | 1.932 | 3207 | | 0.826 | 1.839 | 3206 | | 0.807 | 1.888 | 3440 |
| | 0.819 | 1.935 | 3263 | | 0.810 | 1.883 | 3413 | | 0.799 | 1.912 | 3539 |
| | 0.813 | 1.951 | 3350 | | 0.794 | 1.936 | 3635 | | 0.779 | 2.071 | 3850 |
| | 0.793 | 2.034 | 3619 | | | | | | | | |
| Avg. | 0.822 | 1.946 | | Avg. | 0.818 | 1.865 | | Avg. | 0.825 | 1.871 | |

H₂ binding to M₅H₁₅ (M = Ti, V) and Cr₅H₁₁

The systems discussed thus far show that the early transition metal hydrides can interact with H₂ in a Kubas like fashion to produce dihydrogen complexes. We now progress to larger metal hydride networks, specifically those containing five metals, chosen in part as this is the system size we used in our previous study of H₂ binding to a Mn hydride.

Representations of the pentameric base structures are given in figure 6. All of the structures are networks of mainly bridging and some terminal hydrides. The Ti base structure has five terminal hydrides, two of which are located on the same metal centre. V₅H₁₅ has a similar structure to that of Ti₅H₁₅ with five terminal hydrides. However, performing a geometry optimisation of Cr₅H₁₅ yields the structure shown in figure 6C; two H₂ units are generated, similar to the CrH₃ and Cr₂H₆ structures discussed above, and we take the Cr base structure with five metal centres to be Cr₅H₁₁, figure 6D. H₂ binding calculations are performed on this revised base structure.



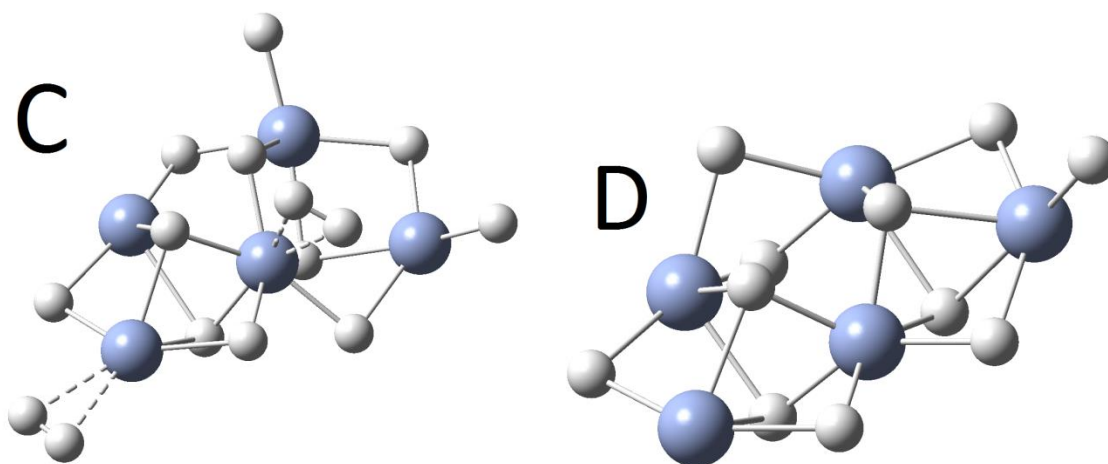


Figure 6. Ball and stick representations of A = Ti_5H_{15} , B = V_5H_{15} , C = Cr_5H_{15} and D = Cr_5H_{11} . Dashed lines show the H_2 units formed from the base structure.

Each system was investigated at loading levels of 1 H_2 per M and 2 H_2 per M. The maximum loading level was then established as discussed in the Methodology. Then, the maximum loading in which the H_2 bind predominantly to the metal centres was determined by removing any H_2 that bind closest to the hydrides; this yields the maximum number of H_2 which bind in a Kubas manner with the base structure, i.e. we distinguish physisorbed H_2 from Kubas-bound H_2 . The data obtained for each of these loading levels on the five-metal centre systems are collected in table 5.

Table 5. Hydrogen Binding Energies (kJ mol^{-1}) and H_2 Geometries (\AA) for M_5H_{15} (M= Ti, V) and Cr_5H_{11}

| Metal | Number of H_2 | Average HBE, ΔE | Average HBG, ΔG | Average $d_{\text{H-H}}$ H_2 | Average $d_{\text{M-H}_2}$ |
|-------|------------------------------------|-------------------------|-------------------------|---------------------------------------|----------------------------|
| Ti | 5 | -43.1 | -1.9 | 0.809 | 1.991 |
| | 10 | -34.1 | 6.1 | 0.805 | 2.156 |
| | Maximum Bound to Metal Centres:9 | -37.1 | 4.8 | 0.811 | 1.982 |
| | Maximum Bound to Base Structure:15 | -25.0 | 9.5 | 0.788 | 2.770 |
| V | 5 | -53.6 | -11.1 | 0.842 | 1.857 |
| | 10 | -32.9 | 4.7 | 0.805 | 2.389 |
| | Maximum Bound to Metal Centres:7 | -44.6 | -1.3 | 0.832 | 1.852 |
| | Maximum Bound to Base Structure:13 | -26.8 | 7.8 | 0.793 | 2.712 |
| Cr | 5 | -46.0 | -2.8 | 0.850 | 1.776 |

| | | | | | |
|------------------------------------|----|-------|----------|-------|-------|
| | 10 | -25.5 | 6.6 | 0.802 | 2.695 |
| Maximum Bound to Metal Centres:5 | | | As Above | | |
| Maximum Bound to Base Structure:12 | | -22.6 | 9.1 | 0.793 | 2.690 |

Ti₅H₁₅ with 1 H₂ per metal centre binds more strongly to H₂ than the analogous TiH₃ monomer (Table 1) with an average HBE of 43.1 kJ mol⁻¹; at the Gibbs level the H₂ binding is maintained, unlike in the monomer, but it is now very weak. The HBE suggests that the first H₂ per metal centre undergoes a Kubas like orbital interaction with Ti; the extension of d_{H-H} H₂ by 0.057 Å is also evidence of this interaction, although this lengthening is smaller than for the analogous MH₃ system. Moving to two H₂ per metal centre reduces the average HBE by 9.0 kJ mol⁻¹ and becomes non-binding at the Gibbs level; the average extension of the H₂ units is slightly reduced.

Table 6 shows the bond lengths, distances from the closest metal centre, and stretching frequency for each dihydrogen in these systems. The final entry for 10 H₂ on Ti₅H₁₅ is distinctly different as it is much further away from its nearest metal centre, has almost no extension in the H-H bond compared with free H₂, and has a much higher stretching frequency; these factors point to this H₂ being bound in a physisorbed fashion rather than through the Kubas orbital interaction. This physisorbed H₂ is the one that is removed to establish the maximum loading in which the H₂ bind predominantly to the metal centres (Table 5), discussed above. The maximum loading including physisorption, *i.e.* the maximum loading of H₂ to the whole base structure, not just to the metal centres, is 15; this system has a much reduced average HBE and smaller average d_{H-H} extension as only a subset of the H₂ bind in a Kubas manner. A more detailed breakdown of the H₂ geometries can be found Table S1, which shows the 9 H₂ bound in a Kubas fashion and the 6 physisorbed H₂.

Table 6. Individual H-H Bond Distances (Å) and Stretching Frequencies (ν, cm⁻¹) for the Maximum Kubas-like Loadings of

H₂ on M₅H₁₅ (M=Ti, and V) and Cr₅H₁₁. Data for maximum bound to base structure can be found in the supplementary information.

| Ti ₅ H ₁₅ + nH ₂ | d _{H-H} H ₂ | d _{M-H2} | Stretching Frequency | V ₅ H ₁₅ + nH ₂ | d _{H-H} H ₂ | d _{M-H2} | Stretching Frequency | Cr ₅ H ₁₁ + nH ₂ | d _{H-H} H ₂ | d _{M-H2} | Stretching Frequency |
|--|--|---------------------------------------|--|---|--|---------------------------------------|--|--|--|---------------------------------------|--|
| 5 | 0.858 | 1.867 | 2798 | 5 | 0.933 | 1.737 | 2169 | 5 | 0.877 | 1.755 | 2625 |
| | 0.818 | 1.958 | 3258 | | 0.849 | 1.817 | 2907 | | 0.877 | 1.722 | 2633 |
| | 0.807 | 2.011 | 3404 | | 0.845 | 1.831 | 2955 | | 0.877 | 1.722 | 2646 |
| | 0.785 | 2.043 | 3748 | | 0.798 | 1.916 | 3578 | | 0.813 | 1.822 | 3350 |
| | 0.778 | 2.075 | 3884 | | 0.787 | 1.982 | 3741 | | 0.805 | 1.859 | 3461 |
| R ² | d _{H-H} and d _{M-H2} : 0.98 | d _{H-H} and v: 0.99 | d _{M-H2} and v: 0.97 | R ² | d _{H-H} and d _{M-H2} : 0.90 | d _{H-H} and v: 0.98 | d _{M-H2} and v: 0.96 | R ² | d _{H-H} and d _{M-H2} : 0.93 | d _{H-H} and v: 1.00 | d _{M-H2} and v: 0.93 |
| 10 | 0.846 | 1.901 | 2921 | 10 | 0.868 | 1.782 | 2721 | 10 | 0.877 | 1.755 | 2625 |
| | 0.846 | 1.890 | 2926 | | 0.853 | 1.820 | 2852 | | 0.877 | 1.722 | 2632 |
| | 0.839 | 1.918 | 3008 | | 0.833 | 1.863 | 3081 | | 0.877 | 1.722 | 2645 |
| | 0.812 | 1.968 | 3355 | | 0.826 | 1.843 | 3195 | | 0.813 | 1.822 | 3351 |
| | 0.806 | 1.974 | 3439 | | 0.815 | 1.846 | 3333 | | 0.805 | 1.859 | 3461 |
| | 0.799 | 1.999 | 3544 | | 0.800 | 1.913 | 3541 | | 0.754 | 3.289 | 4240 |
| | 0.788 | 2.050 | 3697 | | 0.795 | 1.927 | 3611 | | 0.754 | 3.371 | 4243 |
| | 0.781 | 2.067 | 3824 | | 0.755 | 3.456 | 4188 | | 0.754 | 3.259 | 4245 |
| | 0.779 | 2.069 | 3866 | | 0.754 | 3.737 | 4221 | | 0.753 | 4.103 | 4260 |
| | 0.755 | 3.720 | 4204 | | 0.754 | 3.703 | 4230 | | 0.753 | 4.047 | 4263 |
| R ² | d _{H-H} and d _{M-H2} : 0.44 | d _{H-H} and v: 1.00 | d _{M-H2} and v: 0.46 | R ² | d _{H-H} and d _{M-H2} : 0.76 | d _{H-H} and v: 1.00 | d _{M-H2} and v: 0.80 | R ² | d _{H-H} and d _{M-H2} : 0.77 | d _{H-H} and v: 1.00 | d _{M-H2} and v: 0.82 |
| 9 | 0.846 | 1.901 | 2921 | 7 | 0.890 | 1.778 | 2489 | 5 | As Above | | |
| | 0.846 | 1.890 | 2926 | | 0.861 | 1.789 | 2793 | | | | |
| | 0.839 | 1.918 | 3008 | | 0.831 | 1.835 | 3138 | | | | |
| | 0.812 | 1.968 | 3355 | | 0.826 | 1.869 | 3168 | | | | |
| | 0.806 | 1.974 | 3439 | | 0.820 | 1.841 | 3274 | | | | |
| | 0.799 | 1.999 | 3544 | | 0.801 | 1.914 | 3529 | | | | |
| | 0.788 | 2.050 | 3696 | | 0.794 | 1.940 | 3641 | | | | |
| | 0.781 | 2.067 | 3823 | | | | | | | | |
| 0.779 | 2.069 | 3866 | | | | | | | | | |
| R ² | d _{H-H} and d _{M-H2} : 0.97 | d _{H-H} and v: 1.00 | d _{M-H2} and v: 0.98 | R ² | d _{H-H} and d _{M-H2} : 0.87 | d _{H-H} and v: 0.99 | d _{M-H2} and v: 0.90 | | | | |

When the V system is extended to include 5 metal centres the HBE for 1 H₂ per metal centre increases from the analogous VH₃ system by 1.8 kJ mol⁻¹, and significant binding is still maintained at the Gibbs level. The extension of the H-H bond is also greater than that seen for the VH₃ analogue, 0.810 vs 0.842 Å; both of these metrics suggest that the complexation of H₂ is more favoured on the extended system. When the loading is increased to 2 H₂ per metal centre the HBE drops significantly and the average H₂ extension

is reduced; this is because there are 3 physisorbed H₂ present. When these are removed the average HBE increases by 11.7 kJ mol⁻¹ and the bond extension is increased to only 0.010 Å less than the 1 H₂ per V system. Including physisorption, the maximum loading is 13 H₂, Table S1, with 7 Kubas-bound H₂ and 6 H₂ bound via physisorption.

When compared to the CrH₃ monomer, the binding for 1 H₂ per Cr metal centre shows a large increase in HBE. There is a corresponding large increase in the H-H bond extension for the Cr₅H₁₁ system; both metrics indicate stronger Kubas orbital interactions. When an extra H₂ is introduced per metal centre there is a dramatic decrease in the average HBE to about half that at the single H₂ loading level, along with a corresponding change in H₂ d_{H-H}. This large change is because the second 5 H₂ all bind to the base structure *via* physisorption, *i.e.* the maximum binding to the metal centres *via* the Kubas mechanism is only 5 H₂ for this structure. The maximum loading is 12 H₂ when allowing physisorption, Table S1. More specifically, 6 H₂ bind *via* physisorption with the final H₂ bound in a fashion in between Kubas and physisorption; its bond length is lengthened *vs* free H₂, but not to the extent of the 5 Kubas H₂. When the physisorbed H₂ are included, the average the HBE is lower than for the completely Kubas binding system (with 5 H₂), as expected.

In summary, the pentameric Ti system is able to bind the most H₂ through the Kubas mechanism, 9; across the series through V to Cr the maximum amount of Kubas-like H₂ decreases by 2 per element. Each system can bind an additional 6 physisorbed H₂, and Cr₅H₁₁ adds a further H₂ with weak Kubas characteristics, minor extension of the H-H bond and a stretching frequency between Kubas like binding and physisorption. V₅H₁₅ binds H₂ most strongly.

Figures 7 and 8 show how d_{H-H} H₂ correlates with the distance from the metal centre to each H₂, and with the stretching frequencies of H₂ respectively. The former correlation is

reasonable, $R^2 = 0.75$, when considering only the Kubas-bound H_2 . The remaining physisorbed hydrogen behave differently and cluster together at the left of figure 7. The relationship between $d_{H-H} H_2$ and the stretching frequencies, shown in figure 8, is linear with an R^2 value of 0.99, suggesting that these two factors are indeed very strongly linked.

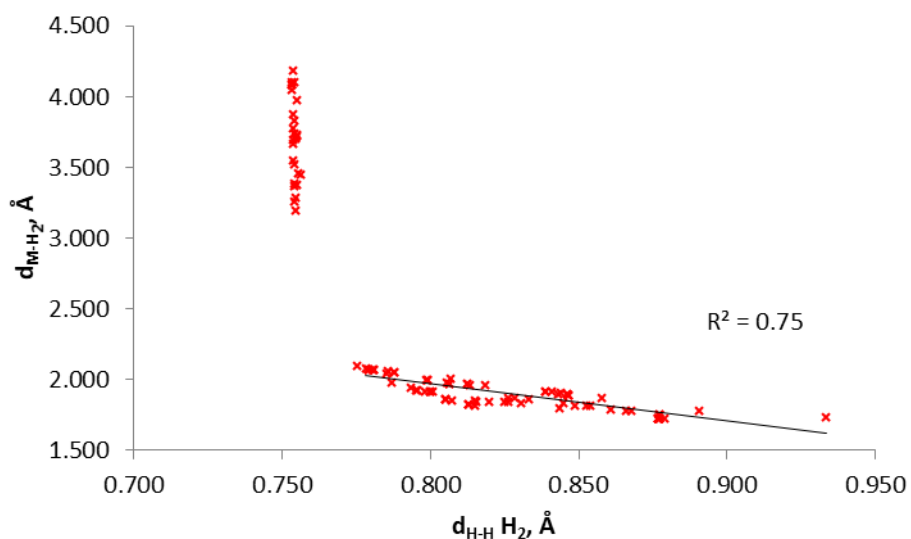


Figure 7. Correlation between $d_{H-H} H_2$ and d_{M-H_2} for the H_2 on the 5 metal centre systems; Ti_5H_{15} , V_5H_{15} , and Cr_5H_{11} . This includes every H_2 detailed in Tables 6 and S2, although the R^2 value is for only the Kubas-bound H_2

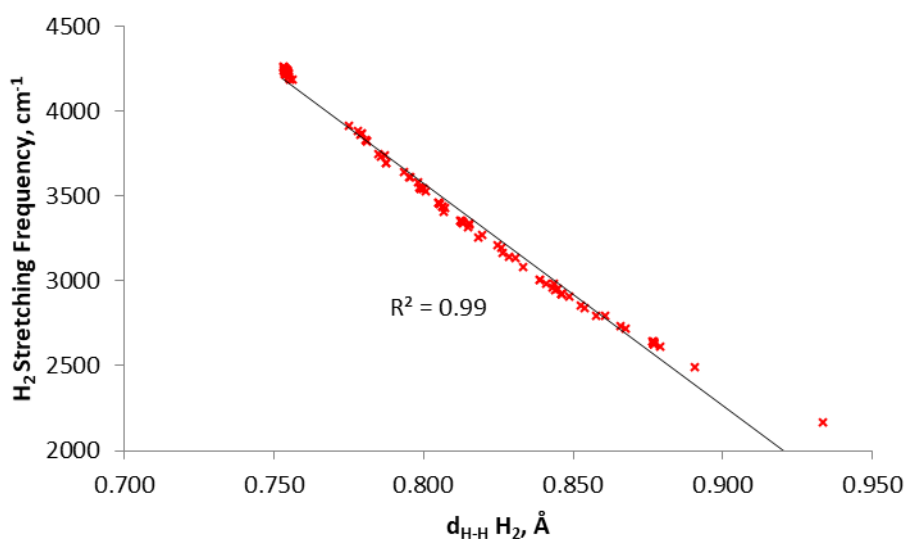


Figure 8. Correlation between $d_{H-H} H_2$ and the stretching frequencies of H_2 for the H_2 on the 5 metal centre systems; Ti_5H_{15} , V_5H_{15} , and Cr_5H_{11} . This includes every H_2 detailed in Tables 6 and S2.

Comparisons with Our Previous Experimental and Computational Work

Our previous experimental work on MH_3 ²⁴⁻²⁶ suggests that each system can bind between 1 and 2 H_2 per metal centre. This is apparent from the gravimetric adsorption, wt%, H_2 stored for each MH_3 system, and the Raman spectra. The experimental data for TiH_3 show 3.49 wt% H_2 at 140 bar and 298 K,²⁵ which is around 1 H_2 per metal centre, projected to be 5.8 wt% when phase pure, which is nearer to 2 H_2 per Ti. The Raman spectrum for H_2 -loaded TiH_3 at 100 bar shows 3 different Kubas H_2 signals at around 3000 cm^{-1} , suggesting multiple binding site types and/or multiple H_2 bound to a metal centre; there is negligible physisorbed H_2 seen under these conditions. In our Ti_5H_{15} model we see a loading of 1.8 Kubas bound H_2 per metal centre, 6.6 wt%, a little above that seen experimentally but close to the projected maximum. When physisorbed H_2 are included we find a maximum loading of 10.6 wt%, 3.0 H_2 per metal centre, much greater than the ideal projected experimental absorption but, as noted, little physisorbed H_2 is seen experimentally. We calculate H_2 stretching frequencies at c. 3000 cm^{-1} , as seen experimentally. The experimental heats of adsorption rise as loading of H_2 is increased, and is projected to maximise at 32 kJ mol^{-1} , very close to the 37.1 kJ mol^{-1} we calculate for just the Kubas bound H_2 . In general, then, there is good agreement between theory and experiment for this system.

The experimental data for VH_3 show a gravimetric storage of 5.8 wt% at 130 bar and 298 K, which is between 1 and 2 H_2 per metal centre²⁶. This compares well with our calculated Kubas-like maximum; 1.4 H_2 per centre, 4.9 wt%, but is somewhat lower than the maximum including physisorption; 2.6 H_2 per centre, 8.8 wt%. The Raman spectrum for VH_3 under 100 bar of H_2 shows a weak signal at 4105 cm^{-1} attributed to physisorbed H_2 and has 3 other signals, assigned to Kubas-bound H_2 , at 2770, 2929 and 3834 cm^{-1} . We find a range of

stretching frequencies from 3489 to 3641 cm^{-1} for Kubas-like H_2 along with stretches around 4200 cm^{-1} for physisorbed H_2 . Hence the quantitative agreement between theory and experiment for the stretching frequencies is less good than for the Ti system, but qualitatively correct in finding both Kubas and physisorbed H_2 . By contrast to TiH_3 , the experimental enthalpy of H_2 adsorption is found to be only 0.52 kJ mol^{-1} for VH_3 , much lower than from our calculations and also lower than that expected for room temperature Kubas binding. This has been attributed²⁸ to the material deforming under pressure and thus buffering the energy release of H_2 complexation, an effect not accounted for in our computational model. We return to this issue below. This discrepancy is not seen for the Ti case as the heat of adsorption given in that study is a linear extrapolation from much lower loading levels.

CrH_3 has a gravimetric storage of 5.08 wt% H_2 at 160 bar and 298 K which, again, suggests the material binds between 1 and 2 H_2 per metal centre.²⁴ We calculate only 3.6 wt% of H_2 from Kubas binding, rather lower than experiment. When the calculated physisorbed H_2 are included we find a gravimetric weight percentage of 8.1 wt%, now well above the experimental value. These data suggest that, like VH_3 , experiment is measuring both Kubas and physisorbed H_2 . Consistent with this, the experimental Raman spectrum shows signals at around 4100 to 4200 cm^{-1} , also seen in our models when physisorbed H_2 are considered. Raman spectroscopy also finds 3 signals at 2789, 2922 and 3188 cm^{-1} attributed to H_2 complexation; we calculate a range of stretching frequencies from 2625 to 3461 cm^{-1} for Kubas-like H_2 suggesting we are finding similar binding motifs. As with VH_3 , the Cr system is found experimentally to have a very low adsorption enthalpy, 0.37 kJ mol^{-1} , whilst still maintaining H_2 binding properties at room temperature. This much lower than expected

value, which again disagrees with our HBE data, is also attributed to pressure causing the system to distort, buffering the binding energy²⁸.

We have previously reported computational work on the H₂ binding properties of hydrazide linked systems of Ti, V and Cr,^{28,29} studying both M(II) and M(III) oxidation states. The M(II) hydrazide monomers,²⁸ with various ancillary ligands including trimethylsilylmethyl, hydrides, hydrazides, and THF, can bind between 1 and 3 H₂ per metal centre. There is a trend across all the systems in which Cr binds fewer H₂ than V which in turn binds fewer than Ti; this is the same as we report above for H₂ Kubas bound to MH₃. The M(II) hydrazide systems show Kubas like binding, although there is no clear trend as to which metal has the strongest binding; the trends are dependent on the ancillary ligand present. The dimers of the M(II) hydrazide systems also show no clear binding energy trends across the series, but still display clear Kubas H-H bond extension and stretching frequencies.

The trend to fewer Kubas bound H₂ across the series is also present in the M(III) hydrazide dimers,²⁹ and once again there is no strong HBE trend at the various loading levels considered. The energies we found for the fully hydrazide based M(III) systems are lower than we observe for the present hydride systems. However, when a hydride is introduced to the Ti(III) hydrazide system there is a large increase in the HBE to a level similar to our hydrides, -47.83 kJ mol⁻¹.

As with the MH₃ systems, the structure of these hydrazine systems is thought to distort under pressure of H₂, buffering the energy gain of H₂ complexation. We previously tested this effect computationally²⁸ by determining the energy differences between the base structures before and after the addition of H₂, finding a destabilising change in the energy per H₂ of between 20.5 and 37.2 kJ mol⁻¹ for V(III) and between 42.2 and 44.6 kJ mol⁻¹ for

Cr(II). When similar data are obtained for the model MH_3 systems under consideration in this study we find an energy difference per H_2 in the pentameric base structures before and after attaining maximum Kubas loading of 8.1 kJ mol^{-1} for Ti_5H_{15} , 12.6 kJ mol^{-1} for V_5H_{15} and, 17.7 kJ mol^{-1} for Cr_5H_{11} , which at least qualitatively suggests that a similar buffering/flexing mechanism to that previously proposed is possible for these materials. Since a real world structure would require reordering of bonds in 3 dimensions rather than only 2 dimensions in the modelled pentamers, greater reorganization energies would be expected in reality.

Conclusions

In this contribution, we have presented quantum chemical computational evidence that mono- and multi-metallic models of MH_3 ($M=Ti, V, \text{ and } Cr$) can all employ Kubas-like complexation to bind dihydrogen *via* interaction between the metal d orbitals and the H_2 σ and σ^* orbitals. All of the models show a large affinity for H_2 , with binding energies at the upper end of those expected for such an interaction; each also shows the Kubas motif of extended H_2 bond lengths. The experimental energies are much lower than those we calculate, the projected HBE for TiH_3 is of the same magnitude as the calculated value. This energy discrepancy is attributed to flexing of the macro structure, which buffers the energy released by hydrogen binding.

The amount of H_2 found to bind to these systems *via* the Kubas mechanism is consistent with our previous experimental data; between 1 and 2 H_2 per metal centre. When all our physisorbed H_2 are included we find that our models bind more H_2 than the experimental systems, with TiH_3 binding as many as 3 H_2 per centre. Qualitatively, however, our models agree well with experiment. Combining data from experiment and computation, we conclude that TiH_3 binds almost exclusively *via* the Kubas interaction, whereas VH_3 and CrH_3 bind using both Kubas and physisorption. It is likely the extent of the latter which is responsible for the quantitative differences between experiment and theory for the amount of H_2 that can bind to VH_3 and CrH_3 , most likely arising from the limitations of a small molecular cluster representation of an extended system.

It has been shown across our previous work, and in this study, that the early transition metals from Ti to Mn can bind H_2 via the Kubas interaction. We have seen trends across these studies that show that when Ti binds H_2 it achieves a greater maximum loading than the other transition metals across the series. However, the HBEs do not correlate well with

the maximum loading throughout; similar trends in binding energies have been seen in this work and our previous systems.^{28, 29}

Consideration of the pentameric models suggests that VH_3 would provide the best practical alternative from a cost/performance perspective as it binds H_2 the most strongly, while also supporting a significant number of H_2 per metal atom, with vanadium costing significantly less than chromium or titanium. The reason that experimental studies have yielded lower values in all three cases is likely related to the lack of convenient metal alkyl precursors and overall control over the decomposition of the metal alkyl into a porous metal hydride with maximum diffusion characteristics and available binding sites. For this reason continued synthetic efforts into this exciting new class of materials are warranted.

Acknowledgments

The authors acknowledge Hydro Quebec and the University of Manchester for funding. We also thank the Computational Shared Facility (CSF) at the University of Manchester for computational resources and associated support services.

References

1. P. Jena, *Journal of Physical Chemistry Letters*, **2011**, *2*, 206-211.
2. M. Balat, *International Journal of Hydrogen Energy*, **2008**, *33*, 4013–4029.
3. J. Ren, H. W. Langmi, B. C. North, M. Mathe, *International Journal of Energy Research*, **2015**, *39*, 607.
4. R. von Helmolt, U. Eberle, *Journal of Power Sources*, **2007**, *165*, 833.
5. N.A.A. Rusman, M. Dahari, *Int. J. Hydrogen Energy*, **2016**, *41*, 12108.
6. L. Schlapbach, A. Züttel, *Nature*, **2001**, *414*, 353.
7. D. Durbin, C. Malardier-Jugroot, *Int. J. Hydrogen Energy*, **2013**, *38*, 14595.
8. J. M. Simmons, T. Yildirim, A. Hamaed, D. M. Antonelli, M. I. Webb and C. J. Walsby, *Chem. Eur. J.*, **2012** *18*, 4170-4173
9. M. Dincă, A. F. Yu, & J. R. Long, *Journal of the American Chemical Society*, **2006**, *128*, 8904–8913.
10. M. Dincă, A. F. Yu, & J. R. Long, *Journal of the American Chemical Society*, **2005**, *127*, 9376–9377.
11. M. P. Suh, H. J. Park, T. K. Prasad, & D. Lim, *Chemical Reviews*, **2012**, *112*, 782–835.
12. A. G. Wong-Foy, A. J. Matzger & O. M. Yaghi, *Journal of the American Chemical Society*, **2006**, *128*, 3494–3495.
13. B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, *International Journal of Hydrogen Energy*, **2007**, *32*, 1121
14. B. Bogdanović, M. Schwickardi, *Journal of Alloys and Compounds*, **1997**, *253*, 1-9
15. G. J. Kubas, *Chem. Rev.*, **2007**, *107*, 4152.
16. G. J. Kubas, *Journal of Organometallic Chemistry*, **2009**, *694*(17), 2648–2653.
17. , T. K. A. Hoang, & D. M. Antonelli, *Advanced Materials*, **2009**, *21*(18), 1787–1800.
18. G. J. Kubas, C. J. Unkefer, B. I. Swanson & E. Fukushima, *Journal of the American Chemical Society*, **1986**, *108*(22), 7000–7009.
19. P. Atkins and D. Shriver, *Inorganic Chemistry*, **2010**, Oxford University Press, 5th Ed.
20. C. V. J. Skipper, A. Hamaed, D. M. Antonelli, & N. Kaltsoyannis, *Dalton Transactions*, **2012**, *41*(28), 8515–23.
21. C. V. J. Skipper, T. K. A. Hoang, D. M. Antonelli, & N. Kaltsoyannis, *Chem. Eur. J.*, **2012**, *18*(6), 1750–60.
22. A. Hamaed, H. Van Mai, T. K. A. Hoang, M. Trudeau, & D. Antonelli, *The Journal of Physical Chemistry C*, **2010**, *114*(18), 8651–8660.
23. C. V. J. Skipper, A. Hamaed, D. M. Antonelli, & N. Kaltsoyannis, *Journal of the American Chemical Society*, **2010**, *132*(48), 17296–305.
24. L. Morris, M. L. Trudeau, D. Reed, D. Book, D. M. Antonelli, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 9480.
25. T. K. A. Hoang, L. Morris, D. Reed, D. Book, M. L. Trudeau, & D. M. Antonelli, *Chemistry of Materials*, **2013**, *25*, 4765–4771.
26. L. Morris, L. A. C. Smith, M. L. Trudeau, D. M. Antonelli, *J. Phys. Chem C*, **2016**, *120*, 11407-11414.
27. L. Morris, J. J. Hales, M. L. Trudeau, P. Georgiev, J. P. Embs, J. Eckert, N. Kaltsoyannis and D. M. Antonelli, *Energy and Environmental Science*, **2019**, DOI: 10.1039/c8ee02499e
28. C. V. J. Skipper, D. M. Antonelli, & N. Kaltsoyannis, *The Journal of Physical Chemistry C*, **2012**, *116*(36), 19134–19144.
29. C. V. J. Skipper, A. Hamaed, D. M. Antonelli, & N. Kaltsoyannis, *Dalton Transactions*, **2012**, *41*(28), 8515–23.
30. C. V. J. Skipper, T. K. A. Hoang, D. M. Antonelli, & N. Kaltsoyannis, *Chem. Eur. J.*, **2012**, *18*(6), 1750–60.
31. J. P. Perdew, K. Burke, M. Erzerhof, *Physical Review Letters*, **1996**, *77*, 3865.
32. J. P. Perdew, K. Burke, M. Erzerhof, *Physical Review Letters*, **1997**, *78*, 1396.
33. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of Chemical Physics*, **2010**, *132*, 154104.
34. A. J. H. Wachters, *The Journal of Chemical Physics*, **1970**, *52*(3), 1033.
35. P. J. Hay, *The Journal of Chemical Physics*, **1977**, *66*(10), 4377.
36. A. D. McLean, & G. S. Chandler, *The Journal of Chemical Physics*, **1980**, *72*(10), 5639.
37. R. Krishnan, J. S. Binkley, R. Seeger, & J. A. Pople, *The Journal of Chemical Physics*, **1980**, *72*(1), 650.
38. E. Tsvion, J. R. Long, & M. Head-Gordon, *Journal of the American Chemical Society*, **2012**, *136*, 17827–17835.
39. R. C. Lochan, & M. Head-gordon, *Physical Chemistry Chemical Physics*, **2006**, *8*, 1357–1370.

40. M. Kocman, P. Jurečka, M. Dubecký, M. Otyepka, Y. Cho and K. S. Kim, *Physical Chemistry Chemical Physics*, **2015**, *17*, 6423.
41. J. Gebhardt, F. Viñes, P. Bleiziffer, W. Hieringer, A. Görling, *Physical Chemistry Chemical Physics*, **2015**, *16*, 5382–5392.
42. A. Mavrandonakis, K. D. Vogiatzis, A. D. Boese, K. Fink, T. Heine, W. Klopper. *Inorganic Chemistry*, **2015**, *54*, 8251–8263.
43. M. Manadé, F. Viñes, A. Gil, F. Illas. *Physical Chemistry Chemical Physics*, **2018**, *20*, 3819–3830.
44. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
45. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.