

Vertical and adiabatic ionization potentials of MH_{k+1}^- anions. *Ab initio* study of the structure and stability of hypervalent MH_{k+1} molecules

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Vertical and adiabatic ionization potentials of the free MH_{k+1}^- anions, where M is a nontransition atom and k is the maximal formal valence of the atom M, have been studied by *ab initio* methods. Thermodynamic stabilities of the corresponding neutral hypervalent MH_{k+1} species have been calculated as well. LiH_2^- , BeH_3^- , MgH_3^- , BH_4^- , AlH_4^- , and SiH_5^- are very stable to loss of the extra electron and are stable geometrically at high symmetry structure, except for SiH_5^- which is not stable thermodynamically. LiH_2 , NaH_2 , BeH_3 , MgH_3 , and BH_4 have minima at C_{2v} (2B_2) structures; however, only BH_4 is thermodynamically stable to all possible dissociation asymptotes. The NaH_2^- anion is not adiabatically electronically stable.

I. INTRODUCTION

Many complex hydride anions MH_{k+1}^- , where M is a nontransition metal element and k is the maximal formal valence of M, are geometrically and thermodynamically stable. *Ab initio* calculations show that LiH_2^- , NaH_2^- , and KH_2^- , $^{1(c)}$ anions have closed shell linear $D_{\infty h}$ ($^1\Sigma_g^+$) structures [Fig. 1(a)]; BeH_3^- and MgH_3^- (Ref. 2) have closed shell D_{3h} ($^1A_1'$) structures [Fig. 1(b)]; BH_4^- and AlH_4^- , 3 have closed shell T_d (1A_1) structures [Fig. 1(c)]; and SiH_5^- , GeH_5^- , and SnH_5^- , 3 have closed shell D_{3h} ($^1A_1'$) structures [Fig. 1(d)]. The lightest group IV hypervalent species, CH_5 and CH_5^- , have both been predicted to be unstable transition states with the radical energetically more stable than the anion,^{4,5} and the SiH_5^- anion has been experimentally characterized.⁶

One of the remarkable physical properties of these MH_{k+1}^- anions is their very high vertical electron detachment energies (VEDE) or vertical ionization potentials (VIP), which recently have been predicted theoretically using Green function methods.⁷ For example, BH_4^- and AlH_4^- have VEDEs of 4.54 eV and 4.75 eV,⁷ respectively. Both values are higher than the VEDE of halide ions (F^- and Cl^- have VEDEs of 3.40 eV and 3.61 eV⁸). This is especially interesting, because H^- , B^- , and Al^- have a low electron detachment energies: 0.7542 eV, 0.277 eV, and 0.441 eV⁸, respectively. The high VEDEs (or VIPs) arise because the extra electron in MH_{k+1}^- fills a bonding HOMO that is delocalized through $(k+1)$ hydrogen atoms.⁷

Unfortunately, we were not able to find in the literature any experimental data on the VEDE or VIP of MH_{k+1}^- species. While MH_{k+1}^- anions are very stable to loss of an extra electron, their adiabatic electron detachment energies (AEDE) or adiabatic ionization potentials (AIP) are not known. Moreover, the geometric and thermodynamic stabilities of corresponding MH_{k+1} species are not known. We would like to point out that if MH_{k+1} is stable, the AEDE or AIP is equal to the adiabatic electron affinity of MH_{k+1} . The last values are important for thermodynamic calculations of the stability of $L^+MH_{k+1}^-$ complex salts, where L^+ is a cation, such as Li^+ or NH_4^+ . Such

complex molecules are known in crystals and in solutions⁹ and $LiBH_4$, $NaBH_4$, KBH_4 have been seen in the gas phase.¹⁰

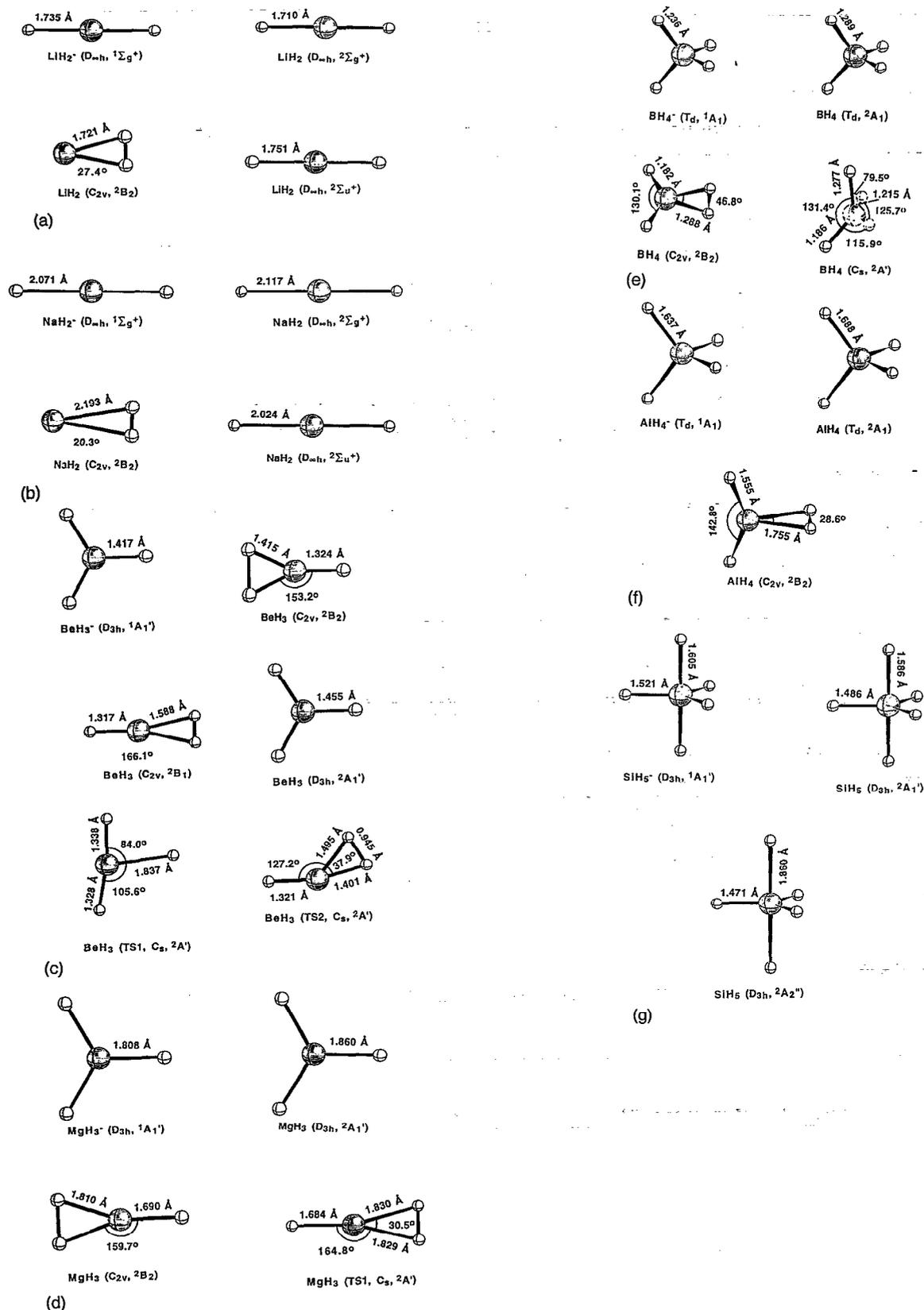
The aim of this work is to study the geometrical and thermodynamic stability of MH_{k+1} species and to calculate the AEDEs or AIPs of the corresponding MH_{k+1}^- anions.

II. COMPUTATIONAL DETAILS

The geometries of LiH_2^- , LiH_2 , NaH_2^- , NaH_2 , BeH_3^- , BeH_3 , MgH_3^- , MgH_3 , BH_4^- , BH_4 , AlH_4^- , AlH_4 , SiH_5^- , SiH_5 , as well as LiH , NaH , BeH^- , BeH , BeH_2 , MgH^- , MgH , MgH_2 , BH_2^- , BH_2 , BH_3 , AlH_2^- , AlH_2 , AlH_3 , SiH_3^- , SiH_3 , and SiH_4 were optimized employing analytical gradients¹¹ at the second-order Møller-Plesset [MP2(full)] level with triple-zeta plus polarization and diffuse bases [denoted 6-311++G** (Ref. 12)]. The fundamental vibrational frequencies, normal coordinates, and zero point energies (ZPE) were calculated by standard FG matrix methods. Finally, higher quality correlated total energies were evaluated in the frozen core approximation both by fourth-order Møller-Plesset perturbation theory¹³ (MP4), and by the quadratic configuration interaction including singles and doubles with approximate triples QCISD(T)¹⁴ method using 6-311++G(2df,2pd) basis sets. For open-shell species, the unrestricted USCF wave functions were projected to produce pure spectroscopic states (whose results, in turn, are labeled PUSCF, PMP2, PMP3, and PMP4).¹⁵ The Gaussian 92 program suite¹⁶ was used to obtain all of the results discussed here. In this article, we report our geometric parameters and vibrational frequencies at the MP2(full)/6-311++G** level and find energies at the QCISD(T)/6-311++G(2df,2pd) level but at the MP2(full)/6-311++G** geometry.

III. RESULTS AND DISCUSSION

LiH_2^- , LiH_2 , NaH_2^- , and NaH_2 . Both LiH_2^- and NaH_2^- have stable linear $D_{\infty h}$ structures with $1\sigma_g^2 1\sigma_u^2$ valence electronic configurations. The calculated geometric parameters, vibrational frequencies, and relative energies are presented in Tables I and II, and in Figs. 1(a) and 1(b).

FIG. 1. Calculated geometries at the MP2(full)/6-311++G** level for MH_{k+1}^- anions and MH_{k+1} neutrals.

The LiH_2^- anion is a geometrically and thermodynamically stable species. Our dissociation energy for $LiH_2^- \rightarrow LiH + H^-$ is +54.0 kcal/mol and $\rightarrow Li^- + H_2$, it is a +5.1 kcal/mol (both including ZPE correction).

These data agree well with earlier predictions +54.1 kcal/mol and +5.3 kcal/mol, respectively by Senekowitsch and Rosmus^{1(b)} at the coupled electron pair approximation (CEPA) with a large basis set. All of the dissociation en-

TABLE I. Calculated molecular properties for LiH_2^- and LiH_2 .

$\text{LiH}_2^- (D_{\infty h}, {}^1\Sigma_g^+)$	$\text{LiH}_2 (C_{2v}, {}^2B_2)$	$\text{LiH}_2 (D_{\infty h}, {}^2\Sigma_g^+)$	$\text{LiH}_2 (D_{\infty h}, {}^2\Sigma_u^+)$
$1\sigma_g^2 1\sigma_u^2$	$1a_1^1 1b_2^1$	$1\sigma_u^2 1\sigma_g^1$	$1\sigma_g^2 1\sigma_u^1$
MP2(full)/6-311++G** $E_{\text{MP2}} = -8.61779$	MP2(full)/6-311++G** $E_{\text{MP2}} = -8.56306$ $\langle S^2 \rangle = 0.752$	MP2(full)/6-311++G** $E_{\text{MP2}} = -8.49690$ $\langle S^2 \rangle = 0.798$	MP2(full)/6-311++G** $E_{\text{MP2}} = -8.50930$ $\langle S^2 \rangle = 0.943$
$\nu_1(\sigma_g) = 1057 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 425 \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 1120 \text{ cm}^{-1}$	$\nu_1(a_1) = 3101 \text{ cm}^{-1}$ $\nu_2(a_1) = 868 \text{ cm}^{-1}$ $\nu_3(b_2) = 1315 \text{ cm}^{-1}$	$\nu_1(\sigma_g) = 997 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 348 \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 1377 \text{ cm}^{-1}$	$\nu_1(\sigma_g) = 990 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 277i \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 1491 \text{ cm}^{-1}$
ZPE = 4.33 kcal/mol	ZPE = 7.55 kcal/mol	ZPE = 4.38 kcal/mol	ZPE = 3.55 kcal/mol
QCISD(T)/6-311++G(2df,2pd) $E_{\text{SCF}} = -8.55965$ $E_{\text{MP2}} = -8.61428$ $E_{\text{MP3}} = -8.62629$ $E_{\text{MP4}} = -8.62998$ $E_{\text{QCISD(T)}} = -8.63150$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -8.51822$ $E_{\text{PMP2}} = -8.55598$ $E_{\text{PMP3}} = -8.56266$ $E_{\text{PMP4}} = -8.56455$ $E_{\text{QCISD(T)}} = -8.56515$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -8.45823$ $E_{\text{PMP2}} = -8.49223$ $E_{\text{PMP3}} = -8.49999$ $E_{\text{PMP4}} = -8.50439$ $E_{\text{QCISD(T)}} = -8.50809$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -8.48477$ $E_{\text{PMP2}} = -8.50930$ $E_{\text{PMP3}} = -8.51421$ $E_{\text{PMP4}} = -8.51828$ $E_{\text{QCISD(T)}} = -8.51916$

ergies reported in this paper have been obtained without correcting for, so called, basis set superposition errors which are expected to be ca. 4–5 kcal/mol. These corrections should therefore affect our conclusions only for weakly bound species.

Substitution of Li by Na leads to the geometrically stable, but thermodynamically unstable NaH_2^- anion. Our calculated dissociation energy for $\text{NaH}_2^- \rightarrow \text{NaH} + \text{H}^-$ is +46.9 kcal/mol and for $\rightarrow \text{Na}^- + \text{H}_2$ it is -12.3 kcal/mol (with ZPE correction). The NaH_2^- ion is a local minimum that should have a potential barrier on the $\text{Na}^- + \text{H}_2$ dissociation pathway because the $1a_1^1 1b_2^1$ (in C_{2v} symmetry) electronic configuration of NaH_2^- does not correlate with the $1a_1^2 2a_1^1$ electronic configuration of the $\text{Na}^- ({}^1S) + \text{H}_2 ({}^1\Sigma_g^+)$ asymptote. The HLiH^- and HNaH^- anions are isoelectronic with linear BeH_2 , MgH_2 , BH_2^+ , and AlH_2^+ for which it was shown¹⁷ that there are large barriers to dissociation C_{2v} and near C_{2v} cuts. Senekowitsch and Rosmus^{1(b)} have found barriers of at least 2 eV above the minimum energy of HLiH^- .

Our calculated VIPs of LiH_2^- are very large for both valence states: 3.06 eV (${}^2\Sigma_u^+$) and 3.35 eV (${}^2\Sigma_g^+$). The VIP of the ${}^2\Sigma_u^+$ state agrees well with that (3.10 eV) of

Senekowitsch and Rosmus^{1(b)} obtained at the CEPA level and with the value (2.95 eV) of Boldyrev and Niessen⁷ calculated at the Green's function level (in both cases, large basis sets were used). This agreement between three different methods confirms that our calculated $\text{VIP}({}^2\Sigma_u^+) = 3.0 \pm 0.1 \text{ eV}$ for LiH_2^- should be a good guide for experimental measurement.

Detachment of the extra electron from the HOMO ($1\sigma_u$) of LiH_2^- leads to the ${}^2\Sigma_u^+$ state of neutral LiH_2 . The optimized structure of the ${}^2\Sigma_u^+$ state of LiH_2 has an imaginary bending frequency [$\nu_2(\pi_u) = 277i \text{ cm}^{-1}$], and therefore is not a local minimum. The total energy of ${}^2\Sigma_u^+ \text{LiH}_2$ at the geometry of the LiH_2^- anion is higher than $\text{LiH} + \text{H}$ by 3.0 kcal/mol, and higher than $\text{Li} + \text{H}_2$ by 50.5 kcal/mol. Optimization following the normal mode of imaginary frequency leads to an angular local minimum structure ($C_{2v}, {}^2B_2$) with electronic configuration $1a_1^1 1b_2^1$. This structure is more stable than $\text{LiH} + \text{H}$ by 21.9 kcal/mol, but unstable with respect to $\text{Li} + \text{H}_2$ by 25.7 kcal/mol. However at the optimal geometry of this $C_{2v} ({}^2B_2)$ structure, a $C_{2v} ({}^2A_1)$ state with $1a_1^2 2a_1^1$ electronic configuration lies lower by 11.3 kcal/mol [QCISD(T)/6-311++G(2df,2pd)]. This $C_{2v} ({}^2A_1)$ state correlates with the

TABLE II. Calculated molecular properties for NaH_2^- and NaH_2 .

$\text{NaH}_2^- (D_{\infty h}, {}^1\Sigma_g^+)$	$\text{NaH}_2 (C_{2v}, {}^2B_2)$	$\text{NaH}_2 (D_{\infty h}, {}^2\Sigma_g^+)$	$\text{NaH}_2 (D_{\infty h}, {}^2\Sigma_u^+)$
$1\sigma_g^2 1\sigma_u^2$	$1a_1^1 1b_2^1$	$1\sigma_u^2 1\sigma_g^1$	$1\sigma_g^2 1\sigma_u^1$
MP2(full)/6-311++G** $E_{\text{MP2}} = -163.11685$	MP2(full)/6-311++G** $E_{\text{MP2}} = -163.07615$ $\langle S^2 \rangle = 0.751$	MP2(full)/6-311++G** $E_{\text{MP2}} = -162.99720$ $\langle S^2 \rangle = 0.847$	MP2(full)/6-311++G** $E_{\text{MP2}} = -163.02514$ $\langle S^2 \rangle = 1.022$
$\nu_1(\sigma_g) = 929 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 314 \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 885 \text{ cm}^{-1}$	$\nu_1(a_1) = 3810 \text{ cm}^{-1}$ $\nu_2(a_1) = 529 \text{ cm}^{-1}$ $\nu_3(b_2) = 949 \text{ cm}^{-1}$	$\nu_1(\sigma_g) = 845 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 182 \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 967 \text{ cm}^{-1}$	$\nu_1(\sigma_g) = 868 \text{ cm}^{-1}$ $\nu_2(\pi_u) = 86i \text{ cm}^{-1}$ $\nu_3(\sigma_u) = 3108i \text{ cm}^{-1}$
ZPE = 3.49 kcal/mol	ZPE = 7.56 kcal/mol	ZPE = 3.11 kcal/mol	ZPE = 1.24 kcal/mol
QCISD(T)/6-311++G(2df,2pd) $E_{\text{SCF}} = -162.94273$ $E_{\text{MP2}} = -162.99602$ $E_{\text{MP3}} = -163.00807$ $E_{\text{MP4}} = -163.01199$ $E_{\text{QCISD(T)}} = -163.01379$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -162.91610$ $E_{\text{PMP2}} = -162.95115$ $E_{\text{PMP3}} = -162.95740$ $E_{\text{PMP4}} = -162.95916$ $E_{\text{QCISD(T)}} = -162.95994$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -162.84661$ $E_{\text{PMP2}} = -162.87760$ $E_{\text{PMP3}} = -162.88468$ $E_{\text{PMP4}} = -162.88967$ $E_{\text{QCISD(T)}} = -162.89597$	QCISD(T)/6-311++G(2df,2pd) $E_{\text{PUSCF}} = -162.88621$ $E_{\text{PMP2}} = -162.90746$ $E_{\text{PMP3}} = -162.91164$ $E_{\text{PMP4}} = -162.91555$ $E_{\text{QCISD(T)}} = -162.91694$

$Li(^2S)+H_2(^1\Sigma_g^+)$ asymptote without any barrier, so it dissociates. The nonadiabatic crossing between the C_{2v} (2B_2) and C_{2v} (2A_1) states takes place only 2.4 kcal/mol above the minimum energy structure of the C_{2v} (2B_2) state, which is less than the ZPE correction to this structure [7.55 kcal/mol at MP2(full/6-311++G**)]. Therefore, the C_{2v} (2B_2) structure is not stable and would quickly dissociate into $Li+H_2$ throughout nonadiabatic transition onto the C_{2v} (2A_1) surface. The adiabatic IP ($^2\Sigma_u^+$) for LiH_2^- may be calculated with respect to the dissociation products $Li+H_2$, and it is only 0.74 eV. This very large adiabatic correction (2.32 eV) is due to geometric and thermodynamic instability of the final neutral state of LiH_2 .

The detachment of an electron from another valence MO ($1\sigma_g$) leads to the $^2\Sigma_g^+$ state with $1\sigma_g^11\sigma_u^2$ electronic configuration. This state has a local minimum at $D_{\infty h}$ symmetry (no imaginary frequencies). The geometrical structures for LiH_2 ($D_{\infty h}$, $^2\Sigma_u^+$) and LiH_2^- ($D_{\infty h}$, $^1\Sigma_g^+$) are very close (the Li–H bond lengths are 1.710 Å and 1.735 Å, respectively), therefore the difference between the vertical and adiabatic IPs for this state is very small (0.01 eV) and a large Franck–Condon factor is expected for this ionization process. Our best values for the VIP and AIP ($^2\Sigma_g^+$) for LiH_2^- are actually the same 3.35 eV.

The NaH_2^- ion is geometrically stable at a $D_{\infty h}$ ($^1\Sigma_g^+$) structure, but thermodynamically it is not a stable species. This is unlike LiH_2^- , where the anion is a thermodynamically stable species. Our calculated dissociation energies for NaH_2^- are +46.9 kcal/mol (into $NaH+H^-$) and –12.3 kcal/mol (into Na^-+H_2 , all with ZPE correction). However, as discussed above for LiH_2^- , on the dissociation pathway for NaH_2^- ($D_{\infty h}$, $^1\Sigma_g^+$) \rightarrow Na^-+H_2 there should be a barrier.

Detachment of an electron from the $1\sigma_u$ -HOMO in NaH_2^- leads to the geometrically and thermodynamically unstable NaH_2 ($^2\Sigma_u^+$) species. The vertical IP ($^2\Sigma_u^+$) of NaH_2^- is 2.63 eV which agrees well with the GF calculation data 2.53 eV.⁷ Geometry optimization of NaH_2 ($^2\Sigma_u^+$) within $D_{\infty h}$ symmetry gives a structure which has three imaginary frequencies [$\nu_2(\pi_u)=86i$ cm⁻¹ and $\nu_3(\sigma_u)=3108i$ cm⁻¹]. This structure ($D_{\infty h}$, $^2\Sigma_u^+$) lies below the $NaH+H$ dissociation asymptote by 1.1 kcal/mol, and because it has an imaginary antisymmetric stretch frequency, it should dissociate without any barrier. However, like LiH_2 , the NaH_2 species has a local minimum at C_{2v} symmetry with a 2B_2 electronic state. All frequencies are positive for this structure (see Table II). This local minimum is stable with respect to dissociation into $NaH+H$ (+21.7 kcal/mol), but unstable with respect to dissociation into $Na+H_2$ (–37.7 kcal/mol). However, as in the case of LiH_2 , this NaH_2 (C_{2v} , 2B_2) local minimum energy is higher than the 2A_1 ($1a_1^22a_1^1$) electronic state at the geometry of this local minimum (by 30.0 kcal/mol). Therefore the adiabatic IP ($^2\Sigma_u^+$) of NaH_2^- should be calculated with respect to the dissociation products $Na+H_2$ and this value is –0.12 eV(!). *The NaH_2^- anion is not adiabatically electronically stable.*

The detachment of an electron from the $1\sigma_g$ -MO in

NaH_2^- leads to the $^2\Sigma_g^+$ state which is a local minimum at $D_{\infty h}$ symmetry (see Table II), with a vertical IP of 3.21 eV. Because the geometries for NaH_2^- ($D_{\infty h}$, $^1\Sigma_g^+$) and NaH_2 ($D_{\infty h}$, $^2\Sigma_g^+$) are very close, the adiabatic correction to this IP is very small (0.01 eV). This first excited state is not thermodynamically stable with respect to either $NaH+H$ (–13.9 kcal/mol), or $Na+H_2$ (–73.4 kcal/mol).

In summary, the result of our calculations LiH_2^- and NaH_2^- have shown that only LiH_2^- anion is a thermodynamically stable species, while NaH_2^- (and we expect¹⁸ KH_2^- , RbH_2^- , and CsH_2^-) is not thermodynamically stable, nor electronically stable if we take into account geometric relaxation.

BeH_3^- , BeH_3 , MgH_3^- , and MgH_3 . Both BeH_3^- and MgH_3^- are known to have planar D_{3h} ($^1A_1'$) structures.² According to our calculations, the BeH_3^- anion is thermodynamically stable both to dissociation into BeH^-+H_2 (+49.6 kcal/mol) and into BeH_2 (this molecule is thermodynamically stable with respect to dissociation into $Be+H_2$ by 34.7 kcal/mol) $+H^-$ (+60.1 kcal/mol). The MgH_3^- ion is also thermodynamically stable both to dissociation into MgH^-+H_2 (+19.9 kcal/mol) and into $Mg+H_2+H^-$ (+56.0 kcal/mol). The MgH_2 molecule is not thermodynamically stable with respect to dissociation into $Mg+H_2$ (by –3.9 kcal/mol, with ZPE correction), however complexation of this molecule with H^- leads to the thermodynamically stable MgH_3^- anion.

The valence electronic configuration for both of the above anions is $1a_1'^21e'^4$. Therefore, vertical electron detachment should lead to two final electronic states 2E ($1a_1'^21e'^3$) and $^2A_1'$ ($1a_1'^11e'^4$). Our best vertical IPs are 3.97 eV (2E) and 6.63 eV ($^2A_1'$) for BeH_3^- , and 3.84 eV (2E) and 5.82 eV ($^2A_1'$) for MgH_3^- . The first VIPs of BeH_3^- and MgH_3^- calculated at the PMP4 and QCISD(T) levels agree well with Green function results 3.86 eV ($BeH_3^-, ^2E$) and 3.74 eV ($MgH_3^-, ^2E$).⁷ The 2E electronic state is geometrically unstable for both BeH_3 and MgH_3 species at the D_{3h} structure due to Jahn–Teller distortion.

The D_{3h} (2E) structure of BeH_3 at the anion geometry is not thermodynamically stable with respect to dissociation into $BeH+H_2$ ($\Delta E=28.4$ kcal/mol) or BeH_2+H ($\Delta E=-15.9$ kcal/mol). Geometry optimization of the 2A_1 (C_{2v}) electronic state ($1a_1^21b_2^22a_1^1$) derived from Jahn–Teller distortion of the 2E state leads directly to the dissociation products BeH_2+H without any barrier; this electronic state correlates with the ground electronic states of the dissociation products. Optimization of the 2B_2 (C_{2v}) ($1a_1^22a_1^11b_2^1$) component of the Jahn–Teller pass leads to the local minimum C_{2v} (2B_2) structure [see Fig. 1(c), and Tables III and IV]. This local minimum is more stable than BeH_2+H (by 7.2 kcal/mol), but it is less stable than $BeH+H_2$ (by 4.0 kcal/mol, with the ZPE correction). However, both dissociation pathways have barriers: 6.4 kcal/mol [BeH_3 (TS₁)] for BeH_2+H and 3.0 kcal/mol [BeH_3 (TS₂)] for $BeH+H_2$. The geometrical structures of the saddle points (TS₁ and TS₂) for these two reactions are presented on Fig. 1(c). Because there are barriers on the BeH_3 (C_{2v} , 2B_2) dissociation pathways, this neutral mole-

TABLE III. Calculated molecular properties for BeH_3^- and BeH_3 .

$BeH_3^- (D_{3h}, ^1A_1')$	$BeH_3 (C_{2v}, ^2B_2)$	$BeH_3 (TS1, C_s, ^2A')$	$BH_3 (TS2, C_s, ^2A')$	$BeH_3 (C_{2v}, ^2B_1)$	$BeH_3 (D_{3h}, ^2A_1')$
$1a_1'^2 1e'^4$	$1a_1'^2 2a_1'^2 1b_2'$	$1a'^2 2a'^2 3a'^1$	$1a'^2 2a'^2 3a'^1$	$1a_1'^2 2a_1'^2 1b_1'$	$1a_1'^1 1e'^4$
MP2(full)/ 6-311++G** $E_{MP2} = -16.44427$	MP2(full)/ 6-311++G** $E_{MP2} = -16.34702$ $\langle S^2 \rangle = 0.757$	MP2(full)/ 6-311++G** $E_{MP2} = -16.31663$ $\langle S^2 \rangle = 0.758$	MP2(full)/ 6-311++G** $E_{MP2} = -16.34240$ $\langle S^2 \rangle = 0.760$	MP2(full)/ 6-311++G** $E_{MP2} = -16.28919$ $\langle S^2 \rangle = 0.778$	MP2(full)/ 6-311++G** $E_{MP2} = -16.19637$ $\langle S^2 \rangle = 0.766$
$\nu_1(a_1') = 1718 \text{ cm}^{-1}$ $\nu_2(a_2') = 869 \text{ cm}^{-1}$ $\nu_3(e') = 1720 \text{ cm}^{-1}$ $\nu_4(e') = 882 \text{ cm}^{-1}$ ZPE = 11.14 kcal/mol	$\nu_1(a_1) = 2216 \text{ cm}^{-1}$ $\nu_2(a_1) = 1727 \text{ cm}^{-1}$ $\nu_3(a_1) = 881 \text{ cm}^{-1}$ $\nu_4(b_1) = 595 \text{ cm}^{-1}$ $\nu_5(b_2) = 1620 \text{ cm}^{-1}$ $\nu_6(b_2) = 552 \text{ cm}^{-1}$ ZPE = 10.85 kcal/mol	$\nu_1(a') = 2273 \text{ cm}^{-1}$ $\nu_2(a') = 2062 \text{ cm}^{-1}$ $\nu_3(a') = 747 \text{ cm}^{-1}$ $\nu_4(a') = 400 \text{ cm}^{-1}$ $\nu_5(a') = 456i \text{ cm}^{-1}$ $\nu_6(a'') = 70i \text{ cm}^{-1}$ ZPE = 8.84 kcal/mol	$\nu_1(a') = 2237 \text{ cm}^{-1}$ $\nu_2(a') = 1999 \text{ cm}^{-1}$ $\nu_3(a') = 1695 \text{ cm}^{-1}$ $\nu_4(a') = 1070 \text{ cm}^{-1}$ $\nu_5(a') = 705i \text{ cm}^{-1}$ $\nu_6(a'') = 659 \text{ cm}^{-1}$ ZPE = 10.95 kcal/mol	$\nu_1(a_1) = 4251 \text{ cm}^{-1}$ $\nu_2(a_1) = 2239 \text{ cm}^{-1}$ $\nu_3(a_1) = 1041 \text{ cm}^{-1}$ $\nu_4(b_1) = 1772i \text{ cm}^{-1}$ $\nu_5(b_2) = 1309 \text{ cm}^{-1}$ $\nu_6(b_2) = 299 \text{ cm}^{-1}$ ZPE = 13.06 kcal/mol	$\nu_1(a_1') = 1586 \text{ cm}^{-1}$ $\nu_2(a_2') = 819 \text{ cm}^{-1}$ $\nu_3(e') = 1884 \text{ cm}^{-1}$ $\nu_4(e') = 908 \text{ cm}^{-1}$ ZPE = 11.42 kcal/mol
QCISD(T)/6- 311++G(2df,2pd) $E_{SCF} = -16.34705$ $E_{MP2} = -16.44370$ $E_{MP3} = -16.46169$ $E_{MP4} = -16.46667$ $E_{QCISD(T)} = -16.46819$	QCISD(T)/6- 311++G(2df,2pd) $E_{PUSCF} = -16.27134$ $E_{PMP2} = -16.34428$ $E_{PMP3} = -16.35782$ $E_{PMP4} = -16.36205$ $E_{QCISD(T)} = -16.36323$	QCISD(T)/6- 311++G(2df,2pd) $E_{PUSCF} = -16.26673$ $E_{PMP2} = -16.33165$ $E_{PMP3} = -16.34425$ $E_{PMP4} = -16.34812$ $E_{QCISD(T)} = -16.34988$	QCISD(T)/6- 311++G(2df,2pd) $E_{PUSCF} = -16.26436$ $E_{PMP2} = -16.33964$ $E_{PMP3} = -16.35335$ $E_{PMP4} = -16.35748$ $E_{QCISD(T)} = -16.35856$	QCISD(T)/6- 311++G(2df,2pd) $E_{PUSCF} = -16.21585$ $E_{PMP2} = -16.28932$ $E_{PMP3} = -16.30306$ $E_{PMP4} = -16.30733$ $E_{QCISD(T)} = -16.30837$	QCISD(T)/6- 311++G(2df,2pd) $E_{PUSCF} = -16.10804$ $E_{PMP2} = -16.19339$ $E_{PMP3} = -16.21217$ $E_{PMP4} = -16.22003$ $E_{QCISD(T)} = -16.22591$

cule may be observable as a temporarily stable species. The adiabatic IP (2E) of BeH_3^- calculated with respect to the C_{2v} (2B_2) structure is 2.86 eV.

Electron detachment from the second valence $1a_1$ -MO of BeH_3^- leads to a $^2A_1'$ (D_{3h}) state. This state of BeH_3 is geometrically stable (all frequencies are positive), and its optimized geometry is very close to that of BeH_3^- . Therefore, in this case there is little difference between the vertical IP (6.63 eV) and the adiabatic IP (6.59 eV) for BeH_3^- . Again, a large Franck-Condon factor is expected for this ionization process. However, this state of BeH_3 is highly thermodynamically unstable; its dissociation energies are -90.7 kcal/mol ($BeH + H_2$) and -79.5 kcal/mol ($BeH_2 + H$).

The D_{3h} (2E) structure of MgH_3 , at the anion geometry, is even more thermodynamically unstable than in

BeH_3 . This structure lies above the dissociation products $MgH + H_2$ by 50.0 kcal/mol, and above $Mg + H_2 + H$ by 18.1 kcal/mol. Again distortion of this structure to C_{2v} symmetry for the 2A_1 electronic state leads directly to dissociation products. However, C_{2v} optimization of the 2B_2 electronic state leads to a local minimum [see Fig. 1(d) and Table IV] that is not thermodynamically stable with respect to the dissociation asymptote $MgH + H_2$ ($\Delta E = -28.0$ kcal/mol), but is thermodynamically stable with respect to $MgH_2 + H$ ($\Delta E = +8.3$ kcal/mol). Because only small barriers are encountered on both dissociation pathways (1.0 kcal/mol and 5.5 kcal/mol, respectively), the C_{2v} (2B_2) structure of MgH_3 may not exist even as a temporarily stable species. The adiabatic IP (2E) of MgH_3^- calculated with respect to MgH_3 ($C_{2v}, ^2B_2$) is 2.89 eV. The detachment of an electron from the $1a_1$ -MO of MgH_3^-

TABLE IV. Calculated molecular properties for MgH_3^- and MgH_3 .

$MgH_3^- (D_{3h}, ^1A_1')$	$MgH_3 (C_{2v}, ^2B_2)$	$MgH_3 (TS1, C_s, ^2A')$	$MgH_3 (D_{3h}, ^2A_1')$
$1a_1'^2 1e'^4$	$1a_1'^2 2a_1'^2 1b_2'$	$1a'^2 2a'^2 3a'^1$	$1a_1'^1 1e'^4$
MP2(full)/6-311++G** $E_{MP2} = -201.51018$	MP2(full)/6-311++G** $E_{MP2} = -201.41177$ $\langle S^2 \rangle = 0.756$	MP2(full)/6-311++G** $E_{MP2} = -201.41209$ $\langle S^2 \rangle = 0.759$	MP2(full)/6-311++G** $E_{MP2} = -201.29053$ $\langle S^2 \rangle = 0.777$
$\nu_1(a_1') = 1392 \text{ cm}^{-1}$ $\nu_2(a_2') = 581 \text{ cm}^{-1}$ $\nu_3(e') = 1311 \text{ cm}^{-1}$ $\nu_4(e') = 613 \text{ cm}^{-1}$ ZPE = 8.32 kcal/mol	$\nu_1(a_1) = 1691 \text{ cm}^{-1}$ $\nu_2(a_1) = 1318 \text{ cm}^{-1}$ $\nu_3(a_1) = 188 \text{ cm}^{-1}$ $\nu_4(b_1) = 381 \text{ cm}^{-1}$ $\nu_5(b_2) = 1214 \text{ cm}^{-1}$ $\nu_6(b_2) = 322 \text{ cm}^{-1}$ ZPE = 7.31 kcal/mol	$\nu_1(a') = 1705 \text{ cm}^{-1}$ $\nu_2(a') = 1491 \text{ cm}^{-1}$ $\nu_3(a') = 1258 \text{ cm}^{-1}$ $\nu_4(a') = 792 \text{ cm}^{-1}$ $\nu_5(a') = 410i \text{ cm}^{-1}$ $\nu_6(a'') = 344 \text{ cm}^{-1}$ ZPE = 7.99 kcal/mol	$\nu_1(a_1') = 1298 \text{ cm}^{-1}$ $\nu_2(a_2') = 481 \text{ cm}^{-1}$ $\nu_3(e') = 1435 \text{ cm}^{-1}$ $\nu_4(e') = 581 \text{ cm}^{-1}$ ZPE = 8.31 kcal/mol
QCISD(T)/6-311++G(2df,2pd) $E_{SCF} = -201.31296$ $E_{MP2} = -201.39950$ $E_{MP3} = -201.41749$ $E_{MP4} = -201.42279$ $E_{QCISD(T)} = -201.42476$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -201.23102$ $E_{PMP2} = -201.29914$ $E_{PMP3} = -201.31266$ $E_{PMP4} = -201.31712$ $E_{QCISD(T)} = -201.31864$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -201.22823$ $E_{PMP2} = -201.29875$ $E_{PMP3} = -201.31239$ $E_{PMP4} = -201.31691$ $E_{QCISD(T)} = -201.31817$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -201.10263$ $E_{PMP2} = -201.17858$ $E_{PMP3} = -201.19688$ $E_{PMP4} = -201.20517$ $E_{QCISD(T)} = -201.21250$

TABLE V. Calculated molecular properties for BH_4^- and BH_4 .

$BH_4^- (T_d, ^1A_1)$	$BH_4 (C_{2v}, ^2B_2)$	$BH_4 (C_s, ^2A')$	$BH_4 (T_d, ^2A'_1)$
$1a_1^2 1t_2^6$	$1a_1^2 2a_1^2 1b_2^1$	$1a'^2 2a'^2 1a''^2 3a'^1$	$1a_1^2 1t_2^6$
MP2(full)/6-311++G** $E_{MP2} = -27.14513$	MP2(full)/6-311++G** $E_{MP2} = -27.03625$ $\langle S^2 \rangle = 0.756$	MP2(full)/6-311++G** $E_{MP2} = -27.02062$ $\langle S^2 \rangle = 0.765$	MP2(full)/6-311++G** $E_{MP2} = -26.74991$ $\langle S^2 \rangle = 0.772$
$\nu_1(a_1) = 2312 \text{ cm}^{-1}$ $\nu_2(e) = 1219 \text{ cm}^{-1}$ $\nu_3(t_2) = 2314 \text{ cm}^{-1}$ $\nu_4(t_2) = 1124 \text{ cm}^{-1}$ ZPE = 21.53 kcal/mol	$\nu_1(a_1) = 2686 \text{ cm}^{-1}$ $\nu_2(a_1) = 2219 \text{ cm}^{-1}$ $\nu_3(a_1) = 1429 \text{ cm}^{-1}$ $\nu_4(a_1) = 1028 \text{ cm}^{-1}$ $\nu_5(a_2) = 870 \text{ cm}^{-1}$ $\nu_6(b_1) = 2809 \text{ cm}^{-1}$ $\nu_7(b_1) = 1078 \text{ cm}^{-1}$ $\nu_8(b_2) = 2098 \text{ cm}^{-1}$ $\nu_9(b_2) = 742 \text{ cm}^{-1}$ ZPE = 21.38 kcal/mol	$\nu_1(a') = 2720 \text{ cm}^{-1}$ $\nu_2(a') = 2425 \text{ cm}^{-1}$ $\nu_3(a') = 1933 \text{ cm}^{-1}$ $\nu_4(a') = 1082 \text{ cm}^{-1}$ $\nu_5(a') = 981 \text{ cm}^{-1}$ $\nu_6(a') = 741 \text{ cm}^{-1}$ $\nu_7(a'') = 2547 \text{ cm}^{-1}$ $\nu_8(a'') = 1180 \text{ cm}^{-1}$ $\nu_9(a'') = 1102i \text{ cm}^{-1}$ ZPE = 19.45 kcal/mol	$\nu_1(a_1) = 2096 \text{ cm}^{-1}$ $\nu_2(e) = 1247 \text{ cm}^{-1}$ $\nu_3(t_2) = 2352 \text{ cm}^{-1}$ $\nu_4(t_2) = 1157 \text{ cm}^{-1}$ ZPE = 21.61 kcal/mol
QCISD(T)/6-311++G(2df,2pd) $E_{SCF} = -26.98661$ $E_{MP2} = -27.15285$ $E_{MP3} = -27.17423$ $E_{MP4} = -27.18166$ $E_{QCISD(T)} = -27.18280$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -26.90610$ $E_{PMP2} = -27.04166$ $E_{PMP3} = -27.06104$ $E_{PMP4} = -27.06710$ $E_{QCISD(T)} = -27.06812$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -26.89182$ $E_{PMP2} = -27.02705$ $E_{PMP3} = -27.04637$ $E_{PMP4} = -27.05305$ $E_{QCISD(T)} = -27.05462$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -26.58836$ $E_{PMP2} = -26.75569$ $E_{PMP3} = -26.78408$ $E_{PMP4} = -26.79845$ $E_{QCISD(T)} = -26.80638$

leads to a $D_{3h} (^2A_1)$ electronic state, which does not distort the structure from its planar triangular symmetry. The calculated vertical and adiabatic IPs (2A_1) of MgH_3^- are 5.82 and 5.78 eV, respectively.

BH_4^- , BH_4 , AlH_4^- , and AlH_4 . Both of these anions have right tetrahedral $T_d (^1A_1)$ structures with $1a_1^2 1t_2^6$ electronic configurations.³

According to our highest level correlated calculations, both anions are very stable thermodynamically, geometrically, and electronically [see Fig. 1(e), and Tables V and VI]. The calculated dissociation energies of BH_4^- into $BH_2^- + H_2$, and into $BH_3 + H^-$ are +87.2 kcal/mol and +74.1 kcal/mol, respectively. The dissociation energies of

AlH_4^- into $AlH_2^- + H_2$ and into $AlH_3 + H^-$ are +69.2 kcal/mol and +76.2 kcal/mol (all with the ZPE correction). The vertical IPs (2T_2) for both anions are very high: 4.62 eV (BH_4^-) and 4.83 eV (AlH_4^-) which agrees well with the previous Green function calculations 4.54 eV (BH_4^-) and 4.75 eV (AlH_4^-).⁷ The second vertical IPs (2A_1) are much higher in energy: 10.36 eV (BH_4^-) and 8.64 eV (AlH_4^-).

The detachment of an extra electron from the $1t_2$ -HOMO for either BH_4^- or AlH_4^- leads to Jahn-Teller distortion. This question has been very carefully studied in the literature for BH_4 (Ref. 19) and several valence isoelectronic species such as CH_4^+ , SiH_4^+ , and others.²⁰

TABLE VI. Calculated molecular properties for AlH_4^- and AlH_4 .

$AlH_4^- (T_d, ^1A_1)$	$AlH_4 (C_{2v}, ^2B_2)$	$AlH_4 (T_d, ^2A'_1)$
$1a_1^2 1t_2^6$	$1a_1^2 2a_1^2 1b_2^1$	$1a_1^2 1t_2^6$
MP2(full)/6-311++G** $E_{MP2} = -244.47360$	MP2(full)/6-311++G** $E_{MP2} = -244.35493$ $\langle S^2 \rangle = 0.760$	MP2(full)/6-311++G** $E_{MP2} = -244.14348$ $\langle S^2 \rangle = 0.766$
$\nu_1(a_1) = 1806 \text{ cm}^{-1}$ $\nu_2(e) = 780 \text{ cm}^{-1}$ $\nu_3(t_2) = 1717 \text{ cm}^{-1}$ $\nu_4(t_2) = 822 \text{ cm}^{-1}$ ZPE = 15.70 kcal/mol	$\nu_1(a_1) = 2492 \text{ cm}^{-1}$ $\nu_2(a_1) = 2071 \text{ cm}^{-1}$ $\nu_3(a_1) = 1069 \text{ cm}^{-1}$ $\nu_4(a_1) = 589 \text{ cm}^{-1}$ $\nu_5(a_2) = 911 \text{ cm}^{-1}$ $\nu_6(b_1) = 2111 \text{ cm}^{-1}$ $\nu_7(b_1) = 603 \text{ cm}^{-1}$ $\nu_8(b_2) = 1544 \text{ cm}^{-1}$ $\nu_9(b_2) = 473i \text{ cm}^{-1}$ ZPE = 16.28 kcal/mol	$\nu_1(a_1) = 1673 \text{ cm}^{-1}$ $\nu_2(e) = 768 \text{ cm}^{-1}$ $\nu_3(t_2) = 1823 \text{ cm}^{-1}$ $\nu_4(t_2) = 787 \text{ cm}^{-1}$ ZPE = 15.78 kcal/mol
QCISD(T)/6-311++G(2df,2pd) $E_{SCF} = -244.24547$ $E_{MP2} = -244.37431$ $E_{MP3} = -244.39855$ $E_{MP4} = -244.40537$ $E_{QCISD(T)} = -244.40754$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -243.91702$ $E_{PMP2} = -244.04278$ $E_{PMP3} = -244.07118$ $E_{PMP4} = -244.08339$ $E_{QCISD(T)} = -244.09293$	QCISD(T)/6-311++G(2df,2pd) $E_{PUSCF} = -243.91702$ $E_{PMP2} = -244.04278$ $E_{PMP3} = -244.07118$ $E_{PMP4} = -244.08339$ $E_{QCISD(T)} = -244.09293$

The potential energy surface of the BH_4 molecule has been studied at the MP2/6-31** level by Paddon-Row and Wong.^{19(c)} The C_{2v} (2B_2) structure [Fig. 1(c)] was found to be the global minimum on the potential energy surface. The C_s ($^2A'$) structure [Fig. 1(e)] is a saddle point on the flexible intramolecular rearrangement from one global-minimum structure C_{2v} (2B_2) into another C_{2v} (2B_2). BH_4 has 12 global minima (C_{2v} , 2B_2) and 24 saddle points (C_s , $^2A'$) on this potential energy surface. The BH_4 (C_{2v} , 2B_2) structure has been found to be thermodynamically stable both with respect to BH_3+H (+12.9 kcal/mol) and BH_2+H_2 (+14.8 kcal/mol, both at UMP4/6-31G(d,f,p)//UMP2/6-31G**+ZPE) dissociations asymptotes.

We optimized geometries of BH_4 for the C_{2v} (2B_2) and C_s ($^2A'$) structures. The first structure is indeed a minimum, and the second is a saddle point on the intramolecular rearrangement with a barrier of 6.54 kcal/mol. BH_4 is thermodynamically stable with respect to dissociation into BH_3+H (+15.0 kcal/mol) and into BH_2+H_2 (+15.5 kcal/mol, all with the ZPE correction). This neutral species has been observed experimentally in ESR (electron spin resonance) spectroscopic studies.^{19(a),19(b)} The BH_4 radical has been generated by radiolysis of a powdered sample of $NaBH_4$ at 77 K. The observed ESR spectrum revealed a very large isotropic hyperfine coupling constant of 107 G^{19(a),19(b)} and is consistent with a C_{2v} structure for BH_4 . The adiabatic IP (2T_2) of BH_4^- with a final C_{2v} (2B_2) structure for BH_4 is 3.12 eV. The adiabatic correction to the IP (2T_2) reduces from 4.62 eV (Vertical IP) to 3.12 eV (adiabatic IP). However, even the adiabatic IP (2T_2) of BH_4^- is very high if we take into account that the boron and hydrogen anions have low electron detachment energies (0.277 eV and 0.754 eV,⁸ respectively).

The detachment of an extra electron from the $1a_1$ -MO of BH_4^- leads to a T_d (2A_1) electronic state which, therefore, does not distort the structure from the its tetrahedral symmetry. The optimized $R(B-H)=1.290$ Å bond length for this BH_4 (T_d , 2A_1) state is longer than that $R(B-H)=1.236$ Å in BH_4^- . This elongation is expected because the electron was removed from a bonding $1a_1$ -MO. The calculated vertical and adiabatic IPs (2A_1) of BH_4^- are 10.36 and 10.24 eV, respectively.

The removal of an extra electron from the $1t_2$ -HOMO of AlH_4^- leads to a 2T_2 (T_d) electronic state that is not geometrically stable with respect to Jahn-Teller distortion. The energy of AlH_4 (T_d , 2T_2) at the equilibrium geometry of the anion is higher in energy than the dissociation asymptotes AlH_3+H (18.9 kcal/mol) and AlH_2+H_2 (39.8 kcal/mol). We optimized the geometry for the C_{2v} (2B_2) structure [Fig. 1(f)], which was a global minimum for BH_4 . However, this structure for AlH_4 has one imaginary frequency (see Table VI) whose normal mode vector leads to a C_s structure. Further optimization of AlH_4 within C_s symmetry leads directly to dissociation into AlH_2+H_2 . Therefore, the C_{2v} (2B_2) structure is not even a local minimum for AlH_4 .

Another low lying C_{3v} (2A_1) structure for AlH_4 has also been examined. However, optimization in C_{3v} (2A_1)

symmetry leads to dissociation into AlH_3+H . Therefore, no local minimum structure for neutral AlH_4 has been found. The adiabatic IP (2T_2) for AlH_4^- calculated relative to AlH_2+H_2 is 3.11 eV. The adiabatic correction to the vertical IP (2T_2) of AlH_4^- is 1.73 eV. Detachment of an extra electron from the $1a_1$ -MO of AlH_4^- leads to a 2A_1 (T_d) electronic state, which also does not distort from the tetrahedral structure. The optimized AlH_4 (2A_1 , T_d) structure has no imaginary frequencies (see Table VI) and its bond length $Al-H$ is 0.05 Å longer than in the anion where the bonding $1a_1$ -MO is doubly occupied. The adiabatic geometric correction to the vertical IP (2A_1) of AlH_4^- is only 0.08 eV.

SiH₅⁻ and SiH₅. The SiH_5^- anion is a local minimum at a trigonal-bipyramidal D_{3h} ($^1A'_1$) structure according to numerous *ab initio* calculations.⁴ However, the isoelectronic CH_5^- anion is a transition state at the trigonal-bipyramidal structure.⁵ The explanation of the difference in these geometric stabilities have been proposed in Refs. 4(h)-4(j). We will not consider CH_5^- here because this is not a geometrically stable species.

SiH_5^- (D_{3h} , $^1A'_1$) is thermodynamically stable with respect to dissociation into SiH_4+H^- (+15.95 kcal/mol), but unstable with respect to dissociation into $SiH_3^-+H_2$ (-11.31 kcal/mol, all at MP4/6-31++G**+ZPE).^{4(c)} While the barrier for dissociation into $SiH_3^-+H_2$ was not found in the study by Reed and Schleyer,^{4(e)} this barrier must be significant in view of the experimental observation of SiH_5^- by Hajdasz and Squires.^{6(b)} This anion is also electronically stable with respect to loss of its extra electron.^{4(j),7} The neutral SiH_5 (D_{3h} , $^2A'_1$) is not a minimum where this structure has one imaginary frequency at the ROHF/6-31++G**,^{4(j),21} level and three at the UHF/6-31++G** level.^{4(j)}

We repeated optimization of SiH_5^- (D_{3h} , $^1A'_1$) at the MP2(full)/6-311++G** level and found that this structure is a local minimum [see Table VII, and Fig. 1(g)]. Our dissociation energies for this anion relative to SiH_4+H^- and $SiH_3^-+H_2$ are +21.8 kcal/mol and -7.5 kcal/mol (all with the ZPE correction), respectively. The electronic configuration of SiH_5^- (D_{3h} , $^1A'_1$) is $1a_1'^2 1e'^4 1a_2''^2 2a_1'^2$, so four different states ($^2A'_1$ ($1a_1'^2 1e'^4 1a_2''^2 2a_1'^1$); $^2A_2''$ ($1a_1'^2 1e'^4 1a_2''^1 2a_1'^2$); $^2E'$ ($1a_1'^2 1e'^3 1a_2''^2 2a_1'^2$); and $^2A'_1$ ($1a_1'^1 1a_2''^2 1e'^4 2a_1'^2$)) may be obtained in the vertical detachment of an extra electron. At the Koopmans' approximation, the vertical IPs are: 2.56 eV ($^2A'_1$); 6.91 eV ($^2A_2''$); 7.26 eV ($^2E'$); and 13.62 eV ($^2A'_1$). We calculate the first two IPs at a correlated level, and at our highest level, these values are 2.19 eV ($^2A'_1$) and 5.98 eV ($^2A_2''$). Our vertical IP from the $2a_1'$ -HOMO agrees well with a Green function calculation 2.02 eV.⁷

Our optimized SiH_5 (D_{3h} , $^2A'_1$) structure has one imaginary frequency $\nu_4(a_2'') = 735i$ at the MP2(full)/6-311++G** level, and therefore, is not geometrically stable. This structure is also higher than the dissociation products SiH_4+H by 12.5 kcal/mol and higher than SiH_3+H_2 by 25.6 kcal/mol. Optimization of this structure within C_{3v} (2A_1) symmetry leads to SiH_4+H without a barrier. The adiabatic IP ($^2A'_1$) of SiH_5^- should be calculated with re-

TABLE VII. Calculated molecular properties for SiH_5^- and SiH_5 .

$SiH_5^- (D_{3h}, ^1A_1')$	$SiH_5 (D_{3h}, ^2A_2'')$	$SiH_5 (D_{3h}, ^2A_1')$
$1a_1'^2 1e'^4 1a_2''^2 2a_1'^2$	$1a_1'^2 1e'^4 1a_2''^1 2a_1'^2$	$1a_1'^2 1e'^4 1a_2''^2 2a_1'^1$
MP2(full)/6-311++G**	MP2(full)/6-311++G**	MP2(full)/6-311++G**
$E_{MP2} = -292.03684$	$E_{MP2} = -291.82965$	$E_{MP2} = -291.96305$
	$\langle S^2 \rangle = 0.787$	$\langle S^2 \rangle = 0.800$
$\nu_1(a_1') = 2060 \text{ cm}^{-1}$	$\nu_1(a_1') = 2283 \text{ cm}^{-1}$	$\nu_1(a_1') = 2219 \text{ cm}^{-1}$
$\nu_2(a_1') = 1453 \text{ cm}^{-1}$	$\nu_2(a_1') = 1093 \text{ cm}^{-1}$	$\nu_2(a_1') = 1617 \text{ cm}^{-1}$
$\nu_3(a_2'') = 1607 \text{ cm}^{-1}$	$\nu_3(a_2'') = 1427 \text{ cm}^{-1}$	$\nu_3(a_2'') = 1579 \text{ cm}^{-1}$
$\nu_4(a_2'') = 1040 \text{ cm}^{-1}$	$\nu_4(a_2'') = 1040 \text{ cm}^{-1}$	$\nu_4(a_2'') = 735i \text{ cm}^{-1}$
$\nu_5(e') = 2027 \text{ cm}^{-1}$	$\nu_5(e') = 2347 \text{ cm}^{-1}$	$\nu_5(e') = 2258 \text{ cm}^{-1}$
$\nu_6(e') = 1079 \text{ cm}^{-1}$	$\nu_6(e') = 893 \text{ cm}^{-1}$	$\nu_6(e') = 863 \text{ cm}^{-1}$
$\nu_7(e') = 557 \text{ cm}^{-1}$	$\nu_7(e') = 663 \text{ cm}^{-1}$	$\nu_7(e') = 112 \text{ cm}^{-1}$
$\nu_8(e'') = 1244 \text{ cm}^{-1}$	$\nu_8(e'') = 603 \text{ cm}^{-1}$	$\nu_8(e'') = 987 \text{ cm}^{-1}$
ZPE = 22.81 kcal/mol	ZPE = 21.24 kcal/mol	ZPE = 19.81 kcal/mol
QCISD(T)/	QCISD(T)/	QCISD(T)/
6-311++G(2df,2pd)	6-311++G(2df,2pd)	6-311++G(2df,2pd)
$E_{SCF} = -291.76905$	$E_{PUSCF} = -291.57559$	$E_{PUSCF} = -291.71696$
$E_{MP2} = -291.95273$	$E_{PMP2} = -291.74445$	$E_{PMP2} = -291.87821$
$E_{MP3} = -291.98249$	$E_{PMP3} = -291.77464$	$E_{PMP3} = -291.90396$
$E_{MP4} = -291.99121$	$E_{PMP4} = -291.78742$	$E_{PMP4} = -291.91312$
$E_{QCISD(T)} = -291.99348$	$E_{QCISD(T)} = -291.79502$	$E_{QCISD(T)} = -291.91373$

spect to $SiH_4 + H$ which gives a value of 1.60 eV. However, the optimized $SiH_5 (D_{3h}, ^2A_2'')$ structure is a local minimum (see Table VII), whose axial Si-H_a bonds are elongated by 0.255 Å and with Si-H_e bonds shorter by 0.051 Å. The adiabatic IP ($^2A_2''$) of SiH_5^- is 5.40 eV.

IV. OVERVIEW

All of the anions studied here (LiH_2^- , BeH_3^- , MgH_3^- , BH_4^- , AlH_4^- , and SiH_5^-) except NaH_2^- are very stable to loss of the extra electron. Their vertical detachment ener-

TABLE VIII. Calculated vertical (IP_v) and adiabatic (IP_a) ionization potentials (in eV) of MH_{k+1}^- anions.

Anion	Koopmans	PUSCF	PMP2	PMP3	PMP4	QCISD(T)	ADC(3) ^a
LiH_2^- IP _v ($D_{\infty h}, ^2\Sigma_u^+$)	3.48	2.04	2.86	3.05	3.04	3.06	2.95
IP _a ($Li + H_2$)		-0.15	0.48	0.65	0.71	0.74	
IP _v ($D_{\infty h}, ^2\Sigma_g^+$)	3.71	2.75	3.32	3.44	3.42	3.35	
IP _a ($D_{\infty h}, ^2\Sigma_g^+$)		2.76	3.32	3.44	3.42	3.36	
NaH_2^- IP _v ($D_{\infty h}, ^2\Sigma_u^+$)	3.12	1.52	2.41	2.63	2.68	2.63	2.53
IP _a ($Na + H_2$)		-0.99	-0.40	-0.22	-0.16	-0.12	
IP _v ($D_{\infty h}, ^2\Sigma_g^+$)	3.68	2.63	3.23	3.37	3.34	3.22	
IP _a ($D_{\infty h}, ^2\Sigma_g^+$)		2.62	3.22	3.36	3.33	3.21	
BeH_3^- IP _v ($D_{3h}, ^2E'$)	4.42	3.12	3.89	4.02	4.02	3.97	3.86
IP _a ($C_{2v}, ^2B_2$)		2.06	2.71	2.83	2.85	2.86	
IP _v ($D_{3h}, ^2A_1'$)	7.36	6.54	6.83	6.82	6.74	6.63	
IP _a ($D_{3h}, ^2A_1'$)		6.50	6.81	6.79	6.71	6.59	
MgH_3^- IP _v ($D_{3h}, ^2E'$)	4.33	2.88	3.66	3.83	3.82	3.84	3.74
IP _a ($C_{2v}, ^2B_2$)		2.23	2.73	2.85	2.88	2.89	
IP _v ($D_{3h}, ^2A_1'$)	6.40	5.75	6.04	6.03	5.96	5.82	
IP _a ($D_{3h}, ^2A_1'$)		5.72	6.01	6.00	5.92	5.78	
BH_4^- IP _v ($T_d, ^2T_2$)	5.19	3.60	4.54	4.60	4.61	4.62	4.54
IP _a ($C_{2v}, ^2B_2$)		2.19	3.03	3.08	3.12	3.12	
IP _v ($T_d, ^2A_1$)	12.28	10.98	10.90	10.72	10.54	10.36	
IP _a ($T_d, ^2A_1$)		10.84	10.81	10.62	10.43	10.24	
AlH_4^- IP _v ($T_d, ^2T_2$)	5.40	4.01	4.76	4.88	4.88	4.83	4.75
IP _a ($AlH_3 + H_2$)		2.15	2.96	3.09	3.12	3.11	
IP _v ($T_d, ^2A_1$)	9.75	9.02	9.09	8.98	8.84	8.64	
IP _a ($T_d, ^2A_1$)		8.94	9.02	8.91	8.76	8.56	
SiH_5^- IP _v ($D_{3h}, ^2A_1'$)	2.56	1.44	2.06	2.16	2.15	2.19	2.02
IP _a ($SiH_3 + H_2$)		-0.08	0.92	1.01	1.04	1.03	
IP _v ($D_{3h}, ^2A_2''$)	6.91	5.76	6.09	6.10	6.03	5.98	
IP _a ($D_{3h}, ^2A_2''$)		5.26	5.67	5.66	5.55	5.40	

^aData from Ref. 7.

gies are higher than the electron detachment energies of corresponding atomic anions H^- , Li^- , Na^- , B^- , Al^- , and Si^- (Be^- and Mg^- are not electronically stable). The BeH_3^- , MgH_3^- , BH_4^- , and AlH_4^- anions have even higher electron detachment energies than halogen atoms F^- (3.401 eV⁸) and Cl^- (3.613 eV⁸). The origin of the high electronic stability of these anions has been discussed by Boldyrev and Niessen,⁷ and is thought to be because the extra electron in such MH_{k+1}^- anions fill a bonding HOMO that is delocalized through $(k+1)$ hydrogen atoms centers. Again, except for NaH_2^- , all of these anions are also *geometrically stable*, (e.g., they have all positive frequencies at high symmetry structures). Except for NaH_2^- and SiH_5^- , all of the anions studied here are stable thermodynamically to all possible dissociation asymptotes. However, only SiH_5^- anion has been observed experimentally.⁶ We therefore believe that all of these anions should be species that may be studied experimentally. Moreover, these anions have very high electron detachment energies.

For the first vertical IPs of the MH_{k+1}^- anions studied in this work, we obtained very good agreement with results of previous Green function method calculations.⁷ In this work, we used indirect methods in which the IP is calculated as a difference between the total energies of the anion MH_{k+1}^- and the neutral MH_{k+1} at the geometry of anion. This approach has certain disadvantages. First, in these calculations, we use the same basis set for both species even though this basis will not be the same quality for neutral and anionic systems. Second, in correlated calculations on the open-shell neutrals, we used the unrestricted Hartree-Fock reference function, which is known to have spin contamination. If instead, we use the spin-projected energies for the neutral, our energy is not SCF-converged. Finally, the energy convergence in the MP2-MP3-MP4 series may be slow. Because of these potential weaknesses, comparison of our IPs with results from direct Green function methods, where the IP is calculated as a correction to an orbital energy, is very important, especially when studying previously unknown molecules.

Several important consequences follow from Table VIII. First, vertical IPs (or vertical EDEs) from the HOMOs of all MH_{k+1}^- anions do not vary strongly within the MP2-MP3-MP4 series (the variation is ca. 0.2 eV). The PMP4 first IPs are close to the QCISD(T) IPs (the variation is less than 0.05 eV) and to Green function [ADC(3)] IPs (variation is 0.1 eV, except for SiH_5^- , where the discrepancy is 0.17 eV). Because of the good agreement between indirectly and directly calculated vertical IPs, and because two large yet distinct basis sets have been used in these calculations, we believe that our values are correct to within 0.2 eV.

While the LiH_2 , NaH_2 , BeH_3 , MgH_3 , and BH_4 neutral species have local minima at C_{2v} (2B_2) structures, only BH_4 is a thermodynamically stable species at this C_{2v} (2B_2) structure; for this species, experimental study of its photoelectron spectrum may give structural and vibrational information. However, because BH_4^- and BH_4 have very different geometries, the pertinent Frank-Condon factors will be rather small. When the extra electron is re-

moved from the MO lying just below the HOMO, all of the neutral MH_{k+1} species studied here have local minima at the symmetry of the anion and with bond lengths close to the respective anions. The Frank-Condon factor, in this case, should be rather large, and transitions will be easier to measure to obtain structural and vibrational information.

Note added in proof. Dr. R. P. Saxon of SRI International has provided us with information²² on the BH_4 molecule that relates to results reported here.

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