stabilization by solvent becomes $S_R > C_R > T$ as shown in Table III. The relative values of the one-center and two-center terms in eq 1 are important in describing the differential solvation correctly. Our results show that eq 3 keeps a good balance between these two terms and therefore gives the correct qualitative picture of solvation energy.

Conclusion

Typical S_N2 reactions of methyl chloride with anions, Cl^- and F^-, were studied on the basis of the MNDO-effective charge model calculation. The potential energy diagram obtained for the reaction in the gas phase ($\epsilon = 1.0$) was the double-well type potential, which has been accepted for the gas-phase reaction profile. For the reaction in solution ($\epsilon > 1.0$), the potential well becomes shallow and the energy barrier becomes higher than that in the gas phase. The shift from a double-well potential to a unimodal type one was shown to occur when the dielectric constant of the solvent is increased. These results support the reaction profile proposed by Brauman et al.[2] and agree well with Monte Carlo simulation by Chandrasekhar et al.[8]

It has been shown that the MNDO-effective charge model represents the differential solvation correctly. Although the effective charge model does not involve the specific interactions between a solute molecule and solvent, the electrostatic interactions between them are fully included. It is thus expected that the method can be applied successfully to qualitatively understand solvation effects due to electrostatic interactions.

Acknowledgment. This work was supported by The University of Tsukuba Research Project.

Registry No. Cl, 16887-00-6; F, 16984-48-8; CH_3Cl, 74-87-3.

Ab Initio Studies of Molecular Structures and Energetics. 2. Energies and Stabilities of PH_n, SH_n, and ClH_n Compounds

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Abstract: The energies and molecular structures of the highly coordinated species PH_5, SH_4, SH_6, ClH_3, and ClH_5 have been derived by ab initio computations. All structure optimizations employed the MP2 approximation, and energies were computed at the SCF, MP2, and MP4 levels and in two quite different basis sets, in each case with polarization functions on H and the heavy atom. Of particular interest are ClH_3, which is of C_{2v} symmetry, and ClH_5, which is C_{4v}. MP2 vibrational frequencies were determined for each species. Each was found to be structurally stable (i.e., exhibiting no imaginary vibrational frequencies), although a similar treatment of ClH_7 found it to be unstable. The values of ΔH°_{298} and ΔG°_{298} were computed for each of the hydrogenation reactions $PH_3 + H_2 \rightarrow PH_5$, $SH_2 + H_2 \rightarrow SH_4$, $SH_4 + H_2 \rightarrow SH_6$, $ClH + H_2 \rightarrow ClH_3$, and $ClH_3 + H_2 \rightarrow ClH_5$ and the analogous reactions for adding two H atoms. In all cases the products are of higher energy than reactants except for the addition of atomic hydrogen to PH_3, SH_2, and SH_4. The energy difference is largest for addition of H_2 to the Cl compounds, ΔH°_{298} being 477 and 503 kJ/mol for formation of ClH_3 and ClH_5, respectively, at the MP4 level. The energy of each species was analyzed by use of the ab initio multicenter energy resolution, a method of analysis that was found to be an especially powerful way of elucidating the nature of its bonding and hence the origins and degree of its structural stabilities. This analysis demonstrates that three-center bonding stabilizes the Cl species more than the others, while increasing three-center repulsions between neighboring H atoms destabilize all the higher coordinations and lead to the instability of ClH_7.

One of the most important advances to take place in quantum chemistry in recent years has been the development of efficient procedures for ab initio computation of derivatives of molecular energies with respect to bond distances and angles. Such procedures permit the optimization of relatively complex molecular structures and also estimation of all their concomitant vibrational frequencies.

The ability to compute vibrational frequencies is of particular importance in dealing with species which have not been observed in the laboratory since the absence of any imaginary frequencies (assuming the energy gradients have been made to vanish) is a rigorous proof that, at the level of approximation employed, the structure corresponds to a local minimum in the energy. Therefore unless the associated zero-point energy level lies above the top of the potential well the species exhibiting this structure is stable (at low temperatures) with respect to spontaneous deformations to all others.

The term "stability" is often misapplied and misunderstood. In discussing the existence of novel chemical species, it is useful to distinguish clearly between three distinct types: (a) structural stability, corresponding to a species with no imaginary vibrational frequencies; (b) kinetic or chemical stability, implying that in addition to the above the species is not readily altered by its chemical or physical environment; and (c) thermodynamic stability, meaning that in addition to property (a) the thermodynamic equilibria between the species and its possible rearrangements or other reaction products permit detectable amounts of it to exist. Of these, (b), kinetic stability, is by far the most difficult to compute. Also (c), thermodynamic stability, is of special concern for compounds of heavier elements such as those studied here. Therefore we will focus primarily on (a) and (c), the structural and thermodynamic stabilities of the species in question.

An important class of compounds that has drawn increasing interest, both experimentally and theoretically, are those in which the sum of the substituents plus the unshared electron pairs on a given central atom is greater than four—structures often termed "hypervalent" species. Although once thought to be structurally unstable in general due to the inherent nature of their bonding, recent theoretical and experimental data have indicated that many such species are in fact structurally quite stable,[1] with the difficulty in their preparation in the laboratory stemming largely from thermodynamic instabilities.

In this paper we describe ab initio calculations bearing on the structures, energies, and the thermodynamic and structural stabilities of the key sets of neutral compounds PH_n, SH_n, and ClH_n where n is 1, 3, or 5 for Cl; 2, 4, or 6 for S; and 3 or 5 for P. Except for PH (which has a triplet ground state) and ClH_7 (which we have found to be unstable) this series of compounds represents

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all possible combinations of lone electron pairs and bonds to H in electrically neutral species. Of the "hypervalent" species (n = 5 for P; 4 and 6 for S; 3, 5 and 7 for Cl) only SH_4 and PH_5 have previously received a detailed theoretical study including the requisite set of normal-mode vibrational frequencies. SH_4 has been studied with particular care by Yoshioka, Goddard, and Schaefer[2] employing CI gradient techniques. The energy surface of PH_5 has been carefully studied by several authors. Perhaps the more accurate of these, which also include vibrational frequencies, are the work of Kutzelnigg and Wallmeier[3] and Reed and Schleyer.[4] The highly coordinated sulfur compounds have received surprisingly little theoretical attention, despite the current high level of interest among synthetic chemists,[5] and the existence of analogous compounds of chlorine has rarely even been postulated. The nature of the bonding in SR_4, based on the Hückel method, has been studied by Chen and Hoffmann.[6] The structure and energy of SH_6 were computed several years ago by Schwenzer and Schaefer.[7] The energies and symmetries of SH_4, ClH_3, and ClH_5 have been examined[8] by the semiempirical MINDO method, but unfortunately this study apparently gave the wrong symmetry for the structure of each species. More recently studies related to the pseudorotation energy surface has been reported for SH_6[9] and ClH_3.[10] However, it should be emphasized that, when computing the properties of any experimentally unknown species, there is no reason to believe that the structure employed (even when geometrically optimized) is stable or that the species even exists at all unless the set of normal-mode vibrational frequencies have first been computed at a reasonably high level of accuracy and shown to consist entirely of real numbers.

In this paper we also report a systematic study of the energies (including nuclear-motion corrections) and molecular structures of the phosphorus, sulfur, and chlorine compounds delineated above. Of particular interest are ClH_3, ClH_5, and ClH_7, since to our knowledge the structures as well as the structural and thermodynamic stabilities of these species have not been previously reported. Because all of these highly coordinated compounds may be considered as being formed by addition of H or H_2 to a smaller species, we have carried out parallel computations on PH_3, SH_2, and ClH in order to assess the thermodynamic stabilities of the higher members of each series with respect to dehydrogenation to known compounds. Finally, in order to explain the structural instability of very highly coordinated species such as ClH_7 we have carried out an ab initio multicenter analysis of the energy of each compound at the SCF level. Multicenter-energy theory, which has not previously been employed for this type of analysis, permits resolution of the total energy into contributions due to all atomic groupings involving one through four atoms, thus producing separate quantitative values for central-atom/hydrogen and hydrogen/hydrogen contributions to the total energy. It therefore permits a level of detail in the study of highly coordinated (and highly crowded) compounds that is not otherwise possible.

Method

Since we have found that equivocal results (particularly the absence of imaginary vibrational frequencies) may result from employing the Hartree–Fock method alone in dealing with species that may prove to be structurally unstable, all molecular structures and vibrational frequencies reported herein were computed with inclusion of the second-order perturbation approximation,[11] MP2, to the correlation energy. (It was found however that for these particular species the Hartree–Fock and MP2 methods agreed regarding the structural stability in each case.) All energies as well as the structures and frequencies were computed employing the GAUSSIAN 86 program.[12] The multicenter analysis of the energy was performed with a new and separate program we constructed for this purpose.

Table I. Optimized Structural Parameters[a]

	basis	symmetry	X–H	H–X–H
PH_3	I	C_{3v}	1.4051	94.53
PH_5	I	D_{3h}	1.4626 ax	
			1.4137 eq	
SH_2	I	C_{2v}	1.3291	92.84
SH_4	I	C_{4v}	1.3817	87.74
SH_6	I	O	1.3987	
ClH	I	$C_{\infty v}$	1.2682	
	II	$C_{\infty v}$	1.2703	
ClH_3	I	C_{2v}	1.5976 ax	170.46 ax–ax
			1.2638 eq	85.23 ax–eq
	II	C_{2v}	1.6153 ax	170.23 ax–ax
			1.2640 eq	85.12 ax–eq
ClH_5	I	C_{4v}	1.5815 ba	89.70 ba–ba
			1.2623 ap	85.88 ap–ba
	II	C_{4v}	1.5928 ba	89.71 ba–ba
			1.2604 ap	85.89 ap–ba

[a] Bond lengths in Å and angles in deg, optimized in the MP2 approximation. For 4-fold equivalent sets the angle refers to that between neighboring H atoms. Angles ordained by symmetry are not given. Basis I is 66-31G** and II is MC(2d,2p).

Two quite different basis sets were employed. The first, which we will refer to as basis I, consisted of the 66-31G* basis[13] plus a set of p functions on the hydrogen[14] to form the 66-31G** basis. This corresponds to maximally contracted sets of functions in the atomic-core region (a contracted 1s and a contracted 2sp, where sp refers to s and p functions sharing the same exponents) and, in the valence shell, a 6-fold d and two contracted sets of sp functions on the heavy atom as well as two contracted s functions plus a polarization p on each hydrogen. The second set was the one proposed by McLean and Chandler[15] for the heavy atoms. This is maximally contracted only for atomic 1s orbitals, with the remaining five s and five p functions (with differing exponents) describing the 2s, 2p and valence-electron distributions. This was augmented by two 6-fold sets of d primitive functions on the heavy atom and two sets of p functions on hydrogen. The d and p functions were the default values chosen by the program. Their exponents generally straddle those of the 66-31G** set and are approximately the same for the added p set as for the d set. This type of basis set, with the 311G set for the hydrogens is sometimes termed 66-311G(2d,2p), although it is much different in construction from the analogous set[16] for first-row atoms not only in the contraction scheme but also in that the valence p functions are allowed to be much more diffuse than the s. We will refer to this as basis II. All structures and frequencies were computed employing basis I. As a test of their sensitivity to choice of basis set, the total energies and the multicenter analyses were calculated for each species in basis II as well. Since the structures of ClH_3 and ClH_5 have not been reported before, these were reoptimized in basis II.

Energies were computed not only at the MP2 level but also, for comparison, in the SCF and in the fourth-order perturbation approximation (MP4) with single, double, triple, and quadruple excitations. All reported perturbation calculations included only the excitations of the valence orbitals.

Molecular Structures

In Table I we list the symmetry and the bond distances and angles of the equilibrium structure of each species, optimized at

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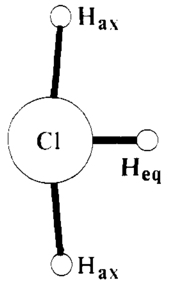

Figure 1. The structure of ClH_3, viewed perpendicular to the plane of symmetry, as computed in the MP2 approximation with the larger basis set (II) and reproduced to scale.

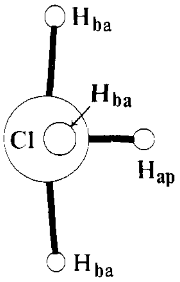

Figure 2. The structure of ClH_5, viewed perpendicular to one of the two H–Cl–H symmetry planes, as computed in the MP2 approximation with the larger basis set (II) and reproduced to scale. Note that one basal hydrogen is obscured by the chlorine.

the MP2/basis I level of approximation. For the smaller species, for which experimental values are known, the accuracy of the computed results is reasonable. The computed bond lengths are 1.405, 1.329, and 1.270 Å for PH_3, SH_2, and ClH, respectively, compared with the reported experimental values[17] of 1.420 (effective), 1.336 (equilibrium), and 1.275 (equilibrium). The bond angles of 94.5° and 92.8° in PH_3 and SH_2 may be compared to the experimental values of 93.3° (effective) and 92.2° (effective), respectively. Clearly PH_3 is particularly difficult to treat accurately, and this may apply to the computed structure of PH_5 as well, as has been described in some detail by Kutzelnigg and Wallmeier.[18] Our computed bond lengths in PH_5 (1.463, 1.414Å) are comparable to the MP2 values in a somewhat smaller basis found by Reed and Schleyer[4] (1.474 and 1.424), the CEPA and CI values reported by Kutzelnigg and Wallmeier[18] (1.47 and 1.42), and the MRD-CI results of Shih, Peyerimhoff, and Buenker[19] (1.48 and 1.43).

Vibrational frequencies were also computed for each of these molecules, and no imaginary frequencies were found, showing that each is structurally stable.

In reporting the structures of the larger molecules, we have employed a nomenclature based on the trigonal bipyramidal structure of PH_5 and the approximate trigonal bipyramidal nature of ClH_3, which lead to distinct axial (ax) and equatorial (eq) positions about the heavy atom (lone pairs occupying equatorial positions in the Cl compound). Similarly ClH_5 is a square pyramid with one apical (ap) and four basal (ba) hydrogen atoms.

For each of these species we have found only one equilibrium conformation. Other symmetric structures, e.g., those obtained by placing lone pairs in axial positions in ClH_3, were found to be unstable in the MP2/basis I approximation. Similarly SH_4, for which early calculations indicated the presence of two conformations, was shown[2] to exhibit only one of C_{4v} symmetry when polarization functions were included in the basis set. We likewise discovered that employing the present level of approximation only one conformation, of C_{4v} symmetry, is found. Thus SH_4 and ClH_5, for reasons that are presently not well understood, prefer the more symmetric structure to one based on a trigonal bipyramid.

The common structural features of ClH_3 and ClH_5 computed in the two basis sets are extremely similar to each other and between basis sets, except for the longer of the two Cl–H bonds which increase noticeably on going to the larger basis. It is tempting to ascribe this difference to the more diffuse nature of the p orbitals in basis II. Therefore as a test we reoptimized ClH_3 in the MP2 approximation but with the 66-31++G** basis (which adds an additional sp set of diffuse primitive functions[20] to both the hydrogen and chlorine). This is the largest of the basis sets employed by Reed and Schleyer[4] in their study of PH_5. The resulting axial and equatorial bond lengths are 1.6149 and 1.2634 Å, respectively, while the bond angles are 170.98° and 85.49°. These bond lengths are essentially the same as in basis II. Hence it seems that the diffuse functions in basis II and in 66-31++G** lead to more accurate values of this parameter.

The computed equilibrium structure of ClH_3 is shown in Figure 1 and ClH_5 in the same orientation in Figure 2. It is remarkable that the bond distances and angles among the chlorine and three coplanar hydrogen atoms are virtually identical between the two compounds. These structures however are analogous to those of ClF_3 and ClF_5, which also exhibit the same symmetries as the hydrogen species. For ClF_3 the experimental values[21] of the axial and equatorial bond lengths are 1.703 and 1.584 Å, respectively, while the F_{ax}–Cl–F_{eq} angle is 87°. In ClF_5 the F_{ap}–Cl–F_{ba} angle is estimated[22] to be 86.5°. The difference between the bond lengths in ClF_5 is apparently not known experimentally.

Optimization of the structure of ClH_7, the chlorine–hydrogen species with all electron pairs involved in bonding, showed that of all species possessing any symmetry, the form of lowest energy is of C_{5v} symmetry, i.e., a pentagonal bipyramid analogous to IF_7.[23] However the frequency calculation showed it to have two imaginary frequencies, indicating that it is a saddle point and not a structurally stable compound.

Minimal Vibrational Frequencies

The computation of all the vibrational frequencies needed to demonstrate structural stability has otherwise little direct bearing on the subject matter of this study, and hence for simplicity these are not explicitly included here. However the magnitudes of the frequencies are indirectly related to the kinetic stabilities of each species since it is highly improbable that a shallow energy well with low barrier to decomposition would be characterized by a high vibrational frequency.

It was found that the vibrational energies were quite similar between compounds with the same corrdination such as ClH_3 and PH_3 or ClH_5 and PH_5. (The phosphorus compounds have somewhat larger average stretching frequencies.) The lowest computed frequency of ClH_3 in the MP2/66-31G** approximation is 1064 cm^{-1}, which is remarkably close to the value of 1078 in PH_3. Similarly the lowest frequency in ClH_5 is 546 compared to 573 in PH_5. The minimum frequencies of SH_2, SH_4, and SH_6 are 1270, 699, and 1422 cm^{-1}, respectively. Since these are all reasonably large values, an argument can be made that the more highly coordinated hydrides will prove to be reasonably stable kinetically as well as structurally.

Energies and Thermodynamic Stabilities

In Table II we list total energies of each species including H and H_2, computed at the MP2/basis I structure, at five levels of approximation: SCF and MP2, both in basis I and II, and MP4

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Table II. Computed Energies[a]

	SCF/basis I	MP2/basis I	SCF/basis II	MP2/basis II	MP4/basis II
H	−0.498 23	−0.498 23	−0.499 81	−0.499 81	−0.499 81
H_2	−1.131 33	−1.157 66	−1.133 00	−1.162 76	−1.170 19
PH_3	−342.454 10	−342.590 14	−342.481 06	−342.629 60	−342.661 03
PH_5	−343.509 56	−343.674 86	−343.545 28	−343.725 25	−343.763 09
SH_2	−398.674 95	−398.821 13	−398.705 34	−398.868 26	−398.895 17
SH_4	−399.663 80	−399.850 04	−399.703 67	−399.909 92	−399.945 96
SH_6	−400.706 89	−400.925 17	−400.761 45	−400.999 94	−401.041 98
ClH	−460.066 21	−460.215 62	−460.097 90	−460.267 76	−460.288 96
ClH_3	−460.969 07	−461.158 35	−461.018 18	−461.243 61	−461.278 43
ClH_5	−461.856 81	−462.113 40	−461.926 57	−462.213 25	−462.259 25

[a] At the MP2/basis I optimized structures, in hartrees. Basis I is 66-31G**, and II is MC(2d,2p).

Table III. Nuclear-Motion Corrections[a]

	E°_{298}	$(TS)^\circ_{298}$		E°_{298}	$(TS)^\circ_{298}$
H	3.72	32.45	SH_4	103.26	63.28
H_2	33.77	38.78	SH_6	166.32	63.10
PH_3	73.97	62.51	ClH	24.90	55.57
PH_5	125.96	64.31	ClH_3	63.27	63.90
SH_2	49.29	61.21	ClH_5	105.76	69.32

[a] Sum of rotational, translational, and vibrational energies computed in the MP2/66-31G** approximation, in kJ/mol.

in basis II. Table III lists the nuclear motion corrections, the sum of rotational, translational, and vibrational terms (not including PV) required to convert energy differences to ΔH°_{298} and ΔG°_{298}. These were likewise computed at the MP2/basis I level.

From these values we may obtain the enthalpies and free energies of the hydrogen addition reactions to go from lower to higher coordination: $PH_3 + H_2 \rightarrow PH_5$, $SH_2 + H_2 \rightarrow SH_4$, $SH_4 + H_2 \rightarrow SH_6$, $ClH + H_2 \rightarrow ClH_3$, and $ClH_3 + H_2 \rightarrow ClH_5$ and also the analogous reactions adding two H atoms rather than H_2. The results are shown in Table IV. All five reactions involving H_2 are seen to be quite endothermic, indicating that with respect to these reactions the highly coordinated species are not thermodynamically stable. The enthalpy and free-energy differences are largest for the chlorine compounds. Thus in the MP4 approximation with basis II, ClH_5 is computed to be higher in free energy than $ClH + 2H_2$ by 1044 kJ/mol (249 kcal/mol).

The enthalpy of the first reaction, $PH_3 + H_2 \rightarrow PH_5$, may be compared to an enthalpy of ca. 176 kJ/mol obtained by applying our nuclear-motion correction to the energy difference of ca. 160 found by Kutzelnigg et al.[3,24] Likewise, we obtain an enthalpy of 232.2 kJ/mol from the energy difference of Reed and Schleyer[4] (which included nuclear-motion corrections). An early estimate of the energy difference between SH_6 and $SH_2 + 2H_2$ was given by Schwenzer and Schaefer[25] as 151. However for the reaction $SH_2 + H_2 \rightarrow SH_4$ Yoshioka, Goddard, and Schaefer[2] estimated the energy difference at their highest level of approximation to be 302.9 which, including the corrections in Table III, gives a ΔH°_{298} value of 320.6, in good agreement with our result.

The enthalpies and free energies for the analogous five reactions which add free H atoms have been less well studied. These are shown in the last two columns in Table IV. The SCF approximation is seen to be quite unreliable for these reactions. However from the MP2 and MP4 results it is clear that PH_5, SH_4, and SH_6 are thermodynamically stable with respect to loss of two hydrogens. In other words, the energy required for homolytic cleavage of the H_2 is more than enough to shift these reactions to the right. Our result for the formation of PH_5 by this route, $\Delta H^\circ_{298} = -229$ kJ/mol, is in qualitative agreement with the rough estimate of Kutzelnigg et al.,[18] $\Delta E \sim -250$. ClH_3 and ClH_5 however are thermodynamically unstable with respect to loss of two H atoms. The relatively small positive enthalpies of the last two reactions at the MP4 level, 52.62 and 79.45, indicate that the "extra" hydrogens are not strongly bound to the chlorine.

Table IV. Computed ΔH°_{298} and ΔG°_{298} for H and H_2 Addition[a]

	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}
	$PH_3 + H_2 \rightarrow PH_5$		$PH_3 + 2H \rightarrow PH_5$	
SCF/basis I	214.95	251.93	−115.30	−52.41
MP2/basis I	207.25	244.23	−192.12	−129.23
SCF/basis II	196.32	233.30	−130.02	−67.13
MP2/basis II	191.95	228.93	−212.54	−149.65
MP4/basis II	194.62	231.60	−229.37	−166.48
	$SH_2 + H_2 \rightarrow SH_4$		$SH_2 + 2H \rightarrow SH_4$	
SCF/basis I	391.81	428.52	61.57	124.19
MP2/basis I	355.75	392.46	−43.61	19.01
SCF/basis II	371.30	408.01	44.96	107.58
MP2/basis II	335.67	372.38	−68.81	−6.19
MP4/basis II	331.20	367.91	−92.78	−30.16
	$SH_4 + H_2 \rightarrow SH_6$		$SH_4 + 2H \rightarrow SH_6$	
SCF/basis I	258.48	297.44	−71.75	−6.88
MP2/basis I	243.50	282.46	−155.87	−91.00
SCF/basis II	224.30	263.26	−102.04	−37.17
MP2/basis II	217.79	256.75	−186.69	−121.82
MP4/basis II	221.55	260.51	−202.44	−137.57
	$ClH + H_2 \rightarrow ClH_3$		$ClH + 2H \rightarrow ClH_3$	
SCF/basis I	601.97	632.42	271.73	328.09
MP2/basis I	566.41	596.86	167.05	223.41
SCF/basis II	560.62	591.07	234.28	290.64
MP2/basis II	492.85	523.30	88.38	144.74
MP4/basis II	476.60	507.05	52.62	108.98
	$ClH_3 + H_2 \rightarrow ClH_5$		$ClH_3 + 2H \rightarrow ClH_5$	
SCF/basis I	645.80	679.16	315.55	374.82
MP2/basis I	538.20	571.56	138.83	198.10
SCF/basis II	595.95	629.31	269.61	328.88
MP2/basis II	513.28	546.64	108.80	168.07
MP4/basis II	503.43	536.79	79.45	138.72

[a] At the MP2/basis I molecular structures and including nuclear-motion corrections. In kJ/mol of product. Basis I is 66-31G**, and II is MC-(2d,2p).

Multicenter Analysis of Molecular Energies

It is an important but often overlooked property of all molecular Hartree–Fock calculations employing the basis set expansion method that the total energy obtained may be resolved exactly and uniquely into multicenter expansion terms, i.e., terms that depend on integration over the cartesian space spanned by basis functions centered on only one locus, a pair of loci, sets of three at a time, and sets of four at a time. Thus

$$E_{\text{total}} = \sum_i E_i^{(1)} + \sum_{ij} E_{ij}^{(2)} + \sum_{ijk} E_{ijk}^{(3)} + \sum_{ijkl} E_{ijkl}^{(4)}$$

where the summations are over all basis set centers. Although meaningful molecular orbital wave functions can be constructed from basis sets consisting of functions centered on positions other than those of the atomic nuclei, the fact that the distribution of total electron density computed from these representations show maxima at the nuclear positions has led to the general employment of nuclei-centered basis sets. Thus the loci in the above equation correspond to the nuclear positions of the constituent atoms of the molecule being studied, and this means that the total SCF energy derived from nuclear-centered basis sets may be decomposed into contributions involving the constituent atoms taken one, two, three, and four at a time. This property was first pointed out by Clementi.[26] We summarize in the Appendix the com-

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Table V. Total One-, Two-, Three-, and Four-Center SCF Energies[a]

	$E^{(1)}$	$E^{(2)}$	$E^{(3)}$	$E^{(4)}$
H_2	-0.430	-0.703		
	(*-0.434*)	(*-0.698*)		
PH_3	-340.555	-2.316	0.425	-0.034
	(*-340.630*)	(*-2.150*)	(*0.362*)	(*-0.036*)
PH_5	-339.846	-6.162	3.100	-0.637
	(*-340.112*)	(*-5.588*)	(*2.751*)	(*-0.560*)
SH_2	-397.394	-1.368	0.058	
	(*-397.606*)	(*-1.114*)	(*0.045*)	
SH_4	-397.176	-4.129	1.987	-0.385
	(*-397.407*)	(*-3.823*)	(*1.910*)	(*-0.344*)
SH_6	-396.149	-8.017	4.661	-1.257
	(*-397.052*)	(*-7.280*)	(*4.766*)	(*-1.141*)
ClH	-459.380	-0.717		
	(*-459.517*)	(*-0.549*)		
ClH_3	-460.153	-1.187	0.297	0.025
	(*-460.275*)	(*-1.036*)	(*0.333*)	(*0.010*)
ClH_5	-460.487	-2.327	0.916	-0.028
	(*-460.913*)	(*-1.749*)	(*0.794*)	(*0.012*)

[a] At the MP2/66-31G** optimized structures. Values in parentheses computed in this basis, others in MC(2d,2p) basis. In hartrees.

putational approach we employ for this analysis.

In rationalizing the structural stabilities of highly coordinated compounds several concepts have been proposed, such as d-orbital participitation in accord with the outmoded sp^3d^n hybridization schemes, high electronegativity differences leading to enhancement of the ionic character of the bonds, and either crowding or attraction between nonbonded atoms. The first two of these are clearly not relevant to relative stabilities of, for example, ClH_5 (stable) and ClH_7 (unstable), since d-function participation in the molecular orbitals (MO's) of such molecules is very small and about the same for both compounds as well as for related compounds in which the central atom exhibits four or less substituents plus electron pairs. In fact with a suitable set of s and p basis functions the shapes of the MO's are hardly affected by omitting d functions entirely. Furthermore the electronegativity differences between hydrogen and the central atom are small for all of the compounds studied here and the same for ClH_5 and ClH_7. On the other hand, Musher[27] has postulated the existence of a "hypervalent bond", a linear three-center four-electron pair of bonding orbitals to account for the stabilities of species such as I_3^-. For the MH_n compounds that are the subject of the present study, these three-center orbitals imply a special stability when three atoms including M are collinear.

The two mechanisms that from the above discussion appear most likely to determine the stabilities of the MH_n compounds, i.e., crowding and "hypervalent bonds," are ones that are directly amenable only to a multicenter analysis. In Table V we list the total $E^{(1)}$, $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ for each of the nine compounds studied. For comparison we show the values computed in both basis I (in parentheses) and basis II, in all cases at the MP2/basis I molecular structure. The results are seen to be somewhat dependent on the choice of basis set, although qualitative differences are well reproduced in both sets. In each case the energies converge rapidly on going from $E^{(1)}$ to $E^{(4)}$. Note that the smaller basis invariably gives a lower $E^{(1)}$ contribution than the larger basis set, the latter giving a lower total energy due to lower $E^{(2)}$ contributions (simple two-center bonding). Perhaps surprisingly, all the three-center bonding terms $E^{(3)}$ are positive, hence destabilizing, whereas the $E^{(2)}$ and $E^{(4)}$ terms confer bonding stability. Both $E^{(3)}$ and $E^{(4)}$ can be quite large in the more highly coordinated species, particularly SH_6.

Table VI. Two-Center SCF Energies,[a] $E^{(2)}$

	centers	individual	total
PH_3	P-H	-0.806	-2.418
	H-H	0.034	0.102
PH_5	$P-H_{ax}$	-1.472	-2.944
	$P-H_{eq}$	-1.191	-3.573
	$H_{ax}-H_{ax}$	-0.040	-0.040
	$H_{ax}-H_{eq}$	0.080	0.480
	$H_{eq}-H_{eq}$	-0.029	-0.087
SH_2	S-H	-0.713	-1.426
	H-H	0.057	0.057
SH_4	S-H	-1.133	-4.532
	$(H-H)_{adj}$	0.132	0.528
	$(H-H)_{opp}$	-0.062	-0.124
SH_6	S-H	-1.431	-8.586
	$(H-H)_{adj}$	0.063	0.756
	$(H-H)_{opp}$	-0.062	-0.186
ClH_3	$Cl-H_{ax}$	-0.009	-0.018
	$Cl-H_{eq}$	-1.152	-1.152
	$H_{ax}-H_{eq}$	0.045	0.090
	$H_{ax}-H_{ax}$	-0.108	-0.108
ClH_5	$Cl-H_{ap}$	-1.690	-1.690
	$Cl-H_{ba}$	-0.176	-0.704
	$H_{ap}-H_{ba}$	0.064	0.256
	$(H_{ba}-H_{ba})_{adj}$	0.009	0.036
	$(H_{ba}-H_{ba})_{opp}$	-0.112	-0.224

[a] Computed in at the SCF/MC(2d,2p) level at the MP2/66-31G** optimized structures. In hartrees.

Table VII. Three-Center SCF Energies,[a] $E^{(3)}$

	centers	individual	total
PH_3	H-P-H	0.137	0.411
	H-H-H	0.013	0.013
PH_5	$H_{ax}-P-H_{ax}$	0.026	0.026
	$H_{ax}-P-H_{eq}$	0.474	2.844
	$H_{eq}-P-H_{eq}$	0.001	0.003
	$H_{ax}-(H_{eq}-H_{eq})$	0.023	0.138
	$H_{eq}-H_{eq}-H_{eq}$	-0.007	-0.007
SH_2	H-S-H	0.058	0.058
SH_4	$(H-S-H)_{adj}$	0.491	1.964
	$(H-S-H)_{opp}$	-0.051	-0.102
	H-H-H	0.031	0.124
SH_6	$(H-S-H)_{adj}$	0.379	4.548
	$(H-S-H)_{opp}$	-0.066	-0.198
	$(H-H-H)_{adj-adj}$	0.030	0.240
	$(H-H-H)_{adj-opp}$	0.006	0.072
ClH_3	$H_{ax}-Cl-H_{eq}$	0.248	0.496
	$H_{ax}-Cl-H_{ax}$	-0.174	-0.174
	H-H-H	-0.026	-0.026
ClH_5	$H_{ap}-Cl-H_{ba}$	0.307	1.228
	$(H_{ba}-Cl-H_{ba})_{adj}$	0.031	0.124
	$(H_{ba}-Cl-H_{ba})_{opp}$	-0.190	-0.380
	$H_{ap}-(H_{ba}-H_{ba})_{adj}$	-0.003	-0.012
	$H_{ap}-(H_{ba}-H_{ba})_{opp}$	-0.012	-0.024
	$H_{ba}-H_{ba}-H_{ba}$	-0.006	-0.024

[a] Computed at the SCF/MC(2d,2p) level at the MP2/66-31G** optimized structures. In hartrees.

In Table VI are listed the individual two-center energies for the seven polyatomic molecules. In this and the following tables we show, for clarity, only values corresponding to the larger basis, basis II. For the species SH_4, SH_6, and ClH_5, for which there are 4 -fold planes of symmetry, atoms and bonds are designated as adjacent or opposed, depending on whether they are on adjoining or opposite sides of the square. Note that P-H, S-H, and Cl-H energies become more negative (stabilizing) on going from PH_3 to PH_5, from SH_2 to SH_4 and SH_6, and from ClH to ClH_3 and ClH_5. The $P-H_{ax}$ and $P-H_{eq}$ energies are quite similar in PH_5, while the $Cl-H_{ax}$ and $Cl-H_{eq}$ energies in ClH_3 are much different, as are the $Cl-H_{ap}$ and $Cl-H_{ba}$ energies in ClH_5. The "through-space" (H-H) energies are smaller but still appreciable, especially in the more highly coordinated species. In all cases where there are three collinear atoms there is a negative energy, as might be expected from a "hypervalent bond", but it is relatively small and tends to be overwhelmed by positive terms arising from repulsions between nearest-neighbor (noncollinear) hydrogens. It is the most negative in ClH_5, tending to stabilize the binding of both diagonal pairs of "extra" hydrogen atoms.

The three-center energies, shown in Table VII, may be considered as corresponding to attractions or repulsions between three atoms, as in "three-center bonds," or between pairs of "two-center

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Table VIII. Multicenter Analysis[a] of the Unstable D_{5h} Optimized Structure of ClH_7

	centers	individual	total
$E^{(1)}$	Cl	−455.820	−455.820
	H_{ax}	−0.287	−0.574
	H_{eq}	−0.415	−2.075
$E^{(2)}$	$Cl-H_{ax}$	−1.323	−2.646
	$Cl-H_{eq}$	−1.911	−9.555
	$H_{ax}-H_{eq}$	0.001	0.010
	$H_{ax}-H_{ax}$	−0.060	−0.060
	$(H_{eq}-H_{eq})_{1,2}$	0.164	0.820
	$(H_{eq}-H_{eq})_{1,3}$	0.023	0.115
$E^{(3)}$	$H_{ax}-Cl-H_{ax}$	−0.124	−0.124
	$H_{ax}-Cl-H_{eq}$	0.388	3.880
	$(H_{eq}-Cl-H_{eq})_{1,2}$	1.266	6.330
	$(H_{eq}-Cl-H_{eq})_{1,3}$	0.019	0.095
	$H_{ax}-(H_{eq}-H_{eq})_{1,2}$	0.060	0.600
	$H_{ax}-(H_{eq}-H_{eq})_{1,3}$	−0.036	−0.360
	$(H_{eq}-H_{eq}-H_{eq})_{1,2,3}$	−0.054	−0.270
	$(H_{eq}-H_{eq}-H_{eq})_{1,2,4}$	−0.105	−0.525
	$(H_{ax}-H_{eq}-H_{ax})$	0.021	0.105
$E^{(4)}$			−2.722

[a] Computed at the SCF/MC(2d,2p) level at the MP2/66-31G** optimized structure. In hartrees.

bonds." The energy contributions (all quite small) due to sets of three hydrogen atoms (H–H–H) are positive except for the equatorial set in PH_5 and all hydrogen triplets in ClH_3 and ClH_5. Many of the H–M–H atom triplets in these MH_n compounds exhibit positive energy contributions that may be considered to be due primarily to "through-bond" repulsions of the hydrogens or alternatively as repulsions between adjacent M–H bonds themselves. Repulsion between the central bonding region of each of a pair of M–H bonds must show up in the H–M–H three-center terms. Except for PH_5, all collinear three-center energies have appreciably negative values (Musher's "hypervalent bonds"), but they are much smaller than the repulsions and hence are not significant contributors to the stability of the molecule. Not surprisingly the H–M–H repulsions between hydrogens increase rapidly with increasing degree of coordination, going from 0.411 hartrees in PH_3 to 2.972 in PH_5, from 0.058 in SH_2 to 1.964 in SH_4 and to 4.548 in SH_6, and from 0.496 in ClH_3 to 1.352 in ClH_5. Comparing Tables VI and VII it is clear that for the more highly coordinated species this repulsion energy tends to cancel out the attractive two-center P–H, S–H, and Cl–H bonding energies.

A verification of the meaningfulness of this interpretation is provided by the detailed study of the orbital electron densities in PH_5 by McDowell and Streitwieser.[28] They found that the canonical molecular orbitals exhibited little or no three-center bonding involving the phosphorus and axial hydrogen atoms. Except for the totally symmetric valence orbital, all orbitals involving the axial hydrogens place virtually all the electron density on the hydrogens, resulting in a two- rather than three-center stabilization of these centers. This is also seen directly from the appropriate values in Tables VI and VII, −0.040 and +0.026, respectively.

In summary, three-center bonding does not stabilize the structure of PH_5, is slightly stabilizing in the sulfur hydrides, and is relatively important only in ClH_3 and ClH_5.

This analysis now suggests a reason why, of all the XH_n compounds in this series, only ClH_7 is structurally unstable. The results of the multicenter analysis for the optimized structure constrained to be of D_{5h} symmetry is shown in Table VIII. The collinear three-center energy is appreciable (−0.124 hartrees), but only one of these is possible while maintaining D_{5h} symmetry. Although the Cl–H binding energy (−12.201) is much larger than in ClH_5 (−2.394), it is almost completely cancelled by the repulsions between hydrogens (+10.511) of which +10.210 hartrees are due to three-center "through-bond" repulsions between neighboring hydrogen atoms. Were it not for the latter, ClH_7 would be an extremely stable species, with seven nearly equal Cl–H bonds.

Conclusions

Although highly coordinated fluorine compounds of second-row elements have been known for many years, the analogous hydrogen compounds have never been prepared. Our present results indicate that this does not mean that the hydrogen compounds are structurally unstable, and in fact it now appears likely that the existence of many such highly coordinated species is possible for atoms throughout the second and further rows of the Periodic Table. The polyhydrides are invariably unstable thermodynamically with respect to loss of H_2, which may complicate their preparation in the laboratory. However, it should be noted in this regard that PH_3 is thermodynamically unstable[29] with respect to dissociation into P_4 and H_2 even at room temperature, but the reaction does not proceed appreciably at temperatures below several hundred deg Celsius. The energies for the decomposition reactions of the MH_n compounds tend to be greater than those involving fluorine. For example, recent ab initio calculations[30] of ΔE for the reaction $ClF + F_2 \rightarrow ClF_3$ gave −59.3 kJ/mol, in comparison with the quoted experimental value of −113. The bond angles of the hydrogen compounds are very similar to those of the fluorine analogues in all cases, including ClH_3 and ClH_5, whose structures, thermodynamic properties, and structural stabilities we report here for the first time.

It is important to note that going from a lower degree of coordination to a higher one does not necessarily imply a decrease in stability. For example, Table IV shows that considerably less energy is required to form SH_6 from SH_4 than to form SH_4 from SH_2. Similarly Tables VI and VIII show a steady increase in two-center bond energy in each case on going from the lower to higher coordination.

The ab initio multicenter analysis is a particularly useful way of examining the nature of the bonding in these systems. It not only allows distinguishing strong from weak bonds and two-center from three-center bonding but also more importantly it gives the first quantitative measure of the factors leading to stability and instability in highly coordinated species such as ClH_7. The three-center "hypervalent bond" is found to be present but relatively weak for these compounds with hydrogen, particularly for the PH_n and SH_n species. It may however be strong enough to influence conformations, and its weakness in the sulfur compounds may explain why SH_4 does not assume a trigonal-bipyramidal structure. Our conclusion that instability in "hypervalent" compounds of this type is due to crowding among substituents agrees with a similar conclusion by Dewar and Healy[31] with respect to carbon compounds. However it is not the "through-space" repulsion between hydrogen atoms that might be expected but rather a three-center "through-bond" interaction via the central atom—a situation that can be interpreted as "interbond repulsion" due to crowding. (Indeed stable carbon–lithium compounds in which the carbon is coordinated to more than four lithium atoms apparently owe their stabilities to attraction and incipient bond formations, as opposed to repulsions, between lithiums.[32]) We believe that, by giving a quantitative measure of the individual stabilizing and destabilizing terms, analyses of multicenter expansions may ultimately lead to a more systematic procedure for searching for stable species with novel types of bonding whose existence would not otherwise be suspected either experimentally or through standard theoretical methods.

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Acknowledgment. This work was supported by the Air Force Office of Scientific Research, AFSC, under Grant AFOSR-86-0146.

Appendix

As noted above the total energy of any molecule in the SCF approximation, assuming the wave function is expanded in terms of basis functions, may be written as a sum of terms each of which is identified only by basis function indices. Thus any criterion that is used to segregate basis functions into unique sets, such as the nuclei on which they are centered, will lead to an exact decomposition of the energy. In general

$$E_{\text{total}} = \sum_{n} E_n^{(1)} + \sum_{mn} E_{mn}^{(2)} + \sum_{lmn} E_{lmn}^{(3)} + \sum_{klmn} E_{klmn}^{(4)}$$

where the sum in each case is over all sets, such as all the functions centered on a particular nucleus, to which a basis function may belong.

This is most readily seen (and computed) in terms of the density matrix. In the case of a multibody expansion in terms of nuclei, the one-center energy for nucleus n, $E_n^{(1)}$, is composed of one-center kinetic, nuclear-attraction and two-electron repulsion terms

$$E_n^{(1)} = \sum_{ij\,\text{on}\,n} d_{ij}(\langle i|-\nabla^2/2|j\rangle + \langle i|-Z_n/r|j\rangle) + \tfrac{1}{4}\sum_{ijkl\,\text{on}\,n} p_{ijkl}(2d_{ij}d_{kl} - d_{ik}d_{jl})$$

$E_{mn}^{(2)}$ consists of kinetic, nuclear-attraction, two-electron, and nuclear–nuclear repulsion terms

$$\begin{aligned} E_{mn}^{(2)} = {} & 2\sum_{i\,\text{on}\,n}\ \sum_{j\,\text{on}\,m\neq n} d_{ij}(\langle i|-\nabla^2/2|j\rangle + \langle i|-Z_m/r|j\rangle + \langle i|-Z_n/r|j\rangle) + \\ & \sum_{ij\,\text{on}\,m\neq n} d_{ij}\langle i|-Z_n/r|j\rangle + \sum_{ij\,\text{on}\,n\neq m} d_{ij}\langle i|-Z_m/r|j\rangle + \\ & \tfrac{1}{4}\sum_{ijkl\,\text{on}\,n,m\neq n} p_{ijkl}(2d_{ij}d_{kl} - d_{ik}d_{jl}) + Z_mZ_n/R_{mn} \end{aligned}$$

where d are the density matrix elements and p are matrix elements of the two-electron repulsion $1/r_{12}$. Similarly $E_{lmn}^{(3)}$ = nuclear attraction and two-electron terms, and $E_{klmn}^{(4)}$ = two-electron terms only.

The physical meaning of these terms is that for a given electron distribution $E^{(1)}$ is the energy obtained computing the requisite integrals by integrating over the region of space occupied by basis functions centered on one atom at a time, $E^{(2)}$ is obtained by integrating the electron distribution over the regions of space occupied by basis functions on two centers simultaneously, $E^{(3)}$ depends on integration over the space of functions on three centers simultaneously, etc. In other words, this accords with the conventional concepts of the energies of "two- and three-center bonds".

It is interesting to compare this approach with the "localized orbitals" proposed by Boys,[33] Edmiston and Ruedenberg,[34] England, Gordon, and Ruedenberg,[35] and others. These are intended primarily to rationalize molecular electron distributions in terms of molecular orbitals that have been transformed among themselves according to various localization criteria. Localized orbitals may involve basis functions on one, two, and in some cases three centers. Their application to three-center bonds involving boron compounds in particular has been discussed by Lipscomb.[36] Although these are powerful methods for analyzing wave functions, they have several drawbacks, primarily due to arbitrariness in the way they are defined and the frequent failure of differing approaches (or even the same approach) to agree for a specific case. The practical and conceptual problems have been described in some detail by Kleier et al.[37]

Once obtained, the importance or unimportance of a particular orbital in stabilizing a molecular structure is to be assayed, generally simply by viewing its graphical representation or determining its orbital population. Hence the greatest drawback to employing localized orbitals for the type of problems studied herein is the difficulty in obtaining quantitative interpretations of them, particularly in terms of energies.[38] By contrast the multicenter resolution of the energy has the advantages of yielding unique and quantitative values of the energy directly (independently of how the orbitals are transformed), which is more widely understood than localized orbital populations and which is connected directly with molecular energetics and thermodynamic quantities such as equilibrium constants.

A major impetus for developing localized orbitals was the desire to force quantum calculations to fit into traditional concepts of chemical bonding. In the widely accepted Pauling description, the energy of formation of a gaseous molecule from its constituent gaseous ground-state atoms is partitioned *in its entirety* between the bonds, whereas the treatment presented here shows that the sum of the values of $E^{(2)}$ for each bonded pair of atoms (the energy contribution due to the two-center bonds) corresponds to only a fraction of the total energy of this molecule-formation reaction. Consider that if an MX_n structure describable in terms of n M–X two-center bonds is chemically converted into an $MX_{n-i}Y_i$ molecule, then not only will the $E^{(2)}$ of i M–X connections be replaced by an equal number of $E^{(2)}$ values corresponding to M–Y but also there will be significant changes in the values of $E^{(1)}$, particularly the $E^{(1)}$ corresponding to M and the $E^{(1)}$ replacements due to substitution of X's by Y's. Moreover, there will be replacements in the $E^{(2)}$ repulsion terms involving X⋯X interactions by some X⋯Y ones, and there will be commensurate changes in the $E^{(3)}$ and $E^{(4)}$ terms. That there is hence a great difference between the energy of a reaction such as those studied herein and the energies of individual bonds is immediately apparent from examination of Tables IV, VI, and VII above.

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