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## On the existence of $MH_n$ species with $M=Al, Ga$ and $n=4, 5, 6$ . Computational study of structures, stabilities and bonding

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**Abstract** Based on second-order perturbation theory (MP2) predictions with large 6-311++G(3df, 3pd) basis set we have reviewed the possible structures and stabilities of a series of neutral  $MH_n$  ( $M=Al, Ga$ ;  $n=4, 5, 6$ ) species. For  $AlH_4$  and  $AlH_5$ , our results confirm the previous theoretical findings, which indicate the dihydrogen  $C_s$  complexes ( $^2A'$ )  $AlH_2(H_2)$  and ( $^1A'$ )  $AlH_3(H_2)$ , respectively, as the lowest energy isomers. We found, similarly,  $C_s$  ( $^2A'$ )  $GaH_2(H_2)$  and ( $^1A'$ )  $GaH_3(H_2)$  van der Waals complexes as the most stable species of the gallium analogues  $GaH_4$  and  $GaH_5$ . The calculated  $H_2$  dissociation energies ( $D_e$ ) for  $AlH_2(H_2)$  and  $AlH_3(H_2)$  are of the order  $1.8$ – $2.5$  kcalmol $^{-1}$ , whereas this range of values for  $GaH_2(H_2)$  and  $GaH_3(H_2)$  is  $1.4$ – $1.8$  kcalmol $^{-1}$ . Symmetry-adapted perturbation theory (SAPT) was used to analyze the interaction energies of these dihydrogen complexes (for  $n=5$ ) to determine why the Ga species show a smaller binding energy than the Al species. The SAPT partitioning of the interaction energy showed significant differences between  $AlH_3(H_2)$  and  $GaH_3(H_2)$ , resulting from the much stronger “hydride” character of the aluminum species. The experimental observation of  $AlH_2(H_2)$  and  $AlH_3(H_2)$ , and likely  $GaH_3(H_2)$ , via low-temperature matrix isolation has been reported recently by Pullumbi et al. and Andrews et al., supporting the theoretical predictions. For  $n=6$ , we found the degenerate  $C_2(^2A)$  and  $C_s(^2A')$   $MH_2(H_2)_2$  “double  $H_2$ ” type van der Waals complexes as the lowest energy species for both  $M=Al$  and  $Ga$ .

**Keywords** Aluminum and gallium van der Waals complexes · Ab initio calculations · SAPT

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### Introduction

The current practical interest in the development of various metal hydrides stems from their potential use as reversible hydrogen-storage devices at low and medium temperatures [1–3]. In particular, the systems including aluminum hydrides, like catalyzed sodium alanate  $NaAlH_4$  or penta- and -hexahydrides of the  $XAlH_5$  and  $X_3AlH_6$  ( $X=Li, Na, K$ ) type have recently been studied for this purpose [2, 3]. Also, aluminum hydrides attract attention because of their possible contribution to the improvement of energetic properties of rocket fuels and their role in catalysis. However, as far as “pure” neutral  $AlH_n$  ( $n=4, 5, 6$ ) polyhydrides are concerned, the experimental reports on their existence (as systems showing  $n$  “regular” Al–H bonds) are lacking. The same holds true for their gallium analogues  $GaH_n$  with  $n=4, 5, 6$ .

By contrast, low-coordinated binary  $AlH_x$  and  $GaH_x$  hydrides for  $x=1, 2, 3$  have been known for some time as metastable species with matrix-isolation techniques used most often to facilitate their isolation and spectroscopic characterization. The simplest AlH monohydride is a short-lived species first observed in the gas phase [4]. The next member of the series,  $AlH_2$  dihydride was detected repeatedly in solid matrices [5–7]. For this radical, highly accurate ab initio calculations have been also carried out [8, 9]. Similarly, matrix isolation and assignment of  $AlH_3$  trihydride (alane) was reported [10, 11]. In a recent work conducted by Andrews group, the three aluminum hydrides  $AlH_x$  ( $x=1–3$ ) were generated in a solid matrix and characterized (in addition to the other species) [11]. In the parallel paper, the same group reported synthesizing under similar conditions the gallium analogues including monohydride  $GaH$ , dihydride  $GaH_2$  and trihydride  $GaH_3$  (gallane) [12]. The above studies extended the earlier gas phase study on  $GaH$  by Urban et al. [13], matrix infrared (IR) studies on  $GaH_x$  ( $x=2, 3$ ) by Pullumbi et al. [7, 10], and electron spin resonance (ESR) work on the  $GaH_2$  radical by Knight et al. [14].

Returning to the issue of the existence of  $MH_n$  ( $M = \text{Al, Ga}$ ;  $n = 4, 5, 6$ ) species, we first note that in the recent experiment aiming at matrix isolation of the  $\text{AlH}_4$  tetrahydride radical [15], only an  $\text{AlH}_2(\text{H}_2)$  van der Waals complex was detected, consistent with the earlier ab initio calculations on  $\text{AlH}_4$  [16]. As mentioned above, the related  $\text{AlH}_4$  anion is well known and stable and is commonly used as a reducing agent ( $\text{LiAlH}_4$ ) [17]. It has been also observed in matrix isolation [15]. No experimental observation of the related  $\text{GaH}_4$  species has been reported. To our best knowledge,  $\text{GaH}_4$  has been the subject of a single low level ab initio investigation [18]. For  $\text{AlH}_5$ , Schreiner et al. [19] carried out high level ab initio calculations. These authors found that the  $C_s$   $\text{AlH}_3(\text{H}_2)$  complex is the lowest energy structure. In fact, successful low-temperature matrix isolation of the latter was reported recently [11]. For the gallium analogue  $\text{GaH}_5$ , no systematical theoretical study exists in the literature. The species of formula  $\text{AlH}_6$  and  $\text{GaH}_6$  are neither known experimentally nor have they been examined theoretically. The issue of the existence of hypervalent  $MH_n$  compounds with  $M$  belonging to Group 13 has been addressed in a very recent highlight review in *Angew. Chem. Int. Ed.* by Mitzel [20].

In this computational paper we systematically investigate structures and stabilities of  $MH_n$  species with  $M = \text{Al}$  and  $\text{Ga}$  and  $n = 4, 5, 6$  from the point of view of their possible existence. We also analyze and compare interaction energies within the selected  $\text{AlH}_n$  and  $\text{GaH}_n$  systems (vide infra).

## Methods

The initial mapping of the potential energy surface (PES) was carried out using density functional theory (DFT) with the hybrid B3LYP functional [21, 22]. The effective core potential of Wadt and Hay [23] on Al and Ga was employed along with the associated valence double-zeta (VDZ) basis set and DZ basis set for H, technically designated as LANL2DZ. This basis set was augmented by a set of d functions on aluminum ( $\zeta_d = 0.198$ ) and gallium ( $\zeta_d = 0.207$ ) [24], resulting in the LANL2DZ(d) basis set. The nature of the stationary points located on the respective PESs was determined by vibrational frequency analysis. Next, all the structures and Hessians were recalculated using ab initio second-order Møller–Plesset (MP2) perturbation theory [25], and a large all-electron (AE) 6-311++G(3df,3pd) [26] basis set. The MP2/6-311++G(3df,3pd) step was also intended to improve the description of dispersion effects important for bonding in the various van der Waals complexes found (note also that the basis set includes diffuse functions important in this case). For comparison purposes, DFT using Perdew, Burke and Ernzerhof (PBE) functional [27, 28], was used to estimate the binding energy of the complexes. This functional has been shown to describe the binding energy of

water–benzene dimer accurately in relation to other functionals [29]. The magnitudes of the basis set superposition error (BSSE) and vibrational zero-point (ZPE) corrections were checked for one representative structure. Spin-restricted and spin-unrestricted calculations were carried out for singlets and doublets, respectively, and Gaussian 03 code was used [30]. The pictures presented below were drawn with the MOLDEN program [31].

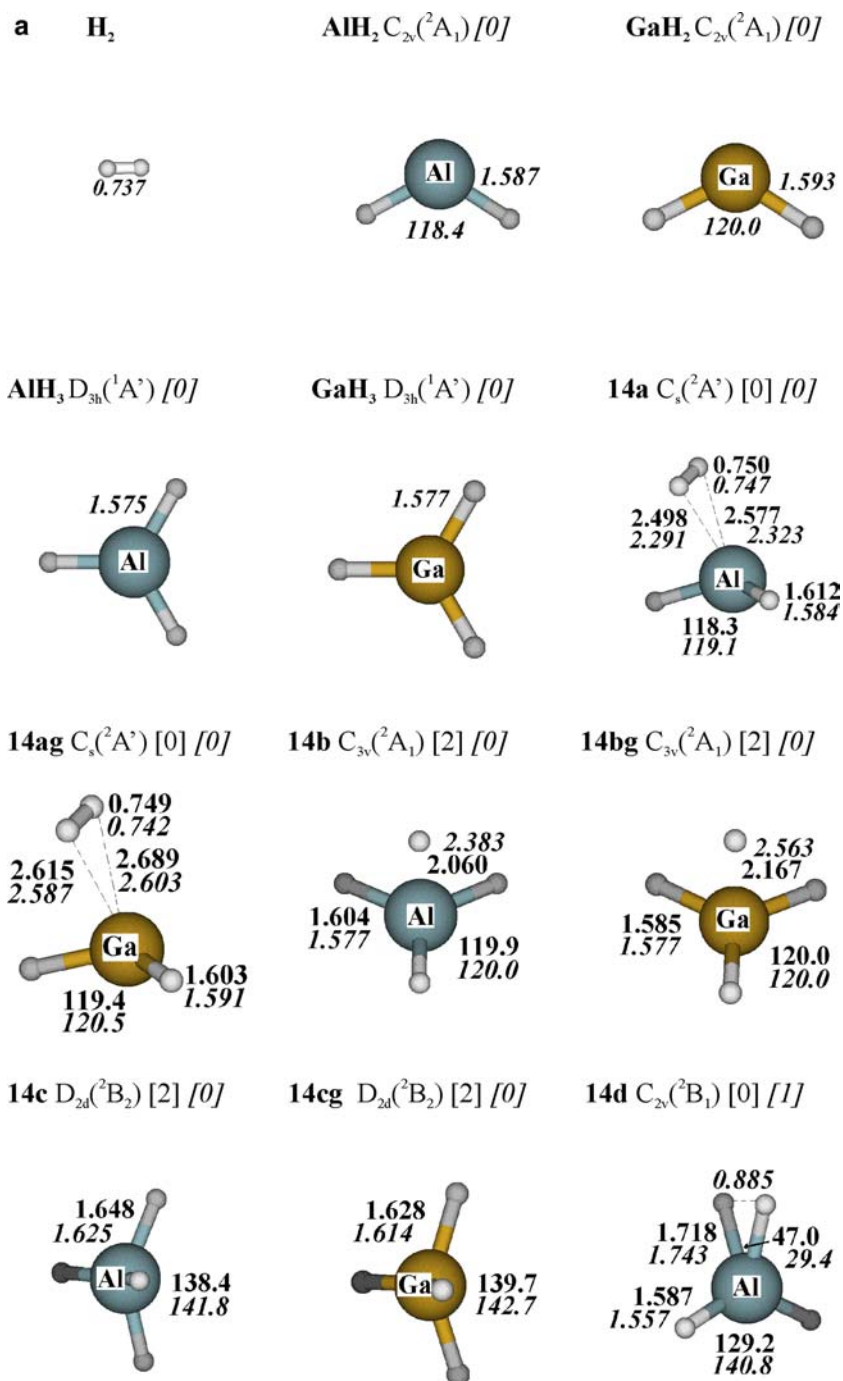
## Results and discussion

The optimized structures are shown in Fig. 1. We consider only those related to genuine minima on the singlet and doublet PESs, with the “method-dependent” cases (for  $n = 4$  and 6) also considered. Our extensive  $MH_n$  ( $M = \text{Al, Ga}$ ;  $n = 4–6$ ) PES search including the plausible high-symmetry “hydride” structures with  $n$  M–H links was recently presented at length [32]. These calculations revealed that for  $n = 5$  and 6, the latter structures correspond to unstable  $m$ th order saddle points ( $m \geq 2$ ), lying appreciably higher in energy than the local minima structures discussed below.

### $MH_4$ ( $M = \text{Al, Ga}$ )

The **14a**  $C_s(^2A')$   $\text{AlH}_2(\text{H}_2)$  van der Waals complex is found to be the ground-state structure of  $\text{AlH}_4$  at both UB3LYP and UMP2. This is consistent with the results of a previous UMP2/6-31G(d,p) study of Wong et al. [16]. Similarly, the **14b**  $C_{3v}(^2A_1)$   $\text{AlH}_3(\text{H})$  species including the alane unit and the **14c**  $D_{2d}(^2B_2)$  structure with four Al–H links are found to lie much higher in energy than **14a**, by 19.9 and 36.1 kcalmol<sup>-1</sup>, respectively, at UMP2/6-311++G(3df,3pd) (Table 1). The two relative energies can be compared with those calculated by Wong et al. of 19.9 and 34.8 kcalmol<sup>-1</sup>, respectively. The extremely long distances between the  $\text{AlH}_2$  and  $\text{H}_2$  moieties within the  $\text{AlH}_2(\text{H}_2)$  complex of 3.10–3.20 Å reported in Ref. [16], could not be confirmed here. At UMP2/6-311++G(3df,3pd), we found actually appreciably shorter  $\text{AlH}_2$ – $\text{H}_2$  separations of 2.29–2.32 Å (Fig. 1). The corresponding UB3LYP/LANL2DZ(d) values of 2.50–2.58 Å are also much closer to our UMP2 results. We note that on the UB3LYP/LANL2DZ(d) PES, the  $\text{AlH}_4(D_{2d}, ^2B_2)$  and  $\text{AlH}_3(\text{H})(C_{3v}, ^2A_1)$  structures are second-order points (showing two imaginary frequencies)—the two do exist as minima on the correlated ab initio UMP2/6-311++G(3df,3pd) PES (Fig. 1). Although we find good agreement between our UMP2 geometry of  $\text{AlH}_4$   $D_{2d}(^2B_2)$  **14c** and that reported in Ref. [16], we notice a serious disagreement in the case of  $\text{AlH}_3(\text{H})(C_{3v}, ^2A_1)$  complex **14b**. Again, the present UMP2 separation between the  $\text{AlH}_3$  and H units within **14b** of 2.38 Å is significantly shorter than the UMP2 result of Ref. [16] of 3.16 Å. The additional  $C_{2v}(^2B_1)$  minimum structure **14d**

**Fig. 1 a)** Structures of the  $MH_n$  ( $M = Al, Ga; n = 4, 5, 6$ ) species optimized with B3LYP/LANL2DZ(d) and MP2/6-311++G(3df,3pd) methods (bond lengths in Å, bond angles in degrees). The number of associated imaginary frequencies is given in square brackets; MP2 geometrical parameters are shown in *italics*  
**b)** Structures of the  $MH_n$  ( $M = Al, Ga; n = 4, 5, 6$ ) species optimized with B3LYP/LANL2DZ(d) and MP2/6-311++G(3df,3pd) methods (continued from Fig. 1a)

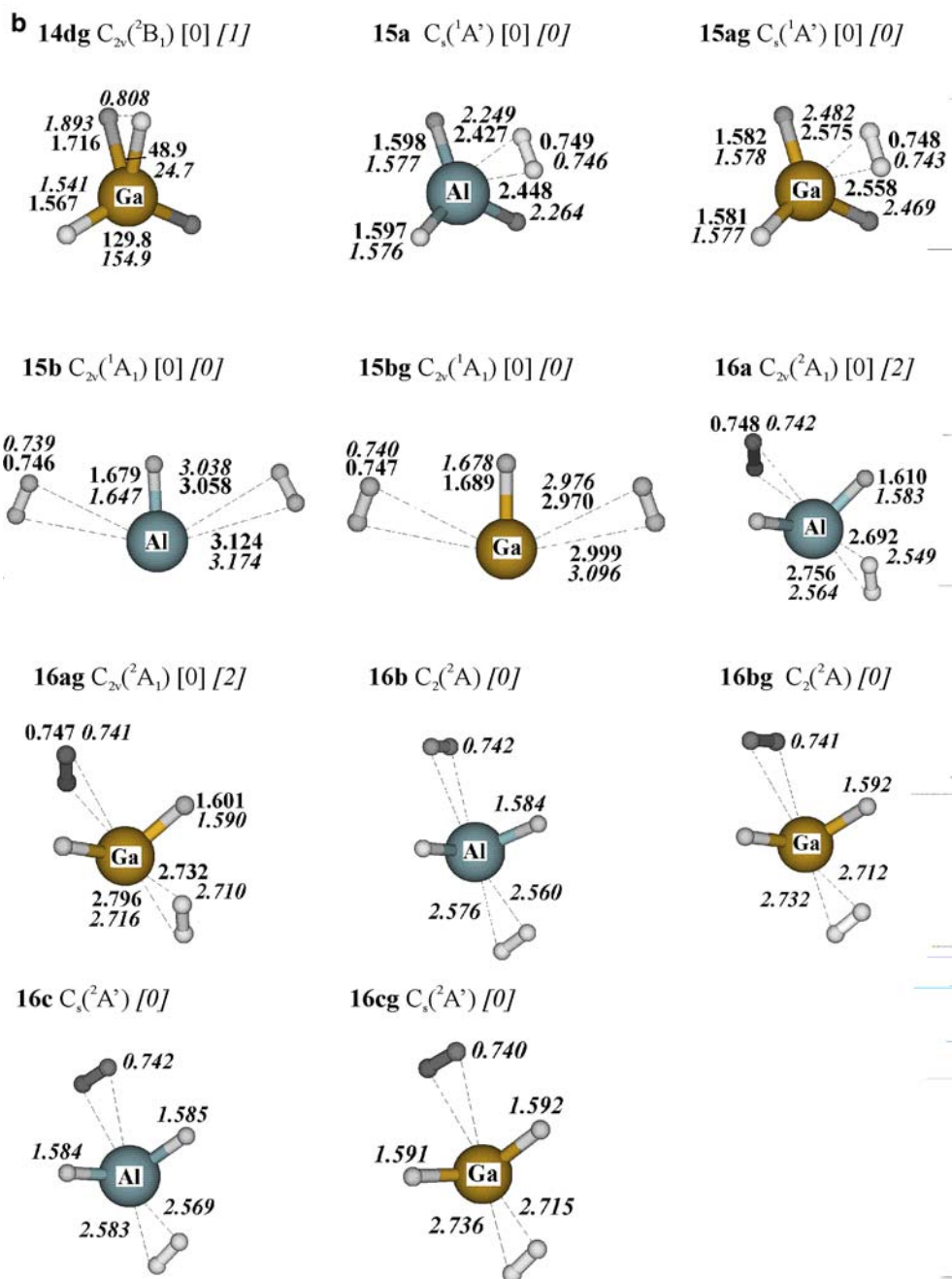


found from the UB3LYP/LANL2DZ(d) calculations (Fig. 1) exhibits four Al–H links and both wide ( $129.0^\circ$ ) and acute ( $47.0^\circ$ ) HAlH angles (also found at the UHF level in Ref. [16]). Assuming next the UB3LYP **14d** structure for the UMP2/6-311++G(3df,3pd) geometry optimization resulted in the  $AlH_2(H_2)$  type complex with a markedly “activated”  $H_2$  unit of 0.88 Å (Fig. 1). However, this UMP2 **14d** complex shows one imaginary frequency ( $393\text{icm}^{-1}$ ) and distortion along the  $b_1$  imaginary mode led eventually to the ground-state complex **14a**. According to the present calculations and consistent with the earlier predictions, [16] **14a** is of low

thermodynamic stability relative to  $H_2$  loss, with an estimated  $H_2$  dissociation energy ( $D_e$ ) of  $1.8\text{ kcalmol}^{-1}$  at UMP2/6-311++G(3df,3pd), (Table 2). Nevertheless, a low-temperature matrix appears to be the appropriate medium to isolate and assign the  $AlH_2(H_2)$  species [15], as already mentioned.

In terms of structure types, the predicted geometries of  $GaH_4$  (Fig. 1) essentially parallel those found for  $AlH_4$ . Furthermore, there is a similar relative stability order of the various  $GaH_4$  forms. Thus, the **14ag**  $GaH_2(H_2)$  ( $2A'$ ) complex corresponds to the lowest energy species of  $GaH_4$ , in agreement with the prior small basis

Fig. 1 (Contd.)



set UMP2 results of Cheung et al.[18]. Our UMP2/6-311++G(3df,3pd) distances between the  $\text{GaH}_2$  radical and  $\text{H}_2$  in **14ag** of 2.59–2.60 Å are again shorter than the UMP2/DZ(d,p) values reported in Ref. [18] (2.71–2.73 Å). The complex  $\text{GaH}_3(\text{H})(C_{3v}, {}^2A_1)$  **14bg** and distorted tetrahedral  $\text{GaH}_4(D_{2d}, {}^2B_2)$  structure **14cg** are less stable isomers, by 23.8 and 37.3 kcalmol<sup>-1</sup>, respectively, at UMP2/6-311++G(3df,3pd) (Table 1). Note that these two structures are not minima on the UB3LYP/LANL2DZ(d) PES (Fig. 1). Likewise, the UB3LYP/LANL2DZ(d) **14dg**  $C_{2v}({}^2B_1)$  tetrahydride minimum structure converged with UMP2/6-311++G(3df,3pd) to the  $\text{GaH}_2(\text{H}_2)$  complex. The latter corresponds to a first-order saddle point (Fig. 1) and

relaxes eventually to **14ag**. Our predicted UMP2  $\text{H}_2$  dissociation energy ( $D_e$ ) for **14ag** of 1.4 kcalmol<sup>-1</sup> is 0.4 kcalmol<sup>-1</sup> smaller than the UMP2 value for the Al analogue (Table 2). The observation of the  $\text{GaH}_2(\text{H}_2)$  complex has not yet been reported, but as in the  $\text{AlH}_2(\text{H}_2)$  case, a low-temperature matrix seems to be the appropriate medium for its isolation by minimizing unfavorable thermal and entropy factors.

$\text{MH}_5$  (M = Al, Ga)

In the recent high-level ab initio study of Schreiner et al. [19], six  $\text{AlH}_5$  isomers were examined using



**Table 1** Relative energies (kcalmol<sup>-1</sup> of MH<sub>n</sub> species (M = Al, Ga; n = 4, 5, 6) at MP2/6-311++G(3df, 3pd)//MP2/6-311++G(3df, 3pd) and B3LYP/6-311++G(3df, 3pd)//B3LYP/LANL2DZ(d)

n	M = Al			M = Ga		
	Species	MP2	B3LYP	Species	MP2	B3LYP
4	<b>14a</b>	0.0	0.0	<b>14ag</b>	0.0	0.0
	<b>14b<sup>a</sup></b>	19.9	20.9	<b>14bg<sup>a</sup></b>	23.8	24.9
	<b>14c<sup>a</sup></b>	36.1	21.4	<b>14cg<sup>a</sup></b>	37.3	23.0
	<b>14d<sup>b</sup></b>	10.3	9.9	<b>14dg<sup>b</sup></b>	13.7	12.9
5	<b>15a</b>	0.0	0.0	<b>15ag</b>	0.0	0.0
	<b>15b</b>	33.4	30.6	<b>15bg</b>	20.7	16.5
6	<b>16a<sup>c</sup></b>	0.1	0.0	<b>16ag<sup>c</sup></b>	0.1	0.0
	<b>16b<sup>d</sup></b>	0.0		<b>16bg<sup>d</sup></b>	0.0	
	<b>16c<sup>d</sup></b>	0.0		<b>16cg<sup>d</sup></b>	0.0	

<sup>a</sup> At UB3LYP/LANL2DZ(d), second-order saddle point

<sup>b</sup> At UMP2/6-311++G(3df, 3pd), first-order saddle point

<sup>c</sup> At UMP2/6-311++G(3df, 3pd), second-order saddle point

<sup>d</sup> Studied only at UMP2/6-311++G(3df, 3pd)

coupled-cluster singles and doubles (CCSD) and CCSD with perturbatively included triples (CCSD(T)) as the most sophisticated methods, together with TZ2P and TZ2P(f,d) basis sets (polarized triple-zeta quality). Our ab initio and DFT predictions concerning the AlH<sub>5</sub> isomers follow the major CCSD (CCSD(T)) findings of Ref. [19], in that: (1) the lowest energy structure is the van der Waals complex of AlH<sub>3</sub> with H<sub>2</sub>, AlH<sub>3</sub>(H<sub>2</sub>) **15a** of C<sub>s</sub> symmetry and (2) the C<sub>4v</sub> and D<sub>3h</sub> structures containing five Al–H links (not shown in Fig. 1) are unstable higher order saddle points [32] that lie considerably higher in energy than **15a**. For **15a**, our Al–H distance in the alane moiety of 1.576–1.577 Å and the AlH<sub>3</sub>(H<sub>2</sub>) separations of 2.264 and 2.249 Å, calculated at MP2/6-311++G(3df,3pd), compare favorably with the corresponding CCSD(T)/TZ2P values of Schreiner et al. [19], of 1.580, 2.295 and 2.331 Å, lending credit to our ab initio geometry optimization level used for the weakly bound H<sub>2</sub> complexes studied here (at least for the Al species). As concerns the thermodynamic stability of **15a**, Table 1 reveals an MP2/6-311++G(3df,3pd) H<sub>2</sub> dissociation energy (D<sub>e</sub>) of 2.5 kcalmol<sup>-1</sup>. Thus, our D<sub>e</sub> result agrees well with the CCSD(T)/TZ2P(f,d) value of 2.9 kcalmol<sup>-1</sup> in Ref. [19]. Schreiner et al. have also shown that temperature and entropy corrections (at

298 K) decrease the stability of the AlH<sub>3</sub>(H<sub>2</sub>) complex by a few kcalmol<sup>-1</sup>, actually causing its instability at room temperature [19]. The recent observation of the existence of the complex AlH<sub>3</sub>(H<sub>2</sub>) in a low-temperature matrix by Andrews [11] is consistent with Schreiner et al. [19] and our thermodynamic considerations.

As in the AlH<sub>5</sub> case, the complex of GaH<sub>3</sub> with H<sub>2</sub>, GaH<sub>3</sub>(H<sub>2</sub>) C<sub>s</sub> **15ag**, was found to be the lowest energy GaH<sub>5</sub> species (Table 1). According to Table 2, the H<sub>2</sub> dissociation energy (D<sub>e</sub>) calculated for **15ag** at the MP2/6-311++G(3df,3pd) level is 1.8 kcalmol<sup>-1</sup>, 0.7 kcalmol<sup>-1</sup> lower than that found for **15a**. Actually, one of the species detected recently in the matrix by Andrews as the product of the reaction of laser ablated Ga atoms with hydrogen during co-deposition at 3.5 K was assigned to a GaH<sub>3</sub>(H<sub>2</sub>) complex (cf. Table 1 in Ref. [12]). The alternative MH<sub>5</sub> species with the MH(H<sub>2</sub>)<sub>2</sub>(M = Al, Ga) type of structure including the MH monohydride with two H<sub>2</sub> molecules attached, can also be envisaged. We actually found local minima corresponding to such structures, denoted **15b** (M = Al) and **15bg** (M = Ga) in Fig. 1. As the species lacking two Al–H(Ga–H) bonds that are present in alane (gallane), they are, at MP2, 33.4 (20.7)kcalmol<sup>-1</sup> less stable than the alane-H<sub>2</sub> **15a** (gallane-H<sub>2</sub> **15b**) complex (Table 1).

#### MH<sub>6</sub> (M = Al, Ga)

For MH<sub>6</sub>, three distinct “double H<sub>2</sub>” type MH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub> complex doublet structures have been located. **16a** (<sup>2</sup>A<sub>1</sub>) (M = Al) and **16ag** (<sup>2</sup>A<sub>1</sub>) (M = Ga) complexes of C<sub>2v</sub> symmetry exist as minima only on the UB3LYP/LANL2DZ(d) PES. On the UMP2/6-311++G(3df, 3pd) PES, these structures show two imaginary frequencies of the order 60–80icm<sup>-1</sup> (they also persist after tightening geometry optimization criteria) (Fig. 1). Further search at UMP2/6-311++G(3df,3pd) led us to the following lower symmetry MH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub> structures: C<sub>2</sub>(<sup>2</sup>A) **16b** (M = Al) and **16bg** (M = Ga), and C<sub>s</sub> (<sup>2</sup>A') **16c** (M = Al) and **16cg** (M = Ga). The latter four correspond to minima and their energy is lower than that of the C<sub>2v</sub> structures by not more than 0.1 kcalmol<sup>-1</sup>. This is understandable because the different MH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub> isomers differ essentially only by the H<sub>2</sub> orientations. The **16b** and **16c**, and **16bg** and **16cg** are degenerate pairs and the lowest energy structures for AlH<sub>6</sub> and GaH<sub>6</sub>, respectively. For the four species, the separations between the MH<sub>2</sub> radical and the two H<sub>2</sub> molecules are calculated to be in the range 2.56–2.58 Å (M = Al) and 2.71–2.74 Å (M = Ga), and are significantly longer than those found at this level for the “single H<sub>2</sub>” MH<sub>2</sub>(H<sub>2</sub>) species (cf. Fig. 1). According to Table 2, the double H<sub>2</sub> dissociation energy from MH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub> (D<sub>e</sub>) is calculated to be 2.8 and 2.4 kcalmol<sup>-1</sup> for M = Al and Ga, respectively. Thus again, the binding energy for this double dihydrogen complex is somewhat smaller for M = Ga compared to M = Al.

**Table 2** The H<sub>2</sub> dissociation energies (D<sub>e</sub>) (in kcalmol<sup>-1</sup>) calculated for the most stable MH<sub>n</sub> species (n = 4, 5, 6) with ab initio MP2 and DFT PBE and 6-311++G(3df, 3pd) basis set

Complex	M = Al		Complex	M = Ga	
	MP2 <sup>a</sup>	PBE <sup>a</sup>		MP2 <sup>a</sup>	PBE <sup>a</sup>
N = 4 AlH <sub>2</sub> (H <sub>2</sub> ) <b>14a</b>	1.8	3.4	GaH <sub>2</sub> (H <sub>2</sub> ) <b>14ag</b>	1.4	2.1
N = 5 AlH <sub>3</sub> (H <sub>2</sub> ) <b>15a</b>	2.5	3.8	GaH <sub>3</sub> (H <sub>2</sub> ) <b>15ag</b>	1.8	2.5
N = 6 AlH <sub>2</sub> (H <sub>2</sub> ) <sub>2</sub> <b>16b</b>	2.8 <sup>b</sup>	4.6 <sup>b</sup>	GaH <sub>2</sub> (H <sub>2</sub> ) <sub>2</sub> <b>16bg</b>	2.4 <sup>b</sup>	3.4 <sup>b</sup>

<sup>a</sup> At the MP2/6-311++G(3df, 3pd) geometries

<sup>b</sup> Relative to MH<sub>2</sub>+2H<sub>2</sub> (M = Al, Ga)

Comparison of DFT PBE and ab initio MP2 binding energies for  $\text{MH}_2(\text{H}_2)$ ,  $\text{MH}_3(\text{H}_2)$  and  $\text{MH}_2(\text{H}_2)_2$  ( $\text{M} = \text{Al}, \text{Ga}$ )

Table 2 reveals that the DFT PBE reproduces both trends in binding energy (b.e.) found at the MP2 level: (1) the b.e. increases on going from  $n=4$  to  $n=6$  for both  $\text{M} = \text{Al}$  and  $\text{M} = \text{Ga}$  (note that this comparison includes “double  $\text{H}_2$ ” complexes for  $n=6$  and “single  $\text{H}_2$ ” complexes for  $n=4, 5$ ); (2) the magnitude of the b.e. for the Ga species is smaller compared to the corresponding Al species (we discuss this issue in more detail in section Interaction energy within  $\text{AlH}_3(\text{H}_2)$  vs.  $\text{GaH}_3(\text{H}_2)$ ). On the other hand, one notices that PBE overestimates the binding effect appreciably compared to MP2 (note that MP2 structures were assumed for the PBE calculations).

Basic set superposition error and zero-point corrections were not included in Table 2, and here we discuss their importance for the two singlet structures: **15a** and **15ag**, further submitted to interaction energy analysis. MP2 calculations give a BSSE estimate of  $0.17 \text{ kcalmol}^{-1}$  for **15a** and  $0.22 \text{ kcalmol}^{-1}$  for **15ag** thus showing that the basis set is flexible and saturated enough. The PBE estimates of BSSE are  $0.05$  and  $0.08 \text{ kcalmol}^{-1}$ , respectively, confirming the fact that DFT is less demanding in terms of basis set quality and that BSSE has very limited impact on the results presented here. The ZPE correction, however, has a much larger destabilizing effect:  $2.15$  and  $2.12 \text{ kcalmol}^{-1}$  for **15a** and **15ag**, respectively, at both MP2 and DFT levels. This means that the gallium species **15ag** is stable with respect to the reactants with the PBE functional, but not within the MP2 treatment.

#### Interaction energy within $\text{AlH}_3(\text{H}_2)$ vs. $\text{GaH}_3(\text{H}_2)$

The nature of the interaction in the corresponding  $\text{H}_2$  complexes of  $\text{AlH}_n$  and  $\text{GaH}_n$  has been compared here for  $n=5$  by using symmetry adapted perturbation theory (SAPT) [33–35]. In the SAPT scheme, the interaction energy is analyzed in terms of electrostatic, dispersion, induction, and exchange-repulsion contributions. The actual analysis was carried out for the  $\text{AlH}_3(\text{H}_2)$  **15a** and  $\text{GaH}_3(\text{H}_2)$  **15ag** pair with the ab initio RHF and correlated methods and using the SAPT2002 code [35] (for results, see Table 3).

The SAPT partitioning of the interaction energy for the  $\text{AlH}_3(\text{H}_2)$  and  $\text{GaH}_3(\text{H}_2)$  structures was performed with the Pople 6-311++G(3df,3pd) basis set used throughout the study. Additionally, four correlation-consistent basis sets were taken for the SAPT study to assess the basis set dependence of the results. They were in the order of decreasing quality: fully augmented, aug-cc-pVTZ triple-zeta basis set with diffuse functions, two reduced aug-cc-pVTZ sets with only  $s+p$  and  $s$  diffuse functions, respectively, and finally cc-pVTZ set without augmentation. Individual energy terms showed virtually

no basis set dependence; the variations rarely reached and did not exceed  $0.3 \text{ kcalmol}^{-1}$ , even for the most sensitive dispersion terms (see Electronic Supplementary Material, Table S1). Further discussion will therefore be restricted to the 6-311++G(3df,3pd) basis set results and the standard notation of the SAPT theory will be used: the two superscript numbers in the particular energy term give the perturbation order for intra- and intermolecular perturbation operator, e.g.,  $E^{10}$  values are first-order intermolecular terms with no electron correlation within monomers.

Table 3 lists the interaction-energy components as calculated by the SAPT scheme. Characteristic differences between the Al and Ga species are visible for the  $E^{10}_{\text{elst}}$  and  $E^{10}_{\text{exch}}$  terms. The first term describes the electrostatic interaction between “static monomer” charge distributions of  $\text{MH}_3$  and  $\text{H}_2$ , its values being  $-5.9 \text{ kcalmol}^{-1}$  for  $\text{M} = \text{Al}$  and  $-3.8 \text{ kcalmol}^{-1}$  for Ga. This is in agreement with significant differences in atomic charges, not only between the metal centers but also the corresponding hydrogen atoms (see Table 4). Despite this, the  $E^{20}_{\text{ind}}$  term, describing *induced-permanent* multipole interactions, is similar for the two systems, showing that the Ga atom is more easily polarizable than Al. However, the most visible difference between the two species is the value of the  $E^{10}_{\text{exch}}$  repulsive exchange term:  $11.2 \text{ kcalmol}^{-1}$  for Al, and only  $6.6 \text{ kcalmol}^{-1}$  for Ga. This difference is large considering that the  $\text{M}-\text{H}_2$  distance increases only from  $2.25$  to  $2.47 \text{ \AA}$  on going from the Al to Ga species, and assuming that the atomic radii of the two metals are similar (Al:125 pm, Ga:130 pm). It can be suggested that the electron density withdrawn to the hydride part of  $\text{AlH}_3$  gives this moiety an additional shield of Pauli repulsion when compared to the Ga analogue. The uncorrelated terms of the interaction energy sum up to a positive value ( $0.85 \text{ kcalmol}^{-1}$  for the aluminum and  $0.61 \text{ kcalmol}^{-1}$  for the gallium structure), but addition of the remaining terms makes the interaction energy slightly negative. However, at the HF level the differences in the terms mainly cancel out and the interaction energies of the two species are similar. The explanation

**Table 3** Selected terms of interaction energy partitioning ( $\text{kcalmol}^{-1}$ ) according to the SAPT scheme. See text for details

	$\text{AlH}_3(\text{H}_2)$ <b>15a</b>	$\text{GaH}_3(\text{H}_2)$ <b>15ag</b>
$E^{10}_{\text{elst}}$	-5,897	-3,842
$E^{10}_{\text{exch}}$	11,175	6,637
$E^{20}_{\text{ind,r}}$	-11,256	-9,030
$E^{20}_{\text{ex-ind,r}}$	6,830	6,844
<b>SAPTSCF</b>	<b>0,853</b>	<b>0,609</b>
$\Delta HF_{\text{int,r}}$	-1,271	-0,637
$E^2_{\text{disp}}$	-3,929	-2,992
$E^{20}_{\text{ex-disp}}$	0,477	0,308
$\text{SAPT}_{\text{corr,r}}$	-2,550	-2,027
<b>SCF + SAPT<sub>corr,r</sub></b>	<b>-2,968</b>	<b>-2,056</b>

<sup>a</sup>Minus sign indicates a stabilizing contribution

**Table 4** Mulliken atomic charges calculated at the MP2/6-311++G(3df, 3pd) level of theory

AlH <sub>3</sub> (H <sub>2</sub> )	15a	GaH <sub>3</sub> (H <sub>2</sub> )	15ag
Al	0,7559	Ga	0,3911
H <sup>a</sup>	0,0270	H <sup>a</sup>	0,0170
H <sup>a</sup>	0,0221	H <sup>a</sup>	0,0160
H <sup>b</sup>	-0,2794	H <sup>b</sup>	-0,1513
H <sup>b</sup>	-0,2627	H <sup>b</sup>	-0,1364
H <sup>b</sup>	-0,2628	H <sup>b</sup>	-0,1365

<sup>a</sup> Belonging to the H<sub>2</sub> unit

<sup>b</sup> Belonging to the MH<sub>3</sub> unit

of the different stabilities of the Al and Ga species must be sought in the correlated terms. Small corrections to the terms present at the HF level do not change the overall picture, but large difference is seen in the dispersion contribution which is surprisingly 1 kcalmol<sup>-1</sup> smaller for the GaH<sub>3</sub>(H<sub>2</sub>). In combination with the uncorrelated terms, this makes the gallium structure almost 1 kcalmol<sup>-1</sup> less stable than its aluminum counterpart in the final SAPT interaction energy (-2.06 vs -2.97 kcalmol<sup>-1</sup>). The fact that the gallium species has a significantly smaller dispersion energy can be explained if we assume that this energy is mostly induced with a participation of the hydride electron clouds. These are indeed larger in case of AlH<sub>3</sub>(H<sub>2</sub>). In short, the SAPT energy partitioning suggests that the increased “hydride” character of aluminum species is responsible for the increased dispersion effect and greater stabilization of this complex with respect to the gallium counterpart. This “hydride” character is again consistent with the well-known properties of aluminum as a strong Lewis acid, and its unexpectedly low electronegativity (Al: 1.47, Ga: 1.82 on the Allred-Rochow scale).

## Conclusions

In summary, we have calculated the possible structures and stabilities for the series of neutral MH<sub>n</sub>(M = Al, Ga; n = 4, 5, 6) species using second-order Møller–Plesset perturbation theory with large 6-311++G(3df,3pd) basis set. For AlH<sub>4</sub> and AlH<sub>5</sub>, we found in agreement with the previous calculations that the dihydrogen C<sub>s</sub> complexes (<sup>2</sup>A') AlH<sub>2</sub>(H<sub>2</sub>) and (<sup>1</sup>A') AlH<sub>3</sub>(H<sub>2</sub>) are the ground-state structures. For the “heavier” analogues we found similarly the C<sub>s</sub> (<sup>2</sup>A') GaH<sub>2</sub>(H<sub>2</sub>) and (<sup>1</sup>A') GaH<sub>3</sub>(H<sub>2</sub>) van der Waals complexes as the most stable species of GaH<sub>4</sub> and GaH<sub>5</sub>. The MP2/6-311++G(3df,3pd) calculated H<sub>2</sub> D<sub>e</sub> for the above complexes lies in the range 1.8–2.5 kcalmol<sup>-1</sup> (M = Al) and 1.4–1.8 kcalmol<sup>-1</sup> (M = Ga). SAPT was used to analyze the interaction energy of the MH<sub>5</sub> systems to determine why the Ga complex is weaker compared to the Al complex. The SAPT partitioning of the interaction energy revealed significant differences between AlH<sub>3</sub>(H<sub>2</sub>) and GaH<sub>3</sub>(H<sub>2</sub>), resulting from much stronger

“hydride” character of the aluminum species. At the bottom line, this increased delocalization of electron cloud in the AlH<sub>3</sub>(H<sub>2</sub>) allows larger dispersion energy and greater stability for this complex than that of GaH<sub>3</sub>(H<sub>2</sub>).

The experimental observations of AlH<sub>2</sub>(H<sub>2</sub>) and AlH<sub>3</sub>(H<sub>2</sub>), and likely GaH<sub>3</sub>(H<sub>2</sub>), *via* low-temperature matrix isolation, have been reported recently by Pullumbi et al. [15] and Andrews et al. [11, 12] thus supporting the theoretical predictions. For n = 6, we found the degenerate C<sub>2</sub>(<sup>2</sup>A) and C<sub>s</sub>(<sup>2</sup>A') MH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub> “double H<sub>2</sub>” type van der Waals complexes to be the lowest energy structures for M = Al, Ga. Estimation of accurate binding energies of the complexes studied here will require a more precise description of dynamic correlation, including anharmonic vibrational effects [8, 9] and, for open-shell systems, spin–orbit effects (especially for the Ga species).

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