Theoretical Study of SN2 Reactions. Ab Initio Computations on HF and CI Level

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Abstract: We report ab initio computations on the Hartree–Fock level and including effects of electron correlation for the following SN2 reactions: $ACH_3 + B^- \rightarrow A^- + H_3CB$ (A, B = H, F, Cl), $FH + F^- \rightarrow F^- + HF$, $H_2 + H^- \rightarrow H^- + H_2$, $FSiH_3 + F^- \rightarrow F^- + H_3SiF$. The corresponding barriers and reaction energies (in vacuo) are determined with an accuracy of a few kilocalories per mole. It is found that electron correlation contributes up to ±7 kcal/mol to the corresponding ΔE and, consequently, cannot be neglected even in these reactions which are of closed shell type.

I. Introduction

Ab initio computations which account for effects of electron correlation, by definition neglected on the HF level, are still rare for chemically interesting molecules although quite efficient methods have recently been developed for this purpose. Since the corresponding computation times are roughly an order of magnitude larger than for a treatment on the HF level, it is desirable to assess in a direct way the reliability of the HF approximation.

Comparison between HF results and experiments as well as direct ab initio computations of correlation effects prove the usefulness of the HF method for the determination of equilibrium geometries and for a conformation analysis. A deviation (between HF and experiment) of about 5% in the interatomic distance as found for F_2[1,2] is already exceptionally large. More pronounced is the error in the force constants k_e which may amount to 74% for F_2[1,2] or 30% for N_2.[2]

It is now also well established that there are only minor changes (less than 1 kcal/mol) of the correlation energy E_c for processes as the internal rotation of ethane (for some recent computations see ref 2-6), inversion of NH_3,[7-10] CH_3^-,[10] SiH_3^-,[11] or the pseudorotation of SiH_5^-.[11] The corresponding effect is slightly larger for the inversion of PH_3 where E_c changes by 2.5 kcal/mol.[12]

The HF approximation, however, is of virtually no use as far as the calculation of reaction energies is concerned if the number of paired electrons changes in the reaction (formation of bonds) as for the formation of F_2 or N_2 from the atoms or the formation of N_2O_4 from $2NO_2$.[13]

The most favorable case for the HF approximation is probably a "closed shell reaction" for which the electronic wave function has closed shell structure along the entire reaction path. It is in fact often assumed that these reactions are comparable to the internal processes just mentioned and that E_c may be considered approximately constant along the reaction path.[14-16]

E_c may change appreciably, however, even in closed shell reactions: For the dimerization of BH_3

$$2BH_3 \rightarrow B_2H_6 \qquad (1)$$

ΔE_c contributes about 16 kcal/mol to the total ΔE_f of 36 kcal/mol.[17,18]

In the present work we report a systematic study of some SN2 reactions

$$ACH_3 + B^- \rightarrow A^- + H_3CB \qquad (2)$$

$$(A, B = H, F, Cl)$$

$$FH + F^- \rightarrow [FHF]^- \qquad (3)$$

$$H^- + H_2 \rightarrow H_2 + H^- \qquad (4)$$

$$F^- + H_3SiF \rightarrow FSiH_3 + F^- \qquad (5)$$

For all these reactions we can treat reactants, products, and transition states (or intermediate states) in a consistent way since we have to deal with electronic closed shell states only. In the discussion we will also include the results of a recent study of SiH_5^- by the present authors.[11]

We thus cover quite different types of reactions with symmetric transition (or intermediate) states showing quite strong bonds (SiH_5^-, $[FHF]^-$, $SiH_3F_2^-$) or rather weak bonds (CH_5^-, $CH_3F_2^-$), unsymmetric transition states (CH_4F^-, CH_4Cl^-), reactions with the same partitioning of valence electrons in reactants and products (reaction 2 with (A, B) = (H, H), (F, F), (Cl, Cl)), and also reactions with quite different partitionings (like (A, B) = (H, Cl), (H, F)).

A discussion of all these results should provide a representative picture of the effects of electron correlation on barriers and reaction energies in closed shell reactions. We note that several extensive theoretical studies (on the HF level) of bimolecular SN2 reactions have been performed.[19-21] Dedieu and Veillard[20] reported reaction paths, geometries of transitions states, barriers, and reaction energies and discussed the theoretical results in connection with the basicity of the incoming and leaving group, the Hammond postulate,[22] and rules given by Thornton.[23] Therefore, we shall not discuss these topics in detail and concentrate on effects of electron correlation. Dedieu et al.[14] have also reported ab initio computations of correlation energies for the reactions involving CH_5^-, $CH_3F_2^-$, and H_3^- as transition states. In the present study we use a more extended basis set and a different method of computation.

Last but not least we point out that experimental results for activation and reaction energies, in vacuo, for the reactions considered in this work are difficult to obtain and, hence, rare and still somewhat uncertain.[24]

II. Theoretical Methods

We have employed the PNO-CI (Pair Natural Orbital Configuration Interaction) and the CEPA-PNO (Coupled Electron Pair Approximation with PNOs) method to compute correlation energies.[25,26] We shall discuss only a few aspects of the theory since the methods used as well as technical details of the corresponding computer programs have been described elsewhere.[26-28] The PNO-CI is virtually identical with a CI which includes all doubly substituted configurations besides the HF wave function. Although this approach accounts for the bulk of the correlation energy it is not suited for the computation of accurate reaction and activation energies.[11,17] This deficiency results from the fact that the number of higher than doubly substituted terms and, hence, their contribution to the energy, increases strongly with the number of electrons.[26] For

Table I. Compilation of Basis Sets

Atom	No.	Huzinaga basis[a]	Contraction	Additional basis functions	
				Type	Exponent η
H	1	4s	(3, 1)	p	0.75
	2	4s	(3, 1)	s/p	0.04/0.3
	3	4s	(3, 1)	p	0.6
	4	5s	(3, 1, 1)	$s/p_1/p_2/d$	0.03/0.17/0.5/0.55
	5	5s	(3, 1, 1)	$p_1/p_2/d$	1.0/0.35/0.8
	6	5s	(3, 1, 1)	$p_1/p_2/d$	0.4/1.6/1.2
C	7	8s; 4p	(5, 1, 1, 1; 3, 1)	d	0.7
F	8	8s; 4p	(5, 1, 1, 1; 3, 1)	p/d	0.09/1.6
	9	8s; 4p	(5, 1, 1, 1; 3, 1)	p/d	0.09/1.2
	10	10s; 6p	(5, 5 × 1; 4, 1, 1)	$p/d_1/d_2$	0.07/0.75/2.25
Cl	11	10s; 6p	(5, 5 × 1; 4, 1, 1)	p/d	0.07/0.6
Si	12	11s; 7p	(5, 6 × 1; 4, 1, 1, 1)	d	0.4
H	13	4s	(3, 1)	p	0.433
H	14	5s	(3, 1, 1)	s/p	0.03/0.75

[a] See ref 32.

a reaction

$$A + B \rightarrow D \tag{6}$$

it is consequently not reasonable to compute the reaction energy ΔE_f from

$$\Delta E_f = E_D^{\text{PNO-CI}} - (E_A^{\text{PNO-CI}} + E_B^{\text{PNO-CI}}) \tag{7}$$

It is certainly more consistent to compare only computations for systems with the same number of electrons. This requires an additional calculation for the system A···B at sufficiently large intermolecular distance and then to obtain ΔE_f according to

$$\Delta E_f = E_D^{\text{PNO-CI}} - E_{A\ldots B}^{\text{PNO-CI}} \tag{8}$$

The deviation between (7) and (8) is by no means negligible and amounts to 6.8 kcal/mol for reaction 1 and to 15 kcal/mol for the process $CH_3F + F^- \rightarrow CH_3F_2^-$. Similar effects occur, of course, in the computation of reaction energies if the partitioning of electrons changes appreciably from reactants to products, as for $CH_3Cl + H^- \rightarrow CH_4 + Cl^-$.

None of the just mentioned difficulties occur in the CEPA. Within this method one includes the higher than doubly substituted configurations in an approximate but consistent way. Within this method one therefore has

$$E_{A\ldots B}^{\text{CEPA}} = E_A^{\text{CEPA}} + E_B^{\text{CEPA}} \tag{9}$$

$$\Delta E_f = E_D^{\text{CEPA}} - (E_A^{\text{CEPA}} + E_B^{\text{CEPA}}) \tag{10}$$

The corresponding eq 8 and 10 give nearly the same result for ΔE_f. Within the CEPA one saves an additional computation for the reacting systems at large intermolecular distance.

The CEPA is, however, not a strictly variational method since the higher than doubly substituted configurations are treated in an approximate way. The PNO-CI is, of course, variational. Various recent applications prove the usefulness of the CEPA which gives, for example, more reliable bond distances, force constants, etc.,[2,10,12,29] than the PNO-CI.

The CEPA has the further advantage that it allows one to split the computation of correlation energies into several independent calculations provided one starts from localized rather than canonical SCF-MO's. In this work we always used localized SCF-MO's determined according to Boys' method.[30]

It can be shown[25,26] that the CEPA correlation energy E_c^{CEPA} can be written as a sum of contributions $\mathcal{E}_n^{\text{CEPA}}$ corresponding to the pairs n of occupied HF-MO's.

$$E_c^{\text{CEPA}} = \sum_n \mathcal{E}_n^{\text{CEPA}} \tag{11}$$

Although the $\mathcal{E}_n^{\text{CEPA}}$ are in principle molecular quantities they are nevertheless of essentially local character. This fact is not only expected by chemical and physical intuition but has also been verified by a detailed analysis of the $\mathcal{E}_n^{\text{CEPA}}$.[2,10-12,17,26] In order to obtain $\mathcal{E}_n^{\text{CEPA}}$ it is therefore sufficient to include in a CEPA treatment besides the pair n only those pairs m which have relatively strong interactions with the pair n.

Let us consider HF_2^- to demonstrate how this fact may be used in the computations. We denote the localized valence shell MO's on F by n_1, n_2, n_3 (lone pair orbitals), and b (bond pair) and use primed labels for the MO's on the second F atom. First of all we can neglect the pair correlation energies for pairs n = (n_i, n_j'), since $|\mathcal{E}_n^{\text{CEPA}}| \leq 0.0001$ au for all these cases. This is an advantage of using localized MO's since no $\mathcal{E}_n^{\text{CEPA}}$ is negligible in general in a delocalized description.

The remaining $\mathcal{E}_n^{\text{CEPA}}$ can then be obtained from a computation in which only the electrons in n_1, n_2, n_3, b, and b′ are correlated. The total correlation energy obtained in this way differs by 0.4 kcal/mol from a treatment in which all valence electrons were correlated simultaneously. The small deviation is due to the fact that interactions between pairs (n, m) like n = (b, b′) and m = (b', n_i') were neglected in this smaller computation.

We have taken advantage of this feature of the CEPA to split the computation of $CH_3F_2^-$, $CH_3Cl_2^-$, and $SiH_3F_2^-$ since the present program could not deal with more than ten occupied MO's simultaneously in the CEPA part.

We note that it is not possible to split a PNO-CI computation. $E_c^{\text{PNO-CI}}$ may be decomposed in analogy to (11), but the contributions $\mathcal{E}_n^{\text{PNO-CI}}$ depend on the number of electrons correlated and are to a much smaller degree than $\mathcal{E}_n^{\text{CEPA}}$ local properties, as has also been shown in recent treatments.[17]

III. Basis Sets

Contracted Gaussian lobes were used as basis sets. A compilation of all basis sets used is given in Table I. AO's of p, d, and f type are constructed as described elsewhere.[31] We started from a contracted Huzinaga basis[32] of about double ζ quality, augmented by additional functions.

For the treatment of negative ions and ionic compounds it is necessary to augment the basis by sufficiently spread out AO's as described in detail in ref 19, 33-36. We consequently included, if necessary, an additional s type AO on hydrogen and a p set for fluorine and chlorine as described in Table I. In all computations we further included a complete set of polarization functions, a p set on H, and a d set for carbon, fluorine, and chlorine. This basis gives 70-80% of the valence correlation energy. The basis set for SiH_5^- also included a second d set and an f set on Si as mentioned in ref 11. The orbital exponents η for the polarization functions were roughly optimized with respect to the total energies (HF + correlation energy) for the respective molecule[10,12] or a corresponding model case. Let us mention an example for this procedure. The orbital exponent η of the fluorine d AO was $\eta = 1.6$, as in HF,[10] or $\eta = 1.2$, as in F^-, depending on the case. We have checked that $\eta = 1.6$ is also optimal for CH_3F and $\eta = 1.2$ for HF_2^-. These exponents are somewhat different from those which one would obtain if one optimizes the exponents with respect to the HF energy only.

As the double ζ type basis sets were augmented by diffuse functions, the basis sets actually used should rather be better than double ζ quality. This does not mean, of course, that our total energies are comparable or even lower than those obtainable with Slater type double ζ sets, since we did not care to obtain highly accurate approximations for the inner shell MO's which contribute most to total energies. What we mean by "double ζ or better" is that we have at least two adjustable linear parameters for valence s and p AO's (and in addition a complete set of polarization functions, of course). In some cases we use a somewhat different basis set as will be discussed in the corresponding context.

IV. Results

(a) **Geometries.** We first list the geometries used for the systems discussed in this work. A detailed comparison of structures of most of the molecules treated here has recently been given elsewhere.[37] For this reason we will compare with previous work for HF_2^- and H_3^- only. The geometries computed in this work have been determined on the HF level if not stated differently. The geometries of transition states have been obtained by multidimensional search for the saddlepoint of the potential hypersurface. We did not vary, however, the $(C\text{-}H_{eq})$ distance in the ACH_3B^- cases since this distance has little influence on the total energy and, as Dedieu and Veillard found,[20] changes very little (about 0.01 au) in different transition states.

The following geometries were used in the final computations; structure parameters given without reference have been determined in this work:

$$H_3^-(D_{\infty h}): \qquad d(\mathrm{H\text{-}H}) = 2.05 \text{ au}$$

This result was obtained from a fit of total energies including correlation. On the HF level we get $d(\mathrm{H\text{-}H}) = 2.04$ au. The rather small deviation of 0.01 au in the H-H distance indicates again the reliability of the HF approximation as far as geometries are concerned.

For comparison we give the distance which was found by Macias,[38] namely 2.02 au.

$HF_2^-(D_{\infty h})$: $\quad d(\mathrm{H\text{-}F}) = 2.1$ au[39]

Other results were 2.12 au[40] and 2.13 au[41]

$CH_4(T_d)$: $\angle \mathrm{HCH} = 109°28'$, $d(\mathrm{C\text{-}H}) = 2.066$ au[42]

$CH_5^-(D_{3h})$: $d(\mathrm{C\text{-}H_{ax}}) = 3.28$ au, $d(\mathrm{C\text{-}H_{eq}}) = 2.01$ au[20]

$$CH_3F(C_{3v}): d(\mathrm{C\text{-}F}) = 2.68 \text{ au}, d(\mathrm{C\text{-}H}) = 2.04 \text{ au}, \angle \mathrm{HCH} = 108°30'$$

$$HCH_3F^-(C_{3v}): d(\mathrm{C\text{-}H_{eq}}) = 2.01 \text{ au}, d(\mathrm{C\text{-}H_{ax}}) = 3.66 \text{ au}, \angle \mathrm{H_{eq}CF} = 90°, d(\mathrm{C\text{-}F}) = 3.70 \text{ au}$$

Additional computations by the present authors confirmed these results of Dedieu and Veillard.[20]

$$CH_3F_2^-(D_{3h}): d(\mathrm{C\text{-}F}) = 3.41 \text{ au}, d(\mathrm{C\text{-}H}) = 2.01 \text{ au}$$

On the HF level we reproduced the result of Dedieu and Veillard:[20] $d(\mathrm{C\text{-}F}) = 3.55$ au. Since inclusion of electron correlation is liable to shorten the C-F distance for the transition state, we performed an additional computation for a C-F distance of 3.41 au. This led to a negligibly higher HF energy (0.0003 au) but to a lowering of the total energy by 0.0011 au on the CEPA level. We therefore discuss in the following the computation with the shorter C-F distance only.

$CH_3Cl(C_{3v})$: $d(\mathrm{C\text{-}Cl}) = 3.37$ au, $d(\mathrm{C\text{-}H}) = 2.098$ au, $\angle \mathrm{HCCl} = 108°25'$[43]

$$HCH_3Cl^-(C_{3v}): d(\mathrm{C\text{-}H_{eq}}) = 2.01 \text{ au}, d(\mathrm{C\text{-}Cl}) = 4.01 \text{ au}, \angle \mathrm{HCCl} = 97°14', d(\mathrm{C\text{-}H_{ax}}) = 4.00 \text{ au}$$

$$CH_3Cl_2^-(D_{3h}): d(\mathrm{C\text{-}Cl}) = 4.518 \text{ au}, d(\mathrm{C\text{-}H}) = 2.01 \text{ au}$$

$$ClCH_3F^-(C_{3v}): d(\mathrm{C\text{-}H}) = 2.01 \text{ au}, d(\mathrm{C\text{-}Cl}) = 3.915 \text{ au}, d(\mathrm{C\text{-}F}) = 4.114 \text{ au}, \angle \mathrm{HCCl} = 98°50'$$

$SiH_3F_2^-(D_{3h})$: $d(\mathrm{Si\text{-}H}) = 2.864$ au, $d(\mathrm{Si\text{-}F}) = 3.18$ au[37]

$SiH_3F(C_{3v})$: $d(\mathrm{Si\text{-}H}) = 2.773$ au, $d(\mathrm{Si\text{-}F}) = 3.013$ au, $\angle \mathrm{HSiF} = 108.7°$[37]

$$H_2(D_{\infty h}): d(\mathrm{H\text{-}H}) = 1.4 \text{ au}$$

$HF(C_{\infty v})$: $d(\mathrm{H\text{-}F}) = 1.73$ au[44]

(b) **Reliability of Computed Reaction Energies and Barriers.** The rather extended basis sets on H and F (line 4 and line 10 of Table I) were used only in computations on reactions 3 and 4 to assess the reliability of the standard basis used in the remaining cases. The larger basis contains at least three adjustable linear parameters in the valence shell and two sets of polarization functions. It should therefore give highly accurate results for reaction energies and barriers. The results obtained in using the two basis sets for ΔE_f of the reaction

$$F^- + HF \rightarrow [FHF]^-$$

differ by about 2 kcal/mol on the HF and on the CEPA level. But the correlation contribution differs by 0.18 kcal/mol only. The computed barriers for reaction 4 differ by 1.5 and 1.8 kcal/mol (see Table III), respectively. The correlation contribution changes by 0.3 kcal/mol only. We are therefore confident that the present results predict barriers and reaction energies with an accuracy of a few kilocalories per mole.

These examples further indicate that we get a quite reliable description of correlation effects since the HF results for the corresponding energy differences change more than the correlation energy contributions if one goes from the small to the larger basis. Larger errors are liable, however, for the reactions including chlorine, since this basis is poorer than those used for the other atoms.

(c) **Discussion of Computed Reaction Energies and Barriers.** The computed total energies are listed in Table II. In discussing the results collected Table III, we refer to the various reactions as numbered in this table. Let us first consider reactions 1, 3, 4, 5, and 6 which have H^- as entering group.

The difference of two barriers in reaction 1 and 3 is easily explained. In H_2 no drastic change in structure is necessary to form the transition state H_3^-, whereas in CH_4 one has to bend three C-H bonds for this purpose. The situation is different in reaction 4. As a consequence of the larger d orbital participation, SiH_5^- is even stable with respect to H^- and SiH_4.[11]

The barrier in reaction 5 is much lower than in reaction 3 in agreement with the chemical experience that F^- is a better leaving group than H^-. This holds even more for reaction 6, where we have a "negative barrier" (which will be discussed immediately). The reason for this is that the three-center four-electron bonds in CH_4F^- and CH_4Cl^- are more stable than in CH_5^- in accordance with the model of Rundle,[45] since F and Cl are much better electron acceptors than H.

Table II. Compilation of Total Energies[a] in au

No.	System	Basis set[b]	HF	PNO-CI	CEPA-PNO
1	H^-	2	−0.4860	−0.5182	−0.5182
2	H^-	4	−0.4875	−0.5241	−0.5241
3	F^-	9	−99.4014	−99.5942	−99.6023
4	F^-	10	−99.4533	−99.6846	−99.6977
5	Cl^-	11	−459.3898	−459.5309	−459.5382
6	H_2	1	−1.1289	−1.1634	−1.1634
7	H_2	6	−1.1330	−1.1720	−1.1720
8	HF	1, 8	−100.0088	−100.2066	−100.2142
9	HF	14, 10	−100.0620	−100.2921	−100.3019
10	CH_4	7, 1	−40.1944	−40.3676	−40.3781
11	CH_3F	7, 1, 8	−139.0256	−139.3485	−139.3765
12	CH_3Cl	7, 1, 11	−498.9417	−499.2230	−499.2527
13	SiH_3F	12, 13, 8	−390.1344	−390.4221	−390.4477
14	H_3^-	2, 3, 2	−1.5914	−1.6635	−1.6661
15	H_3^-	4, 5, 4	−1.5946	−1.6745	−1.6777
16	$[FHF]^-$	9, 1, 9	−199.4809	−199.8592	−199.8901
17	$[FHF]^-$	10, 14, 10	−199.5833	−200.0308	−200.0702
18	CH_5^-	7, 1, 2	−40.5791	−40.7856	−40.8064
19	CH_4F^-	7, 1, 9	−139.4925	−139.8390	−139.8788
20	$CH_3F_2^-$	7, 1, 9	−238.4203	*c*	−238.9647
21	CH_4Cl^-	7, 1, 2, 11	−499.4405	−499.7426	−499.7818
22	CH_3FCl^-	7, 1, 9, 11	−598.3671	*c*	*c*
23	$CH_3Cl_2^-$	7, 1, 11	−958.3280	*c*	−958.7755
24	$SiH_3F_2^-$	12, 13, 9	−489.6203	*c*	−490.1318

[a] The following inner shell electrons were left uncorrected: $F(1s^2)$, $C(1s^2)$, $Si(1s^2, 2s^2, 2p^6)$, $Cl(1s^2, 2s^2, 2p^6)$. [b] These numbers refer to the corresponding rows in Table I. [c] Not computed.

Table III

Reaction	Barrier ΔE_B[a]			Reaction energy ΔE[a]			
	SCF	CEPA	$\Delta E_B{}^C$	SCF	CEPA	ΔE^C	*d*
(1) $H^- + H_2 \rightarrow H_2 + H^-$							
A	+14.75	+9.73	−5.02				1, 6; 14
B	+16.25	+11.55	−4.70				2, 7; 15
(2) $F^- + HF \rightarrow [FHF]^-$[b]							
A	−44.38	−46.20	−1.82				3, 8; 16
B	−42.68	−44.32	−1.64				4, 9; 17
(3) $H^- + CH_4 \rightarrow CH_4 + H^-$	+63.59	+56.43	−7.16				1, 10; 18
(4) $H^- + SiH_4 \rightarrow SiH_5^-$[b]	−13.75	−20.02	−6.27				See ref 11
(5) $H^- + CH_3F \rightarrow CH_4 + F^-$	+11.99	+9.98	−2.01	−52.85	−53.79	0.94	1, 11, 10, 3; 19
(6) $H^- + CH_3Cl \rightarrow CH_4 + Cl^-$	−8.03[e]	−6.84	+1.19	−98.24	−91.27	6.97	1, 12, 10, 5; 21
(7) $F^- + CH_3F \rightarrow FCH_3 + F^-$	+4.21	+8.85	+4.64				3, 11; 20
(8) $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	−15.07[e]	*c*		−45.38	−37.47	7.91	3, 12, 11, 5; 22
(9) $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	+2.20	+9.67	+7.47				5, 12; 23
(10) $F^- + SiH_3F \rightarrow [FSiH_3F]^-$[b]	−53.04	+51.35	+1.69				3, 13; 24

[a] All values in kcal/mol, $\Delta E_B{}^C$ and ΔE^C denote the corresponding correlation contribution. [b] Intermediate state. [c] Not computed. [d] Numbers in this column refer to the corresponding lines in Table II. [e] See text, section IVc.

Let us discuss briefly the "negative barrier" found for reactions 6 and 8. In these cases one has at large intermolecular distances (for the backside attack) an attractive interaction between the incoming ion (H^- or F^-) and the dipole moment of CH_3Cl. (The same situation is found[20] for reactions 5, 7, and 9.) The energy along the reaction path goes through a minimum which corresponds to a van der Waals complex $H^- \cdots H_3CCl$ or $F^- \cdots H_3CCl$. The energy then increases as the reaction proceeds up to a saddlepoint of the potential surface which defines the transition state. For reactions 6 and 8, this transition state now has a lower electronic energy than the reactants, as shown in Table III. We thus have a local barrier (the transition state has a higher energy than the van der Waals complex) but along the entire reaction path we always find an energy lower than that of the reactants.

The difference in reaction energies, by roughly 30 kcal/mol, between reactions 5 and 6 is caused by the fact that the C–F bond is stronger than the C–Cl bond.[46]

In the transition states of reactions 7, 8, and 9 we have very electronegative "axial" ligands (F, Cl) which stabilize the four-electron three-center bonds and, hence, lead to relatively small barriers.

Let us now discuss the effect of correlation on barriers and reaction energies in terms of intra- and interpair correlation energies. The partitioning of the total correlation energy in intra- and interpair contributions depends, of course, on the choice of HF MO's (localized or canonical) on which it is based. Since localized MO's, describing, e.g., a C–H bond or a lone pair, are quite similar in different molecules, it is meaningful to discuss the changes of properties referring to localized MO's. Such a discussion is much less instructive if based on canonical MO's. Previous investigations on SiH_5^- [11] and B_2H_6[17] indicated that the influence of electron correlation on activation and reaction energies is mainly due to the change of interpair terms, which is essentially caused by an increase or decrease of next neighbor bond interactions. It can be seen

Table IV. Changes of Intra- and Interpair Correlation Energies

		au[a,b]	Total au	au[a,c]	Total au
(1) $H^- + H_2 \rightarrow H_2 + H^-$	Intra	−0.0065			
	Inter	+0.0145	+0.0080		
(2) $F^- + HF \rightarrow HF_2^-$	Intra	−0.0131			
	Inter	+0.0160	+0.0290		
(3) $H^- + CH_4 \rightarrow CH_4 + H^-$	Intra	−0.0006			
	Inter	+0.0120	+0.0114		
(4) $H^- + CH_3F \rightarrow CH_4 + F^-$	Intra	−0.0073		−0.0173	
	Inter	+0.0105	+0.0032	+0.0188	+0.0015
(5) $H^- + CH_3Cl \rightarrow CH_4 + Cl^-$	Intra	−0.0090		−0.0175	
	Inter	+0.0071	−0.0019	+0.0064	−0.0111
(6) $F^- + CH_3F \rightarrow CH_3F + F^-$	Intra	−0.0047			
	Inter	−0.0027	−0.0074		
(7) $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$	Intra	*d*	*d*	−0.0003	
	Inter			−0.0123	−0.0126
(8) $Cl^- + CH_3Cl \rightarrow CH_3Cl + Cl^-$	Intra	−0.0054			
	Inter	−0.0065	−0.0119		

[a] A plus sign means increase of correlation energy in absolute value with respect to the reactants. [b] Change of intra- and interpair correlation energy between separate systems and the transition state. [c] Change of intra- and interpair correlation energy between separate reactants and products. [d] Not computed.

from the results collected in Table IV that this reasoning holds also for reactions 1 and 3 which involve negatively charged hydrogen atoms. The change in interpair correlation is more pronounced in H_3^- since the electron pairs have a larger differential overlap than found between the "axial" and "equatorial" pairs in CH_5^-. The change in intrapair correlation energy in reaction 1 is due to exclusion effects, since in H_3^- we can only substitute an occupied MO by virtual MO's which are orthogonal to the other occupied MO. Due to the large C-H_{ax} distance of 3.28 au, this effect is much smaller in CH_5^-.

A consideration of the individual pair contributions reveals a rather complex picture in general, as will now be discussed in some more detail for reaction 7 (see Table III). The most drastic changes occur for intrapair correlation of the C-F bond pair (CH_3F: $\mathcal{E} = -0.0261$ au, $CH_3F_2^-$: $\mathcal{E} = -0.0203$ au; F^-: $\mathcal{E} = -0.0186$ au) and in the interbond interactions between C-H bonds (CH_3F: $\mathcal{E} = -0.0161$ au, $CH_3F_2^-$: $\mathcal{E} = -0.0107$ au). The large $\mathcal{E}$ for the C-F bond pair in CH_3F arises from the relatively large contribution of the $(\sigma^*)^2$ configuration (which is due to the relatively large C-F bond distance), whereas the corresponding pair in $CH_3F_2^-$ is quite similar to free F^-. The change in interpair correlation between the C-H bonds results from the change in the HCH angle which reduces the differential overlap in planar CH_3. Both effects result in a decrease of intrapair and interpair correlation energy in forming the transition state.

The increasing number of interbond interactions on formation of $CH_3F_2^-$ has no net effect on the barrier. The interbond interactions between the incoming F^- with C-H bonds are relatively small and their contributions cancel almost exactly with the decrease of the corresponding terms involving the outgoing F^-.

This discussion shows that we have changes in many pair correlation energies which make it difficult if not impossible to predict the change in total correlation for reactions.

In reaction 8 (see Table IV) we have a similar situation as in 6. The reactions 4 and 5 (which involve H^- as incoming and F^- or Cl^- as out-going ions) are somehow intermediate between reactions 3 and 6 or 8, respectively. It appears that the relatively diffuse charge cloud of H^- (as compared to F^- and Cl^-) leads to larger interbond interactions (as for F^- or Cl^-) and we have a larger interpair correlation energy in the transition states of reactions 4 and 5 than in the reactants (see Table IV).

The most striking changes in individual correlation energy contributions are found for reaction 2. The change in intrapair terms arises from the large correlation of the bond in HF as compared to the corresponding pairs in HF_2^-. This effect is similar to the one discussed for the C-F bond in reaction 6 (see Table IV). Due to a rather small HF distance in HF_2^-, we also find a considerable increase in the interpair terms, as expected. There is, however, only a small net effect of correlation, 1.64 kcal/mol, on the reaction energy since the changes in inter- and intrapair contributions cancel each other to a large extent.

(d) Comparison with Previous Results. The most recent treatment of HF_2^- was published by Stogard et al.[41] These authors investigated mainly the influence of electron correlation on force constants. The energy of formation was obtained as 53 and 56 kcal/mol on the SCF and CI level, respectively. These authors note, however, that due to a limited basis set (polarization functions as well as an additional smooth p function on fluorine were omitted), these results are probably not too reliable. The present result for the energy of formation is 44.32 kcal/mol (see line 2B Table III).

The remaining computations published so far were performed exclusively on the HF level.[39,40] The HF energy obtained in the present work from the large basis (see line 17 of Table II) is 0.01 au lower than the best result published previously.[39]

A recent experimental value $\Delta E_f = 37$ kcal/mol has been published by Harrel and Daniel.[47] These authors performed a measurement of the enthalpy of the reaction

$$(CH_3)_4NF(s) + HF(g) \rightarrow (CH_3)_4NHF_2(s)$$

Dixon et al.[48] criticized the claim of Harrel et al.[47] that the true energy of the hydrogen bond in HF_2^- is within 1-2 kcal/mol of 37 kcal/mol. Harrel et al.'s conclusion rests on the assumption that the lattice energies of $(CH_3)_4NF$ and $(CH_3)_4NHF_2$ are equal, an unproven and unlikely condition.

Computations on H_3^- including correlation effects have been carried out by Macias[38] and Dedieu, Veillard, and Roos.[14] Macias' result for the barrier of reaction including correlation is 9.4 kcal/mol whereas Dedieu et al. reported a value of 7.7 kcal/mol. Our large basis set result, see line 1B of Table III, is 11.55 kcal/mol. The corresponding total energy for H_3^-, line 15 of Table II, is again lower than any previously published result both on the HF and CI levels. The relatively small barrier obtained by Dedieu et al. (7.7 kcal/mol vs. 11.55 kcal/mol, see Table III) results from the fact that a 6s GTO basis still gives a rather poor HF energy for H^-, whereby one underestimates the barrier.

Table V. Comparison of Theoretical and Experimental Results[a]

Reaction	Reaction energy Exptl[b]	Reaction energy Theory[c]	Exptl activation energy[b]	Theoretical barrier[d]
$H^- + CH_3Cl \rightarrow CH_4 + Cl^-$	−88 ± 9	−88	0.62 ± 0.13	−7[e]
$F^- + CH_3Cl \rightarrow CH_3F + Cl^-$	−32 ± 11	−36	0.1 ± 0.10	−15[e,f]
$H^- + CH_3F \rightarrow CH_4 + F^-$	−56 ± 8	−51	3.7 ± 0.10	10

[a] All values in kcal/mol. [b] At 298 K, see ref. 24. [c] CEPA results from Table III, corrected for zero-point vibrations. [d] CEPA results, see Table III. [e] The "negative barriers" are discussed in section IVc. [f] HF result, see Table III.

Several SCF computations on the reaction $H^- + CH_4$ have been reported in the literature.[14,36,37] Dedieu et al.[14] and Dyczmons et al.[36] included effects of electron correlation. The SCF results of the reaction barrier were 59.3,[14] 70,[36] and 61.23 kcal/mol,[37] as compared to the present result of 63.59 kcal/mol. The reason for the rather large barrier reported by Dyczmons et al.[36] is probably due to the fact that the basis set was less well optimized for CH_5^- than for the separated systems CH_4 and H^-, as has already been noted by these authors. The computations of Dedieu et al.[14] and Baybutt[37] probably underestimate slightly the barrier since the HF energies of H^- were −0.4766 and −0.4810 au, respectively, whereas our basis gives −0.4860 au.

The CI values for the barrier obtained up to now were 55.2[14] and 55 kcal/mol,[36] as compared to the present result of 56.43 kcal/mol. The rather large influence of correlation on the barrier height (~15 kcal/mol) found by Dyczmons et al.[36] is certainly an artefact of the IEPA method (see, for example, ref 17). The present investigation yields a decrease of the barrier by 7.2 kcal/mol as a result of correlation effects (CEPA, see Table III). Dedieu et al.[14] reported a decrease of 4.1 kcal/mol only. These authors used eq 7, however, to obtain ΔE_f. Using the same procedure we would obtain an influence of correlation of 0.69 kcal/mol.

The most extensive basis sets for a HF calculation on the reactions $F^- + CH_3F$ was used by Duke and Bader.[33] Their SCF result for the reaction barrier was 7.14 kcal/mol. In the present work we found an SCF barrier of 4.21 kcal/mol. The deviation of the SCF result is due to a somewhat smaller basis set used by the present authors. But there is also another reason: the exponents of our polarization functions were optimized with respect to the total energy (including correlation), which leads to nonoptimal SCF exponents. If, for example, we had used an orbital exponent $\eta = 1.2$ (as is optimal for this case) instead of $\eta = 1.6$ for fluorine d AO's in CH_3F, we would have obtained an SCF barrier of 5.3 kcal/mol. (The d exponent has little influence on the SCF energy of $CH_3F_2^-$.)

A short comment should be made on the SCF computations of Duke and Bader[33] and Baybutt.[37] Although in both cases nearly the same basis set was used, the SCF results for the barriers were quite different, 7.14 and 2.12 kcal/mol. The present authors were not able to explain this difference.

Dedieu et al.[14] describe a correlation computation on this reaction where they did not use any p functions on hydrogen and included d_{xz}, d_{yz} functions on carbon and fluorine only. Using this basis set they got a barrier of 5.9 kcal/mol. Our CEPA barrier was 8.85 kcal/mol. The difference between our correlation result and Dedieu et al. is first caused by the exclusion of the 2s orbitals of fluorine in their correlation computation and second Dedieu et al. used (7) instead of (8) in order to compute the barrier.

(e) **Comparison with Experiment.** Bohme et al.[24] have performed flowing afterglow experiments to determine rate constants k_{exp} in vacuo for some of the reactions treated in this work. The experimental rate constants k_{exp} are then compared with theoretical capture rate constants k_{c} in order to get an estimate of the activation energy E_{a} according to

$$E_{\mathrm{a}} = -RT \ln (k_{\mathrm{exp}}/k_{\mathrm{c}})$$

We note that the experiments were performed at room temperature only. In Table V we compare these experimental results of Bohme with the theoretical barriers obtained in this work. With respect to a comparison of these results it should be mentioned that one has to distinguish between activation energies, obtained from the Arrhenius equation, and barriers, defined as energy difference between reactants and transition state.[49] The corresponding deviations are usually in the order of a few kilocalories per mole.[49] The quite small activation energies of 0.62 and 0.1 kcal/mol found for the first two reactions listed in Table V are in good agreement with our theoretical results, which show that the energy along the reaction path is always lower than for the reactants as has been discussed in section IVc. The only considerable deviation is found for the process $H^- + CH_3F \rightarrow CH_4 + F^-$: activation energy of 3.7 kcal/mol vs. a barrier of 10 kcal/mol. Considering the rather crude approximations that had to be made in the evaluation of the measurements and the fact that the theoretical barriers may be in error by a few kilocalories per mole, the agreement is still satisfactory.

Bohme et al.[24] have also used available experimental data to determine reaction energies. If we correct our reaction energies for zero-point vibrations, as done in Table V, the theoretical and experimental values agree within the experimental errors. These rather large experimental errors arise mainly from uncertainties in the enthalpies of formation of CH_3Cl and CH_3F as discussed by Bohme et al.[24]

V. Conclusions

The computations reported in this work first of all show that electron correlation has a marked influence on barriers (−7.16 to + 7.47 kcal/mol, lines 4 and 9 of Table III) and reaction energies (up to 7.91 kcal/mol, line 8 of Table III) even for closed shell reactions. Although the effect of electron correlation is not as spectacular as for the dimerization of BH_3, where it amounts to 16 kcal/mol, corresponding to 45% of the total ΔE_f, these effects are in general larger than for internal processes where the correlation energy is often virtually constant.

Inspection of the individual pair contributions to the total correlation energy reveals a rather complex situation since we find a simultaneous increase and decrease of the various contributions along the reaction path. The following pattern seems to emerge from the results collected in Table III. For the reactions involving a carbon or silicon center in the transition or intermediate state we find that correlation stabilizes this state by about 7 kcal/mol if H^- is the incoming and outgoing group, we find a destabilization by 2-7 kcal/mol if both groups are F^- and/or Cl^-, whereas correlation contributes between +1 and −2 kcal/mol for incoming H^- and outgoing F^- or Cl^-.

The investigations presented in this work prove again the computational efficiency of using PNO's for the description of correlation effects. The expansion of the total wave function in terms of the partially nonorthogonal set of PNO's[25-27] gives a very compact form for the wave function. One therefore can exhaust a basis set of 70-80 groups for molecules like $SiH_3F_2^-$ even on computers of moderate capacities. (All computations reported have been performed on a UNIVAC 1108; employing double precision arithmetic the present program requires 65K words (36 bits) core storage.)

Ab initio computations which include effects of correlation are still quite expensive. The computations on $CH_3Cl_2^-$ and $SiH_3F_2^-$ require about 15 h of computation time (CPU + IO). Semiempirical treatments would be much cheaper, but even the MINDO/3[50] still gives a dimerization energy for BH_3 of about 80 kcal/mol[51] which is roughly a factor of 2 too large. Due to a lack of thermodynamic data the boron parameters of MINDO/3 are still preliminary, however. The existence of reliable theoretical results for ΔE_f could offer a possibility to fit the semiempirical parameters in those cases where experimental data are not available.

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