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Geometrical-Electronic Relationships between H₂-Containing Molecules

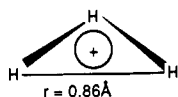
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By use of simple concepts associated with open and closed three-center bonding, the structures of a wide range of systems containing coordinated H₂ are brought together theoretically. H₃⁺(H₂)_n, where n = 0 upwards, ML_m(H₂)_n, where M = transition-metal atom and where to date L = Cp, CO, PR₃ and n = 1, 2, and AH_m(H₂)_n types, where A = main-group atom, m = 1-3, and n = 1-m, join other species such as CH₆²⁺ and CH₅⁺, small-angle states in molecules such as CH₂, and local minima in the approach of H₂ to SiH₂ in being described in essentially the same way by using the isolobal nature of the fragments concerned. H₂ complexes are suggested to be stable for A = O, F (and indeed are known) but less likely for A = C, N, Cl. The H₂ complex with water may well be stable, but that with methanol is less likely.

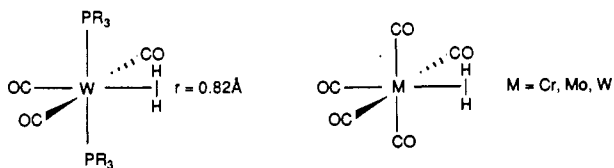
Introduction

Recent years have seen several advances in the study of H₂-containing molecules and complexes. These are distinguished from the traditional hydrides by the presence of a coordinated H₂ unit with a close H-H distance. In the examples where structural data are available, this linkage is stretched no greater than 0.2 Å beyond that in free H₂. The past 8 years have seen the structural characterization of the H₃⁺ molecule¹ (1), the synthesis and



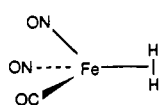
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characterization²⁻⁶ of a series of H₂-containing transition-metal species (2-4) starting with the Kubas molecule² (2), the spec-

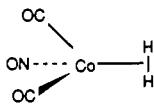


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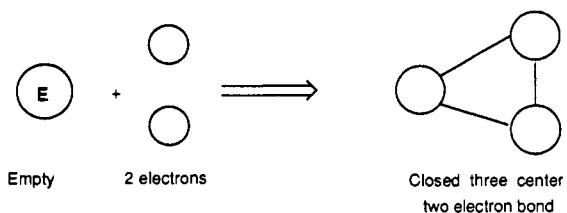


troscopic identification of molecules of the type H⁺(H₂)_n^{7,8} and OH₃⁺(H₂)_n⁸ and the suggestion⁹⁻¹¹ that electronically many of these species are related. In this paper we study some molecules of this type and present an electronic picture that ties together

many of their structures. The discussion is necessarily speculative but is a natural extension of bonding ideas understood quite well by now in small molecules¹² and makes use of the isolobal analogy¹³ in collecting examples scattered across the whole domain of chemistry.

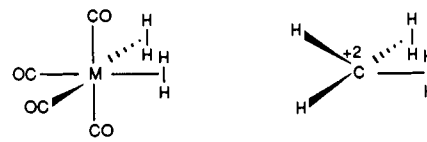
The Three-Center Model

These "H₂" complexes, whether of the H₃⁺(H₂)_n, ML_m(H₂)_n, or AH_m(H₂)_n types (A = main-group atom, M = transition-metal atom), have a common structural feature, namely the presence of a three-membered ring containing two hydrogen atoms and an atom or fragment with an empty LUMO, directed spatially toward the diatomic molecule. In H₃⁺ itself the proton has an empty 1s orbital and the molecule may be written as H⁺(H₂) to emphasize this point. The unsaturated ML_n fragments (as in the Kubas and related molecules of 2-4) have a low-lying transition-metal-centered s/p/d hybrid orbital, and the H₃⁺ fragment has a low-lying pair of orbitals in H₃⁺(H₂)_n, where n = 1-3. A useful way to regard many of these species is then to describe them as containing closed three-center-two-electron bonds (5). We have shown



5

elsewhere¹⁰ that other molecules of this type may be drawn under the same umbrella. These include the SiH₂(H₂) species¹⁴ (a local minimum in the calculated surface for H₂ approach to SiH₂), so-called "small-angle states"¹⁵ in dihydrides such as CH₂⁺ (where the H-H distance is computed to be 0.85 Å in the ²B₂ state), and the Cr(CO)₄(H₂)₂ molecule¹⁶ (6), isoelectronic¹⁷ (in the same way



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that Cr(CO)₅(H₂) and CH₅⁺ are related) with Olah's postulated CH₆²⁺ species ((CH₂²⁺)(H₂)₂) (7). With the exception of 6 and 7, relative to H₂ all of these fragments are isolobal with the proton.

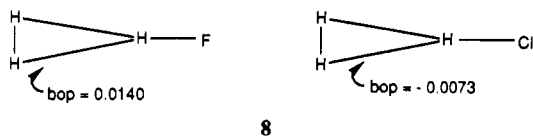
- (1) Oka, T. *Phys. Rev. Lett.* **1980**, *45*, 531.
- (2) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergammi, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *100*, 451. Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473. Kubas, G. J.; Ryan, R. R.; Wroblewski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339.
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- (14) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* **1986**, *106*, 2191.
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Other molecules may be described in this way as we now show.

XH(H₂) Where X = F, Cl

Perhaps the simplest unit to which an H₂ molecule could be attached is a diatomic H-X species where X is a halogen. In HF the hydrogen end of the molecule is quite proton-like as a result of the high electronegativity of fluorine and could be expected to behave in a way similar to that of the H⁺ atom in the conceptual assembly of H₃⁺ from H₂ and H⁺. **8** shows the results of some



8

extended Hückel calculations on XH(H₂) where X = F, Cl. (The parameters are given in the Appendix.) It is very interesting to see that the bond overlap population for the linkages between the two diatomics changes sign on going from fluorine to chlorine. Broadly interpreted, the complex with HF is possible and has indeed been observed¹⁸ (it looks like **8**), but that with HCl should be less stable since the forces of attachment have to be of the van der Waals type, to offset this "molecular orbital based" repulsion. Perhaps even the first vibrational level would lie above the well. (The overlap population shown between HF and (H₂) in FH(H₂) is smaller than that calculated for the H₃⁺ species itself (0.315), a direct result of our choice (the experimental one) of the (H₂)–H distance (see Appendix)). It is easy to understand that, in general, as the H atom electron density in HX increases then the formation of closed, three-center, "electron-deficient" bonding will become less favorable with use of our simple argument above. Figure 1, however, shows the assembly of molecular orbital diagrams for FH(H₂) and ClH(H₂), which give some added insight into the orbital picture. In the former the occupied orbitals of HF are almost entirely fluorine-located so that the interaction of H₂ with HF is well described by the simple donor–acceptor concept. The dominant interaction is between the σ bonding orbital of (H₂) with the LUMO of HF, the latter being strongly hydrogen-located. The H charge from our calculations is found to be +0.61. There is virtually zero interaction of π type between the LUMO of H₂ and the relevant H–F nonbonding orbitals of HF, since the H atom carries no orbitals of this type and the (H₂)–F distance is large.

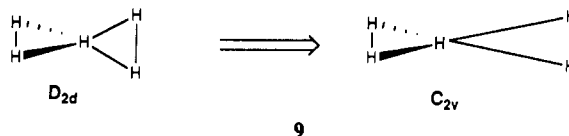
For ClH(H₂) the situation is somewhat different. The occupied orbitals of the HCl molecule have a much larger H 1s contribution (our calculated H atom charge for HCl is +0.39), so that in addition to the interaction described for FH(H₂) there are several two-orbital–four-electron repulsions between pairs of occupied orbitals on the two molecules. Overall the energy of interaction is a destabilizing one. In Figure 1 this shows up as a smaller stabilization of the second lowest orbital of a₁ symmetry. The HOMO is destabilized by approximately the same amount in both cases. The situation in this species is reminiscent of that occurring in the attachment of (H₂) to transition-metal carbonyl and nitrosyl containing fragments. Here¹⁰ the presence of the superlative π -acceptor ligand NO reduces the metal-located electron density in the ML_n fragment and thus the ferocity of the two-orbital–four-electron repulsion terms. As a result (H₂) complexes are found⁵ for ML_n = Fe(CO)(NO)₂ and Co(NO)(CO)₂, but no conclusive evidence is available for a complex with Ni(CO)₃.¹⁹

The FH(H₂) complex is held together by rather weak forces,¹⁸ and as in the H₃⁺(H₂)_n species^{7,8} described in the next section, there are large-amplitude motions that complicate the spectro-

scopic analysis. Even in liquid xenon solution the H–H stretching motion in Cr(CO)₅(H₂) is⁵ very broad, indicating a similar type of situation at lower temperatures and in a different medium.

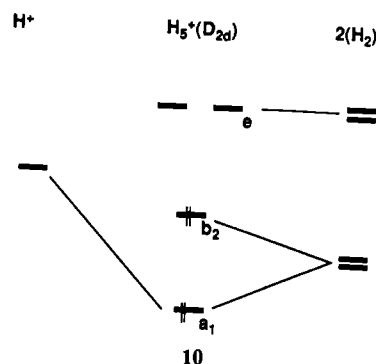
H⁺(H₂)_n

These species have long been known²⁰ as "mass spectrometer molecules" with *n* up to 22, but recently gas-phase spectroscopic information has been obtained^{7,8} on the earlier members of the series. They have also been studied^{21,22} via ab initio molecular orbital methods and some predictions made as to their geometries. The species H₅⁺ has been predicted to have the C_{2v} geometry shown in **9**, distorted away from the symmetrical D_{2d} one. Ex-

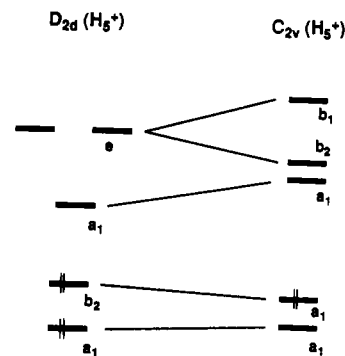


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perimentally^{7,8} it is found that the species in the gas phase is very fluxional. **10** shows the very simple orbital interaction diagram



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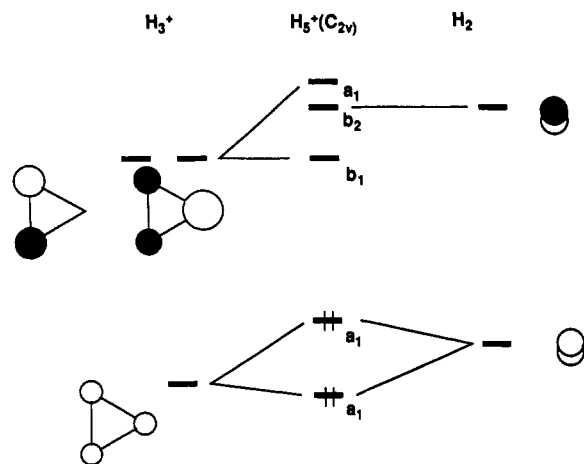


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for construction of the level diagram of the symmetrical molecule from a proton plus two H₂ molecules and **11** the way in which the energy levels change on distortion to C_{2v}. This distortion may be regarded as a second-order Jahn–Teller one that couples the a₁ HOMO and b₂ LUMO via a b₂ distortion. Thus, one of the two H₂ units is bound to the proton more strongly than the other. Another way to regard the resulting structure is one where a single H₂ molecule is bound to an H₃⁺ unit (**12**). The latter provides the empty orbital E of **5**. (In the spirit of the fragment approach the internuclear separations appropriate for **12** are those that exist in the assembled molecule and for the fragments, not the equilibrium geometries themselves.) We may use simple molecular orbital ideas to show why in the C_{2v} geometry it will be bound less strongly to the triatomic than the hydrogen atoms already

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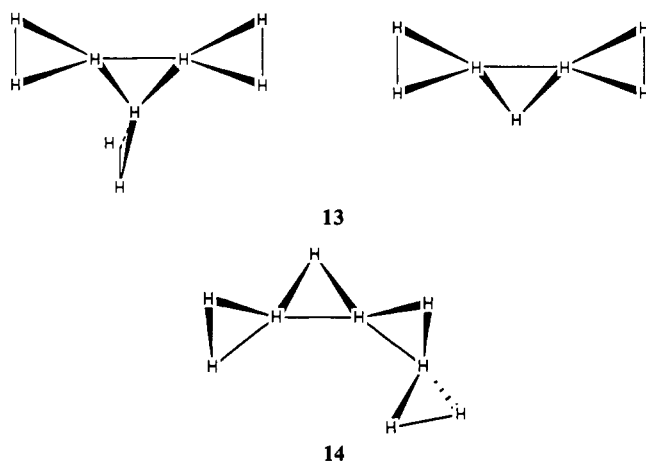


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present in H₃⁺. The interaction energy of the orbitals located on the H₂ molecule with an empty orbital on another unit will depend critically upon the overlap integral between the fragment orbital and the H₂σ bonding orbital of H₂. If the fragment is a proton (to eventually give the H₃⁺ molecule), then at a given distance the overlap integral with H₂σ will be larger by a factor of 2/√6 than the analogous overlap with H₃⁺ (to eventually give the H₅⁺ molecule). This is simply because the orbitals of the latter are diluted by being delocalized over the triatomic molecule. The stated numerical ratio comes straightaway from the form of the LUMO, 1/√6(2φ₁ - φ₂ - φ₃) in Hückel theory, where φ₁₋₃ are the 1s orbitals of the three hydrogen atoms comprising the molecule.

The molecule Cr(CO)₄(H₂)₂ (**6**) is a species similar to H₅⁺, in the sense that replacement of the Cr(CO)₄ unit by H⁺ gives the H₅⁺ molecule. We have calculated the energy change for this species as it undergoes a distortion analogous to the one that takes the D_{2d} H₅⁺ molecule to the C_{2v} form. This is a distortion where one H₂ molecule decreases its H-H separation and becomes bound a little closer to the metal and the other increases its H-H distance and is bound a little further from the metal. We find a somewhat soft potential for this motion from our calculations but note that they are not particularly reliable for this particular type of problem. Such a result is however interesting. Of some considerable interest is the observation¹⁶ that an H₂/D₂ mixture is converted to HD by Cr(CO)₄. The presence of such a soft mode implies that one of the coordinated H₂ molecules may readily open up to give a dihydride. (We discuss possible pathways for H/D exchange elsewhere.¹⁰)

A picture similar to that for H₅⁺ holds for the species H₇⁺ and H₉⁺, where additional H₂ units are attached to the H₃⁺ triangle (**13**). There is an alternative geometry for H₉⁺ (**14**), a chain



14

structure that Schaeffer and co-workers^{21,22} did not examine by ab initio methods. Our theoretical method is not good enough of course to distinguish energetically between such isomers with

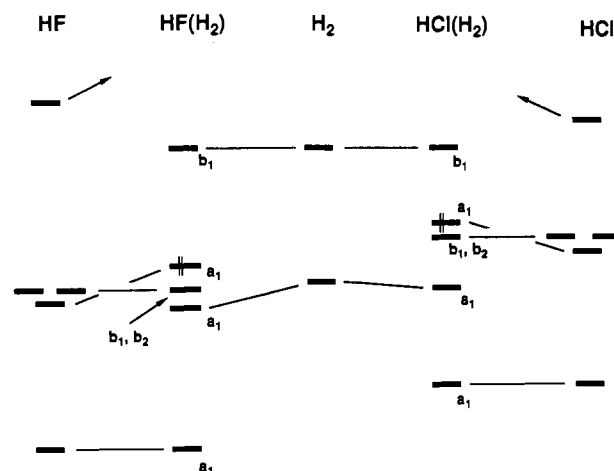


Figure 1. Assembly of molecular orbital diagrams for the molecules FH(H₂) and FCl(H₂).

Table I. Computed Bond Overlap Populations for Various H⁺(H₂)_n Species from Calculations Where All Bonded H-H Distances Are Set Equal

molecule	linkage	calcd overlap population ^a	calcd bond length, Å ^b
H ₃ ⁺	a	0.351	0.850
H ₃ ⁺ (H ₂)	a	0.622	0.764
	b	0.191	1.128
H ₃ ⁺ (H ₂) ₂	a	0.640	0.739
	b	0.143	1.827
	c	0.430	0.845
	d	0.131	0.878
H ₃ ⁺ (H ₂) ₃	a	0.760	0.738
	b	0.106	1.880
	c	0.583	0.856

^aReduced overlap population from calculations where all bonded H-H distances are set at 0.860 Å. ^bCalculated H-H distances from ab initio calculations at the DZ level using D_{3h}, D_{2d}, C_{2v}, and D_{3h} geometries, respectively.²¹

very different coordination numbers, but the experimental results^{7,8} for the H₅₋₉⁺ species do however indicate that the three H₂ molecules in H₉⁺ are bound with a strength similar to those in the other two species, and so **14** is probably not a likely candidate. Figure 2 gives the bond overlap populations for these geometries from calculations where the same values for the three sets of H-H distances were set equal (see Appendix) for all the molecules. Since there are as yet no distances known (with the exception of that in H₃⁺), we have used results from ab initio calculations^{7,8} on H₅⁺ to define the geometries. Table I shows the results from a different set of calculations, those where all H-H distances between bonded atoms are set equal. We expect the actual H-H distances to inversely follow the populations from such a set of calculations, as a direct response to the electronic preferences set by the variation in orbital topology. This, of course, is really what calculations of this type report. Thus, the bond overlap populations that are listed here are to be used in a fashion analogous to that of the interpretation of the structures of conjugated organic molecules. The bond lengths from these ab initio computations and the calculated overlap populations track inversely quite well. For H₅⁺ we chose the D_{2d} geometry where the two H₂ molecules are symmetrically attached to the central proton. Notice that as the number of coordinated H₂ molecules increases so the bond overlap population describing their strength of attachment decreases. This is a well-known result from other areas of chemistry. As the number of ligands increases, their individual bond strengths decrease. In the present series of molecules the central H₃⁺ core with its delocalized orbitals plays the role of a single central atom. We shall see rather different behavior below for complexes of the type AH_m(H₂)_n.

Let us examine other possibilities for the coordination of more H₂ units beyond H₉⁺. Experimental results^{7,8} indicate that these

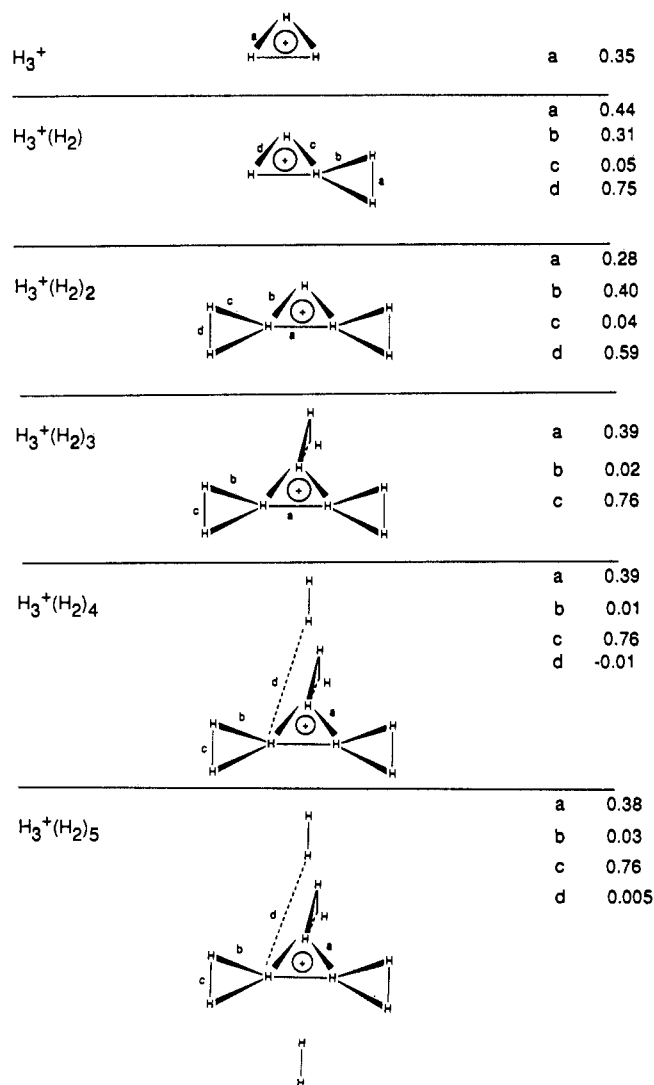
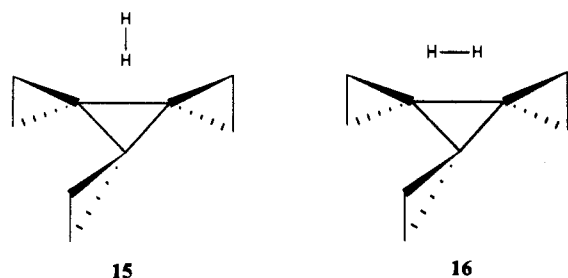
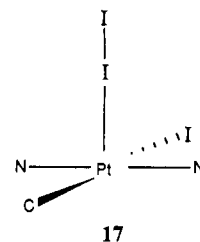


Figure 2. Computed bond overlap populations for various $H^+(H_2)_n$ species.

extra H_2 molecules are bound less strongly than the first three. There are two clear possibilities; positions above and below the plane of the H_3^+ triangle or coordination to the H_2 molecules at the periphery. The one-electron stabilization energy from the end-on approach (15) is calculated to be larger than that for the sideways-on geometry (16). This is in spite of the fact that the

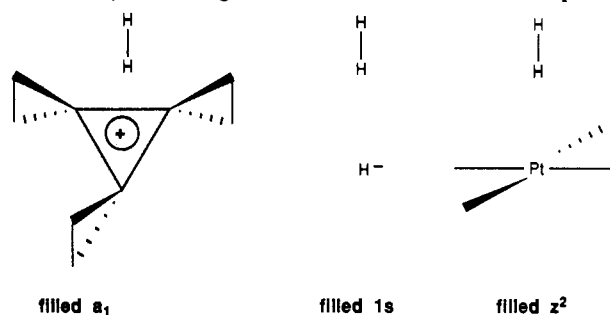


number of atomic contacts between the two units is smaller in the former. There is a clear electronic advantage for the end-on arrangement. The two hydrogen molecule 1s orbitals (containing one electron each) plus the doubly occupied a_1 orbital of the planar triangle produce an orbital situation analogous to that in a linear (but hypothetical) H_3^- molecule. In the latter the role of a filled 1s orbital in electron-rich (two pairs of electrons) three-center bonding should give rise to a linear geometry as found, for example, in the triiodide ion, I_3^- , and in the hypothetical ion H_3^- . This possible structure for the H_{11}^+ molecule is thus analogous to the molecule²³ 17, $[Pt^{II}\{C_6H_3(CH_2NMe_2)_2-o,o\}(\eta^1-I_2)]$, which may



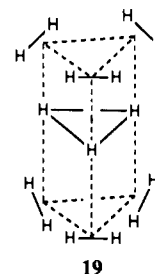
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similarly be regarded as being characteristic of this type of three-center interaction. Here, however, the electronic picture involves an I_2 (rather than H_2) unit coordinated to a molecule with a judiciously located HOMO (a z^2/s metal-centered hybrid in this case) containing two electrons. 18 shows the comparison



18

between the three systems. From the overlap populations of Figure 2, the model suggests that the two extra H_2 molecules coordinated in H_{13}^+ should be bound more strongly than the one extra H_2 molecule in H_{11}^+ . There are no experimental data yet to support this possibility. Clapitt and Gowland, though, noted²⁰ a maximum in the mass spectral intensity at H_{15}^+ , which they suggested could be due to the special stability of an octahedral array of six H_2 molecules set around a central H_3^+ core. From the point of view of providing an interaction with the orbitals of H_3^+ , a trigonal prism is perhaps better as in 19. Using the same geometrical



19

parameters as before, we find a positive overlap population for the H_2 attachment. All of the results presented here focus, of course, on the traditional molecular orbital based forces of chemical bonding. In some of these molecules these forces will be weak and van der Waals interactions may well dominate the picture, a consideration we should always bear in mind. In this way our ideas presented here are to be viewed with a philosophy similar to those we have described²⁴ for the geometries of van der Waals molecules themselves.

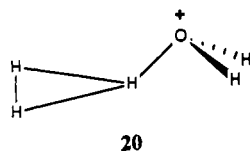
$AH_n(H_2)_n$ Complexes

The picture expounded above concerning the electronic requirements for H_2 complexes requires a judiciously located (both spatially and energetically) LUMO for electron-deficient closed three-center bonding. This orbital not only needs to be strategically located spatially, so as to be capable in principle of good overlap with the orbitals of H_2 , but also needs to be largely localized on the atom to which the molecule is coordinated. We noted above a decrease in the calculated $XH-H_2$ overlap population as delocalization increased. A similar picture should apply to molecular

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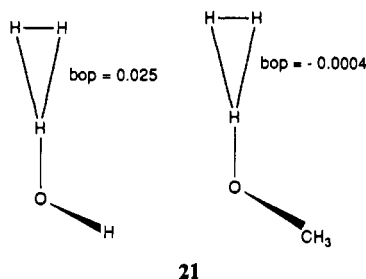
(24) Burdett, J. K. J. *Chem. Phys.* **1980**, *73*, 2825.

hydrogen complexes with the polyhydrides AH_n of the main-group elements such as the example shown in 20. Again it will be quite

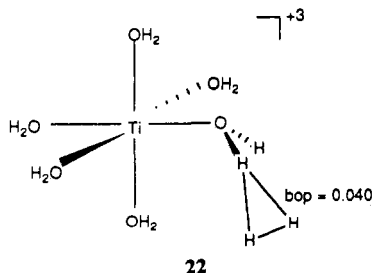


important to choose the identity of A so as to ensure that the relevant orbitals are well localized. This will clearly occur for a main-group atom with an electronegativity as different as possible from that of hydrogen. The main-group hydrides OH₂ and NH₃ and the positive ions NH₄⁺ and OH₃⁺ immediately spring to mind. CH₄ is probably not a likely candidate since we know from experience that the C-H linkage is only slightly polar. Complexes of the type we seek have in fact been identified⁸ in the form of OH₃⁺(H₂)_n with n up to 4, and some theoretical calculations have been performed²⁵ at the *ab initio* level. Figure 3 shows some computed bond overlap populations for a variety of species. The actual geometries have been used for the AH_n units, and the H-(H₂) distance is the same as used in Figure 1. Notice the correlation between the H-(H₂) overlap populations and the electronegativity of the central atom, A. The populations increase with an increase in the hydrogen 1s character in the 2a₁ orbital of the AH_n parent. There is a calculated negative H-(H₂) overlap population for the case of hydrogen interaction with ammonia, ammonium ion, and methane; the nitrogen and carbon atoms are not electronegative enough to attach an extra H₂ in this way. A similar electronegativity dependence is found in our computations on the hypothetical species H₂O₂(H₂) and H₂N₂(H₂). The first is a possibility since a positive bond overlap population exists between the H₂O₂ and (H₂) units, but the second is less likely from the sign of the same parameter. Since the electronegativity of the central A atom is important, OH₃⁺ will be better than OH₂ itself. The complexes with OH₃⁺ have recently been identified, but those with water are presently unknown. We reserve comment until later on the possible structure of OH₃⁺(H₂)₄.

A particularly nice result is shown in 21 and describes the attachment of H₂ to methanol and to water. Notice that the



H-(H₂) overlap population is negative for the methanol case but positive for water, a direct result of the electron-donating property of the methyl group. One can speculate forever, of course, about the type of molecule that may be stabilized in this way. 22 shows



a final example, that of a computed positive overlap population for an (H₂) unit coordinated to a hydrogen atom in the transition-metal hexaquo complex Ti(H₂O)₆³⁺.

Although there is a correlation between the electronegativity of the A atom and the sign of the bond overlap population found

H ₃ O ⁺		a	0.61
H ₃ O ⁺ (H ₂)		a	0.58
		b	0.03
		c	0.75
		d	0.61
H ₃ O ⁺ (H ₂) ₂		a	0.58
		b	0.03
		c	0.75
		d	0.60
H ₃ O ⁺ (H ₂) ₃		a	0.58
		b	0.03
		c	0.75
H ₃ O ⁺ (H ₂) ₄		a	0.57
		b	0.03
		c	0.75
		d	0.26
		e	0.60
NH ₃ (H ₂)		a	0.73
		b	0.36
		d	0.45
NH ₃ (H ₂)		a	0.72
		b	0.73
		c	-0.005
		d	0.77
NH ₄ ⁺ (H ₂)		a	0.73
		b	0.42
		c	-0.003
		d	0.77
CH ₄ (H ₂)		a	0.82
		b	0.86
		c	-0.05
		d	0.81
H ₂ O ₂ (H ₂)		a	0.58
		b	0.02
		c	0.75
H ₂ N ₂ (H ₂)		a	0.73
		b	-0.01
		c	0.78

Figure 3. Computed bond overlap populations for various AH_n(H₂)_m species.

for -H...(H₂), there is only a rough correlation between the size of this overlap population and the computed H atom charge in the parent hydride (Table II). The details of the two-orbital-four-electron interactions, similar to those described above for HCl(H₂), varying from system to system, are clearly important.

End-on Hydrogen Molecules

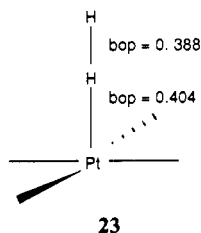
So far we have almost exclusively described (H₂) units attached in a sideways fashion to give closed three-center electron-deficient

(25) Schaefer, H. F., unpublished calculations.

Table II. Computed H Atom Charges in Free Molecules and Corresponding H-(H₂) Overlap Populations

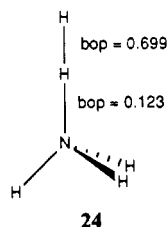
molecule	calcd charge on H atom bound to (H ₂)	calcd H-(H ₂) overlap population
HF	0.6102	0.013
H ₂ O ₂	0.4258	0.019
CH ₃ OH	0.4219	-0.0004
H ₂ O	0.4193	0.025
Ti(H ₂ O) ₆ ³⁺	0.3997	0.040
HCl	0.3869	-0.007
H ₃ O ⁺	0.3685	0.025
N ₂ H ₂	0.2619	-0.009
NH ₃	0.2328	-0.005
NH ₄ ⁺	0.2151	-0.003
CH ₄	0.0571	-0.045

bonds. In many of these systems, though, the possibility exists for end-on coordination. **23** shows, for example, the computed

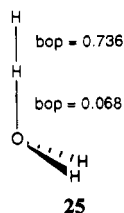


bond overlap populations for the molecule PtH₄(H₂)₂²⁻ used as a model for the hydrogen analogue of the species **17**. Even for a Pt-H_{ap} distance of 2.0 Å the metal-hydrogen overlap population is large. Molecules of this type have yet to be characterized, but Shustorovitch, Baetzold, and Muettterties²⁶ have suggested that such a perpendicular geometry should be the norm for coordination of all closed-shell diatomics to metal surfaces. We note a theoretical treatment by Saillard and Hoffmann²⁷ for the approach of H₂ to a metal surface. We believe that similar geometries for hydrogen in transition-metal-containing molecules should be possible and are probably similar to the route of initial approach in oxidative-addition reactions at square-planar d⁸ centers.

Another possibility is the replacement of the doubly occupied z²/s hybrid orbital in the molecule **23** by a doubly occupied s/p hybrid in some main-group molecule. **24** shows the calculated



overlap populations for the molecule NH₃(H₂) where the extra (H₂) unit is attached in an end-on fashion. Our results naturally will be dependent on the geometry we choose, but for an N-H_{ap} distance of 1.5 Å, a distance roughly 50% larger than the corresponding N-H_{bas} distances, the relevant overlap population is positive. **25** shows the computed overlap populations for the



corresponding OH₂(H₂) molecule. The observation of a positive overlap population is not a guarantee of course that these molecules will exist but is an indication of the electronic factors that are important in the stabilization of such molecules.²⁸ A particularly important point for these linear species is their stability relative to (for example) water and H₂. Such considerations have attracted the attention of several theorists²⁹ interested in the factors that select bond localization versus delocalization in a variety of molecules. Three-center bonds of this type are quite notorious for their instability.³⁰ For these particular systems the general result is that delocalized bonding, of the type shown in **18**, is much less appropriate for hydrogen than for heavier elements such as iodine. In the latter case, though, structural correlation plots show³¹ quite a soft potential for I₃ ↔ I₂ + I⁻. It will be interesting to see if molecules of this type can be made and especially intriguing to see if in the molecule OH₃⁺(H₂)₄ the fourth (H₂) unit is attached in this way.

Conclusions

At this stage it is important to put our results into some kind of perspective. The calculation of a positive bond overlap population between two atoms, in itself, does not guarantee the stability of a particular complex, of course, as we have mentioned above. There are several presently unknown molecules where theory, at perhaps many different levels of sophistication, suggests chemical stability. What we have done in this paper is to weave a linking theoretical thread through some of the observed systems and extrapolate the underlying theoretical basis to some presently unknown systems. The conclusions are based on the identification of stable orbital topologies rather than the accurate computation of bond dissociation energies etc. That there is much more chemistry to be unearthed in this area and that ideas such as these are useful are illustrated by the recent synthesis³² of a complex containing coordinated trihydrogen (H₃) following our prediction^{9,10} of the existence of this type of molecule in earlier theoretical studies.

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Appendix

The calculations used in this study for the molecules H₃⁺(H₂)_n, ML_m(H₂)_n, and AH_m(H₂)_n (A = main-group atom, M = transition-metal atom) were of the extended Hückel type. These calculations are not at all reliable when changes in internuclear distances are investigated, and so all of the calculations in a particular series used the same geometrical parameters. Figure 2 and Table I show two sets of calculations; the first used an H-H distance in the H₃⁺ triangle of 0.86 Å and distances to the coordinated H₂ atoms of 1.2 Å. The distance within the H₂ unit itself was 0.74 Å. In the second set all H-H distances were fixed at 0.8 Å to investigate how the topology of the orbital network determines the different bond lengths. In H₃⁺(H₂)_n (n = 4, 5) the distance *d* was set to 1.1 Å. In the AH_m(H₂)_n complexes (m ≠ 1) all A-H distances were fixed at 1.0 Å and the H-(H₂) distance was set at 1.4 Å. For the HF and HCl complexes the actual H-X distances were used. M-H in ML_m(H₂)_n was set at 1.7 Å. Standard³⁰ orbital parameters were used for all atoms.

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- (28) It has recently been shown that a linear C-H-H geometry is found at the transition state for the reaction CH₃⁺ + H₂ → CH₄ + H⁺: Gordon, M. S.; Baldinger, K., unpublished results.
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