Molecular Orbital Theory of the Electronic Structure of Molecules. 29. The Interaction of H_2 with Simple Lewis Acids

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Abstract: Ab initio molecular orbital theory is used to study the interaction of the weak Lewis base, H_2, with simple Lewis acids, H^+, Li^+, BeH^+, BH_2^+, CH_3^+, LiH, BeH_2, and BH_3. Geometry determinations are made by variation of all symmetry-independent degrees of freedom using both minimal (STO-3G) and extended (4-31G) basis sets. The influence of polarization functions and electron correlation is calculated using geometries determined with the extended basis. The most extensive calculation gives binding energies to H_2 of 104.5 kcal for H^+ and 43.2 kcal for CH_3^+ in close agreement with experiment. Li^+, BeH^+, BH_2^+, LiH, and BH_3 are predicted to have binding energies of 4.5, 21.3, 3.9, 2.0, and 1.7 kcal, respectively. BeH_2 does not form a bound complex.

The simplest molecule that can function as an electron pair donor or Lewis base is H_2. Interaction with a vacant orbital will lead to a three-center, two-electron, donor-acceptor bond. The archetypal example is H_3^+ ($H^+ \cdot H_2$) first observed in 1911 by passing charged species through orthogonal electric and magnetic fields[2] and recently implicated as an intermediate in super acid media.[3] LiH_2^+ ($Li^+ \cdot H_2$)[4] and BeH_3^+ ($HBe^+ \cdot H_2$)[5] have been detected by mass spectrometry. CH_5^+ ($CH_3^+ \cdot H_2$) is known in the gas phase[6] and has also been suggested to be involved in reactions in superacids.[7] Furthermore, the intermediacy of BH_5 ($BH_3 \cdot H_2$) has been claimed on the basis of isotopic scrambling on deuterolysis of BH_4^-.[8,9]

In order to begin a systematic investigation of such interactions, we have carried out ab initio molecular orbital studies of complexes of H_2 with the simple Lewis acids H^+, Li^+, LiH, BeH^+, BeH_2, BH_2, BH_3, and CH_3^+. Some of the resulting species have been the subject of previous theoretical work, H_3^+,[10] LiH_2^+,[11] BeH_3^+,[12] CH_5^+[13] BH_5.[13f] Our approach has been to use several levels of sophistication in a uniform manner, including the simple technique of correlation energy estimation suggested by Moller and Plesset.[14] We have chosen to examine isoelectronic pairs of Lewis acids, one positively charged and one neutral. This allows some distinction between charge transfer effects involving vacant orbitals and polarizability attraction due to ionic charge. In addition we compare the calculated equilibrium structures for AH_4 hydrides having six valence electrons (BeH_4, BH_4^+, and CH_4^{2+}) with the square planar geometries which have been proposed to be the most favorable arrangements on the basis of Walsh diagrams or similar qualitative arguments.[15]

Methods and Results

Calculations were performed at several levels of approximation. In the first, geometries of all species were optimized (subject only to imposed symmetry constraints) according to procedures previously described[16] using the unrestricted Hartree-Fock (UHF) UHF/STO-3G procedure of Hehre et al.[17] At the second level, single point calculations were carried out at the geometry determined in the first step using the "split-valence" 4-31G basis.[18] Next, geometries were reoptimized using the UHF/4-31G method. Single point calculations on these structures were then carried out using both the 6-31G* basis set,[18c,19] which contains d-type polarization functions on heavy atoms, and the 6-31G** basis, which is identical with 6-31G* plus p functions on hydrogen. Finally, unrestricted Moller-Plesset (UMP) second-order perturbation theory[14] was applied to the UHF/6-31G* and UHF/6-31G** wave functions to obtain an estimate of the correlation energy. These results are designated UMP2/6-31G* and UMP2/6-31G**, respectively.

A complete set of structures is given in Tables I and II; the corresponding total energies are given in Table III. Data for H_2,[20] CH_3^+,[20] and CH_5^+[13d] have been taken, in part, from previous papers.

Reference Molecules

H_2. The UHF/6-31G** energy lies 0.00231 hartree above the Hartree-Fock limit while the UMP2/6-31G** result is 0.01680 hartree above the nonrelativistic limit.[21] The UMP2/6-31G** method gives 65% of the correlation energy.

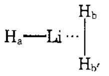
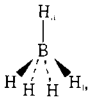
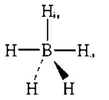
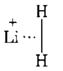
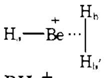
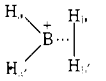
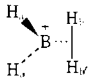
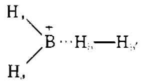
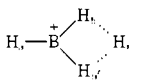
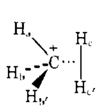
Li^+. The UHG/6-31G* energy is 0.00087 hartree above the Hartree-Fock limit while the UMP2/6-31G* result is 0.04345 hartree above the nonrelativistic limit.[22] The UMP2/6-31G* method gives 4% of the correlation energy.

LiH. The calculated bond length for LiH is short at the UHF/STO-3G level (R = 1.510 vs. 1.595 Å (exp)[23]). The error is reduced at the UHF/4-31G level but is of the opposite sign (r = 1.637 Å). Cade and Huo[24] calculate a bond length of 1.605 Å at the Hartree-Fock limit and find a total energy which is 0.00598 hartree lower than that found with the UHF/6-31G** procedure. Bender and Davidson[25] find a total energy, including electron correlation, of −8.06062 hartrees which is 0.05845 lower than that found by the UMP2/6-31G** method. Thus, about 28% of the correlation energy is obtained using the perturbative method with the UHF/6-31G** procedure.

BeH_2. No experimental bond length for BeH_2 is known as this is a polymeric species.[26] The bond lengths calculated with the minimal and extended basis sets bracket that found by Ahlrichs and Kutzelnigg[27] (r = 1.291, 1.369, and 1.344 Å, respectively) who used a more extensive basis. Their total energy is lower by 0.0191 hartree than the UHF/6-31G* result. The UMP2/6-31G* result is higher by 0.0493 hartree than Ahlrich's Independent Electron Pair Approximation (IEPA) calculation corresponding to 56% of the IEPA correlation energy.

BH_3. No bond length for BH_3 is known as dimerization in the gas phase prevents observation of the monomer.[28] The bond lengths calculated with both the minimal and extended basis sets are in agreement with the value determined by Lipscomb[29]

Table I. Calculated Geometries of AH_n Molecules and Ions (Distances in Å, Angles in deg)

Molecule		Symmetry	Parameter	UHF/STO-3G	UHF/4-31G
H_2		$D_{\infty h}$	r(H–H)	0.712	0.730
LiH		$C_{\infty v}$	r(Li–H)	1.510	1.637
BeH_2		$D_{\infty h}$	r(Be–H)	1.291	1.369
BH_3		D_{3h}	r(B–H)	1.160	1.183
BeH^+		$C_{\infty v}$	r(Be–H)	1.323	1.362
BH_2^+		$D_{\infty h}$	r(B–H)	1.187	1.162
CH_3^+		D_{3h}	r(C–H)	1.120	1.076
	I	C_{2v}	r(Li–H_a)	1.510	1.683
			r(Li–(H_2))^a	2.226	2.368
			r(H_b–$H_{b'}$)	0.728	0.732
$H_a{-}Li\cdots H_b{-}H_{b'}$	II	$C_{\infty v}$	r(Li–H_a)	1.510	1.635
			r(Li–H_b)	2.337	2.504
			r(H_b–$H_{b'}$)	0.718	0.729
BeH_4	I	D_{4h}	r(Be–H)	1.288	
	II	T_d	r(Be–H)	1.369	
	IIIa–h	C_{2v}	Table II		
BH_5	Ia–h	C_s	Table II		
	II	C_{4v}	r(B–H_a)	1.141	1.174
			r(B–H_b)	1.185	1.215
			∠H_aBH_b	118.8	120.4
	III	D_{3h}	r(B–H_a)	1.164	1.191
			r(B–H_b)	1.170	1.208
H_3^+		D_{3h}	r(H–H)	0.967	0.845
		C_{2v}	r(Li–(H_2))^a	2.187	2.229
			r(H–H)	0.738	0.736
		C_{2v}	r(Be–H_a)	1.309	1.344
			r(Be–(H_2))^a	1.761	1.714
			r(H_b–$H_{b'}$)	0.778	0.753
BH_4^+	I	D_{4h}	r(B–H)	1.209	1.202
	II	T_d	r(B–H)	1.265	1.299
	IIIa	C_{2v}	r(B–H_a)	1.177	1.161
			r(B–(H_2))^a	1.764	1.982
			r(H_b–$H_{b'}$)	0.761	0.747
			∠$H_aBH_{a'}$	101.7	98.9
	IIIb	C_{2v}	r(B–H_a)	1.180	1.161
			r(B–(H_2))^a	1.952	2.257
			r(H_b–$H_{b'}$)	0.742	0.739
			∠$H_aBH_{a'}$	97.9	93.5
	IIc	C_{2v}	r(B–H_a)	1.183	1.161
			r(B–H_b)	1.932	2.215
			r(H_b–$H_{b'}$)	0.726	0.735
			∠$H_aBH_{a'}$	94.3	92.3
	IV	C_{2v}	r(B–H_a)	1.172	
			r(B–H_b)	1.231	
			r(B–H_c)	1.270	
			∠$H_bBH_{b'}$	131.9	
		C_s	r(C–H_a)	1.106	1.086
			r(C–H_b)	1.098	1.077
			r(C–H_c)	1.370	1.242
			r(C–$H_{c'}$)	1.367	1.241
			r(C–(H_2))^a	1.298	1.166
			∠$H_bCH_{b'}$	117.7	116.2
			∠$H_cCH_{c'}$	37.2	40.1
			∠H_aCH_b	140.0	131.6
			∠H_aCH_c	83.8	84.8
CH_4^{2+}	I	T_d	r(C–H)	1.285	
	II	D_{4h}	r(C–H)	1.220	

[a] Distance to center of H_2 molecule.

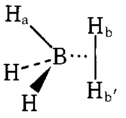
at near Hartree–Fock accuracy (1.160, 1.183, and 1.19 Å), respectively. Lipscomb's total energy is 0.00856 hartree below the UHF/6-31G** result. Jungen and Ahlrichs, using a somewhat less accurate basis, calculate a correlation energy of 0.1203 hartree using IEPA.[30] The UMP2/6-31G** method gives 0.09806 hartree, 82% of the IEPA result.

CH_3^+. The total energy is 0.00966 hartree above that found by Millie and Berthier.[31] The UMP2/6-31G** correlation energy is 78% of that found by Kutzelnigg with the IEPA approach.[13c]

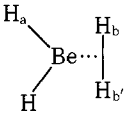
BeH^+. The UHF/STO-3G value, r = 1.323 Å, agrees well with experiment (r = 1.312 Å)[23] but the UHF/4-31G method gives a somewhat longer bond (r = 1.362 Å). The total energy is 0.01138 hartree above the Hartree-Fock limit calculated by Cade and Huo.[32] The UMP2/6-31G** value is 0.05260 hartree above Brown's 38 term configuration-interaction result.[33] The UMP2/6-31G** method gives 40% of Brown's correlation energy.

BH_2^+. Both the UHF/STO-3G and UHF/4-31G results are in good agreement with the bond length calculated by

Table II. Geometries of BH_5 and BeH_4 as a Function of $A-(H_2)$ Distance (4-31G)



	Ia	Ib	Ic	Id	Ie	If	Ig	Ih	Ii
$r(B-(H_2))$,[a] Å	1.0	1.15	1.3	1.45	1.6	1.9	2.2	2.5	∞
$r(B-H_a)$, Å	1.189	1.190	1.186	1.189	1.184	1.183	1.183	1.183	1.183
$r(H_b-H_{b'})$, Å	0.958	0.804	0.767	0.751	0.742	0.734	0.732	0.731	0.730
$\angle H_aB(H_2)$[b]	106.4	104.0	101.7	99.4	96.8	93.3	91.5	90.6	90.0



	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIg	IIIh	IIIi
$r(Be-(H_2))$,[a] Å	1.0	1.15	1.3	1.45	1.6	1.9	2.2	2.5	∞
$r(Be-H_a)$, Å	1.363	1.373	1.377	1.377	1.376	1.372	1.369	1.369	1.369
$r(H_b-H_{b'})$, Å	0.867	0.769	0.751	0.744	0.740	0.735	0.732	0.731	0.730
$\angle H_aBe(H_2)$[b]	110.6	108.5	106.5	104.3	102.0	97.6	94.2	92.1	90.0

[a] Distance to center of $H_b-H_{b'}$ bond. [b] Angle to bisector of $H_b-H_{b'}$ bond (deg).

Jungen using an extensive basis set with the inclusion of correlation (IEPA)[34] (1.187, 1.162, and 1.174 Å, respectively). Jungen's total energy is 0.0018 hartree lower than the UHF/6-31G** result and with the inclusion of correlation is 0.0158 hartree lower than the UMP2/6-31G** result indicating that the latter method obtains 82% of the correlation energy.

Lewis Acid-Base Complexes

H_3^+. H_3^+ has been known for some time to be an equilateral triangle[10a,35] (the linear form is calculated to be 39.6 ± 0.1 kcal/mol less stable[10d,10e]) so only D_{3h} symmetry was considered here. The H-H distance of 0.845 Å compares with 0.875 Å[10e] found with extensive configuration interaction and 0.868 Å[10p] at near Hartree-Fock accuracy. The UHF/6-31G** total energy lies 0.00631 hartree above the Hartree-Fock limit and with the inclusion of correlation lies 0.0156 hartree above the nonrelativistic limit. The UMP2/6-31G** method thus gives 41% of the correlation energy.

LiH_2^+. An isosceles triangle arrangement has been established as the most stable structure for this species[11c] being ~4 kcal/mol lower in energy than linear LiH_2^+. The distance from Li to the center of H_2 (2.23 Å) is in fair agreement with that found by Kutzelnigg,[11e] 1.984 Å, and by Ruedenberg,[11a] 2.07 Å, both of whom used more extensive basis sets in the geometry determination. The UHF/6-31G** energy is 0.00110 hartree above that found in the latter calculation.

LiH_3. A bound state of C_{2v} symmetry was found for LiH_3, being 2.03 kcal/mol lower in energy at the UMP2/6-31G** level than separated LiH and H_2. Linear $HLi-H_2$ is also bound but is ~1 kcal/mol higher in energy than the C_{2v} form. To our knowledge, this is the first such calculation on LiH_3.

BeH_3^+. The C_{2v} geometry found by Ahlrichs[12] was reoptimized and the expected bound state was found although at a somewhat greater separation between Be and H_2 (1.714 vs. 1.609 Å). Ahlrichs found the linear form to be ~10 kcal/mol higher in energy than the C_{2v} geometry and therefore only the latter was considered here. The total energy (UHF/6-31G**) lies 0.00856 hartree above Ahlrich's value while the correlated total energy is 0.02203 hartree higher than the IEPA result. About 81% of Ahlrich's correlation energy is obtained by the perturbative method.

BeH_4. No structure was found using the UHF/STO-3G method that had a total energy more negative than that of BeH_2 and H_2 separated to infinity. Consequently, a potential energy surface scan was conducted using the UHF/4-31G level by fixing a H_2 molecule at various distances from BeH_2 assuming planar, C_{2v} symmetry and optimizing all remaining geometrical parameters (Table II). Using these geometries, UHF/6-31G* and UMP2/6-31G* calculations were performed but still no bound state was found. It should be noted that this species had been predicted to be square planar (D_{4h}) by several authors.[15] While this form is more stable than tetrahedral by 109.6 kcal/mol (UHF/4-31G), it is calculated to be unstable to dissociation by 94.7 kcal/mol (UHF/4-31G).

BH_4^+. Several symmetries were considered for this molecule which also has been predicted to be square planar.[15] Three closely related structures were found that correspond to bound states. All are of C_{2v} symmetry and consist of a slightly bent BH_2^+ fragment forming a weak complex with an H_2 molecule. Three different orientations of H_2 (in plane, IIIa; perpendicular, IIIb; and "end on", IIIc) are very similar in energy indicating that H_2 can easily rotate at the binding distance. "Bridge protonated" (C_{2v}, IV), square planar (D_{4h} I), and tetrahedral (T_d, II) forms are found to be much higher in energy (27.5, 31.2, and 196.3 kcal/mol, respectively). All of the latter group are unbound relative to BH_2^+ and H_2.

BH_5. No structure was found, using the UHF/4-31G method, that was lower in energy than BH_3 and H_2 separated to infinity. This agrees with an earlier ab initio result in which the state having D_{3h} symmetry was studied. However, in view of the experimental claim that BH_5 participates in chemical reactions[8,9] and of the semiempirical (CNDO/2) calculation of its stability[8] further study of the structure was warranted. By analogy to the structure of CH_5^+ [13d,e] and in cognizance of the semiempirical results, a potential energy surface scan of a C_s form of BH_5 was undertaken similar to that done for BeH_4. Two C_s forms are possible, one in which H_2 eclipses a B-H bond and one in which H_2 lies perpendicular to a B-H bond. Previous calculations on CH_5^+ show these forms to be nearly identical in energy and more stable than any other geometry. Consequently we have selected the first of these forms and carried out UHF/4-31G geometry optimizations over a range of fixed $B-H_2$ distances (Table II). Local C_{3v} symmetry around BH_3 and C_{2v} symmetry around $B-H_2$ was assumed. Relaxation of this condition in CH_5^+ resulted in very little change and the assumption was further checked by allowing complete geometrical relaxation for one structure of BH_5 (r = 1.3), restraining only the $B-H_2$ distance. This led to an improvement in the total energy of only 0.00047 hartree. Single point UHF/6-31G* and UHF/6-31G** calculations were

Table **III.** Calculated Total Energies (hartrees)

Molecule		STO-3G optimized geometry		4-31G optimized geometry				
		UHF/STO-3G	UHF/4-31G	UHF/4-31G	UHF/6-31G*	UMP2/6-31G*	UHF/6-31G**	UMP2/6-31G**
H_2		−1.117 51	−1.126 58	−1.126 83	−1.126 83	−1.144 10	−1.131 33	−1.157 65
LiH		−7.863 38	−7.975 16	−7.977 35	−7.980 87	−7.996 51	−7.981 33	−8.002 17
BeH_2		−15.561 35	−15.731 46	−15.735 01	−15.750 73	−15.788 33		
BH_3		−26.070 70	−26.348 45	−26.349 27	−26.389 97	−26.468 49	−26.392 84	−26.490 9
Li^+		−7.135 45	−7.233 26		−7.235 54	−7.235 94		
BeH^+		−14.664 77	−14.830 22	−14.830 68	−14.841 44	−14.863 69	−14.842 58	−14.869 36
BH_2^+		−25.174 43	−25.432 88	−25.432 93	−25.470 79	−25.522 43	−25.743 38	−25.535 33
CH_3^+		−38.779 48	−39.171 29	−39.175 12	−39.230 63	39.329 10	−39.236 26	−39.351 05
LiH_3	I	−8.984 79	−9.103 85	−9.106 17	−9.109 93	−9.143 37	−9.115 28	−9.163 05
	II	−8.981 47	−9.102 30	−9.104 53				
BeH_4	I	−16.544 87		−16.707 09				
	II	−16.346 72		−16.532 48				
	IIIa			−16.707 34	−16.740 36	16.808 05		
	IIIb			−16.773 45	−16.802 31	−16.865 86		
	IIIc			−16.810 63	−16.836 44	−16.898 25		
	IIId			−16.830 73	−16.853 79	−16.914 28		
	IIIe			−16.841 71	−16.862 46	−16.921 75		
	IIIf			−16.852 14	−16.869 73	−16.926 98		
	IIIg			−16.857 05	−16.873 23	−16.929 26		
	IIIh			−16.859 71	−16.875 52	−16.930 98		
BH_5	Ia			−27.403 65	−27.451 09	−27.575 61	−27.462 31	−27.616 91
	Ib			−27.436 21	−27.482 94	−27.600 39	−27.494 56	−27.641 93
	Ic			−27.450 93	−27.496 90	−27.609 64	−27.507 86	−27.650 42
	Id			−27.457 64	−27.502 47	−27.611 04	−27.512 79	−27.651 26
	Ie			−27.462 04	−27.505 46	−27.610 50	−27.515 14	−27.650 11
	If			−27.469 00	−27.510 34	−27.610 68	−27.518 79	−27.648 73
	Ig			−27.473 34	−27.514 01	−27.612 04	−27.521 82	−27.649 06
	Ih			−27.475 32	−27.515 94	−27.612 83	−27.392 84	−27.490 90
	II	−27.101 80	−27.402 71	−27.404 79				
	III	−27.082 54	−27.384 62	−27.386 96				
H_3^+		−1.246 86	−1.262 86	−1.274 29	−1.274 29	−1.296 38	−1.293 62	−1.324 12
LiH_2^+		−8.259 96	−8.364 47	−8.364 47	−8.366 11	−8.384 53	−8.373 33	−8.400 70
BeH_3^+		−15.807 86	−15.979 64	−15.980 58	−15.997 50	−16.039 19	−16.006 01	−16.060 98
BH_4^+	I	−26.244 13	−26.512 34	−26.512 43				
	II	−25.970 38	−26.247 90	−26.249 25				
	IIIa	−26.295 70	−26.560 44	−26.561 48				
	IIIb	−26.294 51	−26.560 06	−26.562 09	−26.600 25	−26.671 32	−26.608 42	−26.699 10
	IIIc	−26.292 12	−26.560 30	−26.561 50				
	IV	−26.247 77	−26.516 43	−26.518 26				
CH_5^+		−39.918 87	−40.322 07	−40.327 15	−40.388 22	−40.534 04	−40.405 71	−40.577 47
CH_4^{2+}	I	−38.348 06	−38.740 80					
	II	−38.595 46	−38.992 54					

then carried out at the UHF/4-31G geometries. With the inclusion of correlation energy, estimated from the most extensive basis, a very shallow minimum is found corresponding to a binding energy of 1.70 kcal/mol (r = 1.45 Å).

CH_5^+. The Hartree-Fock UHF/6-31G** energy is 0.00439 hartree above the value recently found by Dyczmons and Kutzelnigg.[13e] With the inclusion of the Moller-Plesset correlation, the energy is 0.04413 hartree above the IEPA result. The UMP2/6-31G** method gives 81% of the correlation energy found by IEPA. Kutzelnigg's geometry is in close agreement with that found previously by Hariharan et al.[13d]

CH_4^{2+}. Since several groups have predicted that this molecule, isoelectronic with BeH_4 and BH_4^+, should be square planar (D_{4h}),[15] a study of its structure was undertaken. While the square-planar form is found to be 158 kcal/mol (UHF/4-31G) more stable than the tetrahedral form, dissociation to CH_3^+ and H^+ is exothermic by 112 (UHF/4-31G) kcal/mol. Consequently, no further study of this species was made.

Discussion

All charged species studied (H^+, Li^+, BeH^+, BH_2^+, CH_3^+) form bound complexes with H_2 (Table IV). However, the magnitudes of the binding energies show wide variations. A proton binds H_2 with an energy of 104.5 kcal/mol (UMP2/6-31G**). This, of course, is also a protonation energy and is expected to be large.[36] Both this value and those for the remaining ions can be rationalized with the aid of simple perturbation molecular orbital theory.[37] The stabilizing interaction of the filled σ orbital of H_2 with a vacant acceptor orbital, A, of the Lewis acid (Figure 1) will be increased by lowering the energy of A. The energies (6-31G**) of the lowest lying vacant orbitals of each ion (H^+, −0.5000; Li^+, −0.1958; BeH^+ −0.2838; BH_2^+, −0.2355; CH_3^+, −0.2803) reflect both the nature of the vacant orbital and the electronegativity of the central atom. Lithium is less electronegative than hydrogen and therefore the vacant Li^+ 2s orbital lies higher in energy than the 1s of H^+. Similarly, beryllium is more electronegative than lithium and therefore the HBe^+ orbital is lower in energy than that of Li^+. Although boron is more electronegative than beryllium, the vacant orbital in BH_2^+ is pure p and no longer possesses any s character. Consequently, the lowest vacant orbital of BH_2^+ actually lies higher in energy than that of BeH^+. This effect, in addition to those arising from the magnitude of the overlap of A with the σ orbital of H_2 and from nuclear reorganization upon complex formation, results in the unusual ordering of the binding energies: $BH_2^+ < Li^+ < BeH^+ < CH_3^+ < H^+$.

The uncharged species (LiH, BeH_2, BH_3) behave quite differently from their charged isoelectronic analogues. BeH_2 does not form a stable complex with H_2. However, LiH, the only neutral species studied possessing a permanent dipole moment, forms a complex but has less than 10% of the binding energy of the isoelectronic BeH^+. BH_3 binds H_2 with only 4% of the strength of CH_3^+.

Table IV. Calculated Binding Energies, $AH_n + H_2$ (kcal/mol)

	STO-3G optimized geometry		4-31G optimized geometry					
Molecule	UHF/ STO-3G	UHF/ 4-31G	UHF/ 4-31G	UHF/ 6-31G*	UMP2/ 6-31G*	UHF/ 6-31G**	UMP2/ 6-31G**	Exptl
H_3^+	81.17	85.52	92.54	92.54	95.56	101.84	104.50	99 ± 1[a]
LiH_2^+	4.39	2.91	2.75	2.35	2.82	4.05	4.46	
BeH_3^+	16.05	14.23	14.47	18.35	19.71	20.14	21.32	
BH_4^+	2.4	0.90	1.46	1.66	3.02	2.33	3.84	
CH_5^+	13.73	15.19	15.81	19.30	38.18	23.92	43.15	37.9[b]
LiH_3	2.45	1.32	1.25	1.40	1.73	1.64	2.03	
BH_5	0.0	0.0	0.0	0.0	0.0	0.0	1.70	

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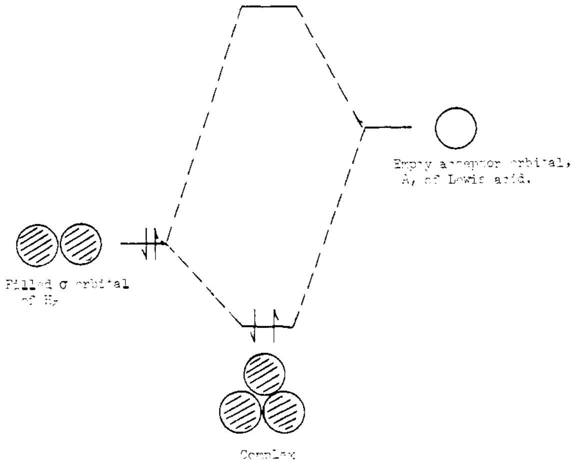

Figure 1. Stabilizing interaction of filled σ orbital of H_2 with empty acceptor orbital A of Lewis acid.

Table V. Comparison of Binding Energies with Binding Distance and H_2 Bond Length (4-31G)

Molecule	Dissociation energy, kcal	r(H–H), Å	r(A–(H_2)), Å
LiH_3	1.25	0.732	2.368
BH_4^+	1.46	0.739	2.257
LiH_2^+	2.75	0.736	2.229
BeH_3^+	14.47	0.753	1.714
CH_5^+	15.81	0.851	1.166
H_3^+	92.54	0.845	0.732

The orbital interaction diagram (Figure 1) may also be used to rationalize the qualitative relationship connecting the metal-H_2 binding distance, the H-H bond length, and the dissociation energy (Table V). As the orbital of H_2 and the acceptor orbital A approach one another in energy, the interaction between them increases leading to an increased binding energy and decreased metal-H_2 binding distance. There is a concomitant withdrawal of bonding electron density from the H-H bond which is consequently lengthened. In the scan of the potential energy hypersurface of BH_5 (Table III), a similar relationship is observed between the fixed B-H_2 distance and the H-H bond length. In this case, however, the binding energy is actually negative and becomes more so as the H_2 molecule approaches boron more closely.

No simple picture emerges of the effect of correlation energy. One expects that correlation energy will increase with increasing number of electron pairs and also that it will depend upon the proximity of H_2 to the binding fragment. Since this distance changes markedly one cannot draw any general conclusions from the calculated correlation energies of the bound complexes. However, in one comparison both the number of electrons and the distance from H_2 to the heavy atom are comparable, i.e., CH_5^+ (r(C-H_2) = 1.17 Å) and BH_5 (r(B-H_2) = 1.3 Å). For CH_5^+ correlation accounts for about half of the binding energy of 43 kcal/mol, or 20 kcal/mol. For BH_5 (r = 1.3 Å) the complex is unstable toward dissociation by 10.2 kcal/mol (UHF/6-31G**). With the inclusion of correlation the complex actually becomes bound by 1.7 kcal/mol having overcome a large Hartree-Fock repulsion. Similarly for BeH_4 (r = 1.3 Å) the complex is unstable by 25.8 kcal at the UHF/6-31G* level but by only 21.4 with the inclusion of correlation.

The Moller-Plesset method of correlation energy estimation gives about a third of the total correlation energy when applied to the relatively limited 6-31G* basis, and nearly half of the correlation energy using the 6-31G** basis, as compared to cases in which full configuration interaction results are known. By contrast, UMP2/6-31G* gives two thirds of the energy obtained by the IEPA approach while UMP2/6-31G** obtains four fifths of the IEPA correlation. Since a polarized, "split-valence" basis set presumably describes the valence region more accurately than the core, it is likely that the influence of correlation on chemical phenomena is more accurately estimated than is the total correlation energy. Viewed in this light the low estimate of the Li^+ correlation energy (4%) is not so disturbing since the ion has only core electrons and this region is described by a single basis function.

The very low binding energy for BH_5 casts some doubt on the claim that this is an intermediate in protonolysis reactions. However, the results suggest that pentavalent boron is a highly likely candidate for a transition state in the exchange of hydrogen atoms.

Summary

Several conclusions may be drawn:

(1) The ability of an electron-deficient species to bind a hydrogen molecule derives almost entirely from charge polarizability and very little from the mere availability of an unoccupied valence molecular orbital. This is similar to conclusions reached when boron compounds are used to model carbonium ions.[38]

(2) Correlation effects in H_2-Lewis acid complexes become significant at distances of about 1.5 Å or less.

(3) Hartree-Fock binding energies are given fairly well at the UHF/4-31G level. The inclusion of polarization functions generally leads to a modest increase in the binding energy.

(4) BeH_4 is not expected to exist at any temperature.

(5) H_3^+, BeH_3^+, and CH_5^+ are the only complexes studied that are expected to be stable at ambient temperatures.

(6) LiH_3, BH_5, LiH_2^+, and BH_4^+ should be observable only at low temperatures where the small enthalpy of association can overcome the entropy of dissociation, which is estimated to be between 25[39] and 35[40] eu.

(7) Finally, D_{4h} structures proposed from qualitative arguments[15] for isoelectronic BeH_4 and BH_4^+ are found to dissociate into AH_2 and H_2. Similarly, CH_4^{2+} is unstable and dissociates to CH_3^+ and H^+.

Note Added in Proof. Hoheisel and Kutzelnigg[41a] have now studied BH_5 extensively with and without electron correlation. The minimum energy geometry and binding energy (2.0 kcal/mol) are quite comparable to our results. The excellent agreement between the binding energies for LiH_2^+ (5.1), BeH_3^+ (24.7), CH_5^+ (43.0), and H_3^+ (107.1 kcal/mol) summarized in this paper and the UMP2/6-31G** results (Table IV) should also be noted. Similar conclusions on BH_5 have also been reached by Pepperberg, Halgren, and Lipscomb.[41b]

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