to efforts to characterize the photoelectrochemical effect of Ru^{3+} on GaAs by investigating changes in the interface trap density of GaAs that has been exposed to Ru^{0} in ultra-high-vacuum,[49] and to the general usefulness of the Ru^{3+} ion as a surface passivant when in contact with air,[46] aqueous I^-/I_3^-,[50] and other potentially reactive interfaces.[51]

In summary, the interfacial reactions of Co(III) and Co(II) complexes with GaAs surfaces have been identified, and the structure of the surface-bound species has been identified by a combination of methods. Other metal ions may employ different modes of binding to chemisorb on GaAs surfaces, and a complete set of spectroscopic studies would be needed in order to elucidate the chemical state of the various other surface treatments that have been identified in the literature. Such studies would be especially important for ions that can drastically change the rate of surface recombination under high-level-injection conditions (implying a reduction in surface state trapping rates as opposed to a chemisorption-induced shift in surface potential), although no such metal ion systems have yet been identified in the literature. We have also shown that the initial metal binding state need not be representative of the species relevant to the electrical behavior of semiconductor electrodes and that in situ characterization methods are required in order to address these issues. Ongoing efforts to discover suitable systems for surface passivation, and to characterize the chemical state of these surfaces, are continuing in this laboratory.

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Theoretical Study of Potential Wells and Barriers for S_N2 Rearrangement in the Systems $(XCH_3X)^-$ with X = F, Cl, and Br

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Abstract: Potential energy characteristics (well depths and barrier heights) for S_N2 rearrangement of the three symmetrical systems $(XCH_3X)^-$ with X = F, Cl, and Br have been calculated by using quantum chemical configuration interaction (CI) approaches with extended basis sets. The ion–dipole complex stabilities are found to be 11–13 kcal/mol for X = F and 8–9 kcal/mol for X = Cl and Br. The barrier heights (relative to the energy of the separate reactants) are obtained as 1–3 kcal/mol for X = F and Br but 7–8 kcal/mol for X = Cl. These results show some unexpected features; at present, they cannot be conclusively compared with experimental data. Therefore, our study should stimulate, on the one hand, further experimental investigations together with careful analysis of the measured quantities and, on the other hand, further refined quantum chemical treatments.

I. Introduction

Bimolecular nucleophilic substitution (S_N2) is an important reaction type of organic chemistry that has been the subject of extensive studies for many years. Experimental results on these reactions in solution[1a–c] revealed a number of regularities relating the reactivity to the nature and structure of the nucleophile, the leaving group, and the substrate. These findings, however, are strongly dependent on the solvent, and no unambiguous information can be obtained from this source about the "genuine" molecular mechanism. This became only possible in the early 1970s when experimentalists succeeded in studying these reactions in the gas phase. Most research work of this kind has been done on simple prototype S_N2 reactions

$$X^- + CH_3Y \rightarrow XCH_3 + Y^- \tag{1}$$

by Bohme et al.,[2a–e] Brauman et al.,[2a,f–k] and more recently, DePuy

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et al.[2l,m] applying flowing afterglow and ion cyclotron resonance techniques. As one of the main results of these investigations, it was found that such gas-phase reactions are up to 20 orders of magnitude faster than the corresponding reactions in solution. Using simple theoretical models for extracting molecular interaction parameters from the measured rate constants, one arrived at the conclusion that the potential profile along the reaction path exhibits minima both on the reactant and on the product sides, separated by a barrier.

Almost parallel to the experimental investigations and crude model considerations, theoretical studies tried to confirm these data, to interpret the results, and to make predictions. The major part of this work concentrated on the static aspects: the relevant parts of the interaction potential energy surface, mostly the potential profile along a (guessed or calculated) reaction coordinate, or even the potential well depths and barrier height only.[3,4] A small number of the hitherto published papers deal with the (approximate) dynamics[5a-e] and the kinetics,[6a,b] i.e., the rate constants. For completeness the theoretical description of the S_N2 reactivity based on qualitative schemes (see, e.g., refs 3o,r and 7–9) should also be mentioned.

Table I. Summary of Basis Sets

	basis set		
atom	all-electron (AE)[a]	pseudo-potential (PP)[b]	abbrev
H	(4s)/[2s][c]	(4s)/[2s][c,d]	DZ
C	(9s5p)/[3s2p]	(4s4p)/[2s2p]	
F	(9s5p)/[3s2p]	(4s4p)/[2s2p]	
Cl	(11s7p)/[6s4p]	(4s4p)/[2s2p]	
Br	(14s11p5d)/[8s6p2d][e]	(4s4p)/[2s2p]	

Additional Functions to DZ Basis Sets[a,f]

atom	type	exponent	abbrev
H	p	1.0	DZDP
C	d	0.75	
F	p, d	0.074, 0.90	
Cl	p, d	0.049, 0.68[g]	
Br	p, d	0.05,[h] 0.35[h]	

[a] Reference 16 if not otherwise noted. [b] Pseudo-potentials and basis sets from ref 17 if not otherwise noted. [c] Scaling factor 1.2. [d] Reference 18. [e] Reference 19. [f] The same exponents were used for AE and PP calculations. [g] Reference 20. [h] Reference 21.

Concerning the potential profile calculations, it became clear that, at least for the barrier height, powerful ab initio methods beyond the Hartree–Fock level with the use of extended basis sets must be applied; standard ab initio Hartree–Fock and semiempirical SCF approaches are in general not adequate. One should notice, however, the extensive study of a broad variety of systems $(XCH_3Y)^-$, undertaken by Mitchell et al.[3j,k,r] in ab initio Hartree–Fock approximation to deduce structure–reactivity relationships. We restrict our discussion from the very beginning, as far as energetical data are concerned, to ab initio approaches that include a "sufficiently large" part of the electronic correlation contribution.

The application of advanced quantum chemical methods to systems of the type $(XCH_3Y)^-$ is still a highly demanding task. For various combinations of X and Y (taken to be hydrogen or halogen atoms or simple functional groups like OH, NH_2, etc.), calculations on a post-Hartree–Fock level of different quality and, consequently, differing results have been carried out.[4] Altogether, until now there are no reliable theoretical predictions of interaction potential energy parameters for any of the reactions 1, and there is still no definite answer to the question of which level of treatment (basis set, wave function ansatz) is required for making predictions of the barrier heights. This situation was one of our motivations to start a series of studies of which the present work is a part.

The main objectives, taking into consideration our experience from the investigation[4h,l] on $(HCH_3F)^-$, are the following: (i) calculation of ion–dipole complex structures and stabilities as well as transition configuration geometries and barrier heights for the symmetrical S_N2 rearrangements

$$X^- + CH_3X \rightarrow XCH_3 + X^- \qquad (2)$$

with X = F, Cl, and Br, on a common level of accuracy (same quantum chemical method, basis sets of comparable quality) allowing for predictions and interpretative conclusions on the sequence X, F–Cl–Br, in terms of electronic structure arguments; (ii) generation of input data for statistical theories to predict rate constants of the identity reactions 2 (since these reactions are expected to be very slow, experimental data are difficult to obtain so that theoretical estimates should be desirable); (iii) providing reference and input data for subsequent estimates of solvent effects.

The paper is organized as follows: In section II the necessary information on the computations is given. The results for geometries and energies of the ion–dipole complexes and the transition configuration are presented and discussed in section III. The final section, IV, summarizes the main conclusions.

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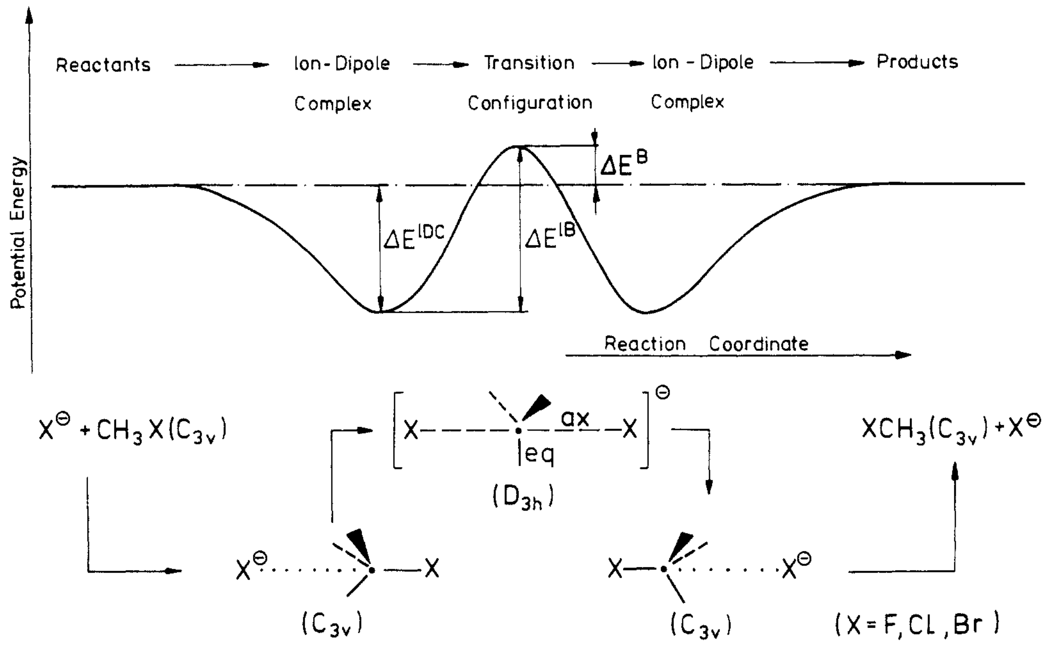

Figure 1. Potential profile of symmetrical gas-phase S_N2 reactions $X^- + CH_3X$ (schematically).

Table II. Optimized Structural Parameters for Methyl Halides CH_3X (C_{3v}) and Ion–Dipole Complexes $X^-\cdots CH_3X$ (C_{3v}) (X = F, Cl, Br)[a]

dist and angles[b]	F			Cl			Br		
	AE	PP	exp[c]	AE	PP	exp[d]	AE[f]	PP	exp[e]
				CH_3X (C_{3v})					
C–H	1.083	1.08	1.090	1.079	1.08	1.085	1.08	1.08	1.082
C–X	1.369	1.37	1.382	1.787	1.79	1.776	1.95	1.97	1.934
∠XCH	108.8	108.6	108.4	108.5	108.2	108.6	107.7	107.2	107.7
				$X^-\cdots CH_3X$ (C_{3v})[g,h]					
X^-–C	2.74	2.73		3.40	3.37		3.58	3.54	

[a] Hartree–Fock results with DZDP basis. Distances are in angstroms, and angles are in degrees. [b] See Figure 1. [c] Reference 22. [d] Reference 23. [e] Reference 24. [f] Without p polarization functions on hydrogen. [g] Only X^-–C distance optimized, other parameters taken from CH_3X. [h] Results of complete geometry optimization in AE SCF approximation with DZDP basis sets for $F^-\cdots CH_3F$ and $Cl^-\cdots CH_3Cl$: C–H 1.077 Å, C–F 1.411 Å, ∠FCH 108.4°, F^-–C 2.724 Å and C–H 1.074 Å, C–Cl 1.823 Å, ∠ClCH 107.8°, Cl^-–C 3.384 Å, respectively.

II. Computational Method

The geometrical structures corresponding to stationary points (local minima, saddle points) along the assumed C_{3v}-symmetric reaction path for the S_N2 rearrangements have been determined on the Hartree–Fock SCF level. Two sets of calculations were performed: (i) with inclusion of all electrons (AE) with the HONDO4[10] and HONDO5[11] programs and (ii) by approximating the influence of the nonvalence electrons by the nonempirical semilocal pseudo-potential (PP) of Durand and Barthelat;[12] in the latter approach, the PSHONDO[13] program package was employed requiring for the geometry search a manual step-by-step procedure (intervals of distances 0.01 Å and angles 0.1°). For X = F and Cl, the eigenvalues of the Cartesian force constant matrix were used to characterize the nature of the stationary points; for X = Br an analogous behavior was presumed.

For these geometries found for the stationary points, the energies have been recalculated to account for correlation contributions by applying the multireference single- and double-excitation configuration interaction (MRD-CI) method of Buenker and Peyerimhoff with configuration selection and energy extrapolation.[14a–e] Energy contributions from some higher order excitations have been estimated by a generalized Davidson correction (DC).[15] Reactants and products were treated as supermolecules at a $X^-\cdots CH_3X$ distance of 100 Å, in order to reduce the size-consistency error that is of considerable magnitude for the type of systems studied here: 17.0, 14.5, and 12.6 kcal/mol for X = F, Cl, and Br, respectively, at the MRD-CI level and 6.8, 5.7, and 4.9 at the MRD-CI(DC) level.

For X = F and Cl, we performed AE as well as PP MRD-CI calculations; for X = Br, only the PP MRD-CI approach has been used to keep a reasonable computational expense. In the AE variant, for X = F a core of 3 and for X = Cl a core of 11 molecular orbitals resembling essentially the inner shells of carbon (1s), fluorine (1s), and chlorine (1s,2s,2p), respectively, were assumed to remain doubly occupied in all configurations. Moreover, in the case of X = Cl the two energetically highest virtual orbitals were not included in the CI treatment. Throughout only one reference configuration was found to be sufficient: the leading configuration had in all calculations a weight of $C_0^2 > 0.88$ whereas all

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Table III. Vibrational Frequencies (cm^{-1}) for the Stationary Points of S_N2 Identity Reactions $X^- + CH_3X$ (X = F, Cl)[a]

	CH_3X (C_{3v})[c]		$X^-\cdots CH_3X$ (C_{3v})		$(XCH_3X)^-$ (D_{3h})	
vibration[b]	F	Cl	F	Cl	F	Cl
$\omega_1(a_1/a_1')$	3280 (2919.6)	3299 (2950.2)	3354	3361	3401	3420
$\omega_2(a_1/a_2'')$	1604 (1459.4)	1512 (1354.9)	1475	1421	1370	1211
$\omega_3(a_1/a_1')$	1071 (1048.6)	679 (732.9)	862	522	375	219
$\omega_4(a_1/a_2'')$			192	111	525*i*	324*i*
$\omega_5(e/e')$	3395 (2999.0)	3434 (3039.3)	3503	3526	3626	3647
$\omega_6(e/e')$	1640 (1467.8)	1624 (1452.2)	1596	1590	1526	1539
$\omega_7(e/e'')$	1256 (1182.7)	1108 (1018.1)	1172	1044	1150	959
$\omega_8(e/e')$			120	77	339	195

[a] Calculations in AE Hartree–Fock SCF approximation with DZ basis sets. [b] Symbols in parentheses: symmetry type (C_{3v}/D_{3h}). [c] Numbers in parentheses: experimental values.[25]

Table IV. Calculated Stabilization Energies $\Delta E^{\rm IDC}$ (kcal/mol) of Ion–Dipole Complexes $X^-\cdots CH_3X(C_{3v})$ (X = F, Cl, Br)[a,b]

	$\Delta E^{\rm IDC}$							
	F			Cl			Br	
method	AE(C)[c]	AE[d]	PP[d]	AE(C)[c]	AE[d]	PP[d]	AE[d,e]	PP[d]
SCF	−12.6	−11.9	−11.9	−9.4	−9.1	−9.1	−8.4	−8.7
CI(SD)	−13.3	−12.2	−11.9	−9.2	−9.2	−9.2		−8.8
	(−13.1)	(−11.7)	(−11.3)	(−8.8)	(−8.7)	(−8.7)		(−8.4)

[a] See Figure 1. [b] Hartree–Fock SCF and CI(SD) results with DZDP basis for the geometries of Table II. Values in parentheses obtained with the Davidson correction. [c] Completely optimized geometry parameters, see footnote *h* of Table II. [d] Only X^-–C distance optimized; see Table II. [e] Without p polarization functions on hydrogen.

other configurations contributed as less as $C_i^2 < 0.0025$. Thus we employed de facto a CI(SD) approach. A selection threshold of $t = 5\ \mu H$ was chosen, and advantage was taken only of C_s symmetry. The resulting dimensions of the CI matrices, which have been actually solved, were in the range 5000–9000.

The basis sets used are compiled in Table I. The PP basis functions were contracted to valence-shell double-ζ (DZ) quality by means of a 3+1 procedure. To increase the flexibility, the DZ basis sets were augmented by diffuse functions (D) on the halogens and polarization functions (P) on all atoms thus giving basis sets denoted by DZDP. As previous potential profile calculations for these S_N2-type reactions have shown, at least basis sets of such DZDP quality are necessary to obtain reliable energetic data;[3i,l] they are applied throughout the paper, only in some cases (mainly for comparison purposes and in the determination of vibrational frequencies) calculations with DZ basis sets are carried out.

III. Results and Discussion

The potential energy profile of a symmetric S_N2 gas-phase reaction 2, as shown in Figure 1, is characterized by two energetic quantities: (i) the stabilization energy ($\Delta E^{\rm IDC}$) of the ion–dipole complexes and (ii) the barrier height ($\Delta E^{\rm B}$ relative to the reactants or $\Delta E^{\rm IB}$, the intrinsic barrier, relative to the ion–dipole complex) for the rearrangement. The two relevant structures, the ion–dipole complex and the transition configuration, will be discussed separately.

Ion–Dipole Complexes. A. Geometric Structure. The results of the geometry optimization for the reactant methyl halides, as well as for the ion–dipole complexes, are presented in Table II. For the former, we obtained close agreement with available experimental data for both AE and PP treatments.

For negative ion–dipole complexes of the type considered here, commonly two geometrical arrangements are discussed:[3j] face-centered structures (C_{3v} symmetry) and vertex-centered structures (C_s symmetry). According to Mitchell's extensive theoretical study (at the Hartree–Fock SCF level with 4-31G basis sets),[3j] halide–halomethane face-centered complexes should be more stable, whereas for highly symmetrical molecular partners (e.g., CH_4[3j,4h,i] and CX_4[3u]), the vertex-centered complexes would be energetically preferred. Vibrational analysis of the face-centered structures performed in an AE Hartree–Fock SCF approach with DZ basis sets for the systems with X = F and Cl (see Table III) shows the local minimum character (all normal frequencies real) in accordance with the finding of Mitchell.[3j]

The complete geometry optimization of the ion–dipole complexes with X = F and Cl was carried out in AE SCF approach with DZDP basis sets (see Table II, footnote *h*). The results show that CH_3X appears in the complex only slightly distorted. This fact should justify an approximate procedure in which only the X^-–C distance is varied, keeping the geometry of the free CH_3X molecule fixed. Indeed, the optimum value of the X^-–C distance obtained in this way is quite close to the value found in the complete calculation (Table II, last line). This limited-geometry variation procedure was applied also in the PP approach. Important to note finally that AE and PP results agree very well.

B. Energy. In Table IV the calculated stabilization energies $\Delta E^{\rm IDC}$ of the halide–halomethane complexes are listed. The Hartree–Fock SCF approximation gives already the major part of the energy gain in the complex formation as can be expected for interactions dominated by electrostatic forces. That the correlation contribution is so small (a few tenths of a kilocalorie per mole) seems somewhat surprising, considering results for other van der Waals complexes of similar kind ($F^-\cdots CH_4$,[4h,i] $F^-\cdots CH_3OH$,[4e] $OH^-\cdots CH_3F$,[4e] $Cl^-\cdots CH_3OH$[4g]). This may be characteristic for the special type of complexes considered here, but it may also indicate persisting inaccuracies of our treatment (basis set, geometry, CI truncation) as well. We note again the very good agreement between the AE and PP results, including (for X = Br only in the SCF approach) the systems containing higher row halogens.

Test calculations and the experience from our earlier studies showed that for the DZDP basis sets the basis set superposition error (BSSE) is sufficiently small to be neglected (0.3–0.7 kcal/mol). Therefore no BSSE correction has been accounted for in the present results. We note, however, that with DZ basis sets the stabilization of the complexes would be strongly overestimated (−20.2, −15.3, and −12.0 kcal/mol for X = F, Cl, and Br, respectively, in the SCF approach) and the BSSE correction is large; the same conclusion holds for the results of Mitchell[3j] obtained with 4-31G basis sets.

Concerning other previous Hartree–Fock SCF investigations, a study of Dedieu and Veillard[3d] gives a stabilization energy of −13.2 kcal/mol for $F^-\cdots CH_3F$, whereas Morokuma et al.[3n] and Chandrasekhar et al.[3p] obtained −9.0 and −10.3 kcal/mol, respectively, for $Cl^-\cdots CH_3Cl$. All these results are in close agreement with ours. For completeness it should be mentioned that semiempirical SCF approaches like MNDO do not give reasonable values for the stabilization energies of these complexes, as shown by the studies of Dewar et al.[3l,q] and Lee et al.[3s]

For comparison with experimental data on stabilization enthalpies $\Delta H_T^{\rm IDC}$ for a given temperature *T*, the calculated $\Delta E^{\rm IDC}$ values must be corrected according to relation 3 where ΔE_v^0 is the

$$\Delta H_T^{\rm IDC} = \Delta E^{\rm IDC} + \Delta E_v^0 + \Delta\Delta E_v^T + \Delta E_t^T + \Delta E_r^T + \Delta(PV) \quad (3)$$

vibrational zero-point energy (ZPE) difference of reactants and

Table V. Optimized Interatomic Distances (Å) for S_N2 Transition Configuration Structures $(XCH_3X)^-$ (D_{3h}) (X = F, Cl, Br)[a]

	F		Cl		Br	
dist[b]	AE	PP	AE	PP	AE[c]	PP
C–H$_{eq}$	1.065	1.06	1.064	1.06	1.06	1.06
C–X$_{ax}$	1.851	1.86	2.408	2.40	2.55	2.56

[a] Hartree–Fock SCF results with DZDP basis. [b] See Figure 1. [c] Without p polarization functions on hydrogen.

Table VI. Theoretical Barrier Heights ΔE^B (kcal/mol) of Symmetrical S_N2 Reactions $X^- + CH_3X$[a]

	method	basis set quality	SCF	SCF + corr	ref
X = F	CI(SD)	TZP[b]	5.9	5.9	4a
	CEPA	DZDP	4.2	8.8	4b
	MBPT(4) SDTQR	DZDP	5.7	1.1	4c
	CI(SD)[c,d]	DZDP	7.4	3.8 (2.4)[e]	this
		DZDP	6.1	3.4 (2.2)[e]	work
X = Cl	CEPA	DZDP	2.2	9.7	4b
	MP2	6-31G*	1.2	2.9	4f
	CI(SD)[c,d]	DZDP	6.3	8.9 (8.7)[e]	this
		DZDP	4.3	7.3 (7.2)[e]	work
X = Br	CI(SD)[c,d]	DZDP[f]	4.3		this
		DZDP	1.0	2.8 (2.5)[e]	work

[a] See Figure 1. [b] Triple-ζ basis plus an incomplete set of d polarization functions (d_{xz}, d_{yz}). [c] Geometry parameters from Tables II and V. [d] Upper line, AE calculation; lower line, PP calculation. [e] Values in parentheses obtained with the Davidson correction. [f] Without p polarization functions on hydrogen.

complex, $\Delta\Delta E_v^T$ the temperature correction to the ZPE term, ΔE_t^T and ΔE_r^T the translational and rotational energy contributions, and $\Delta(PV)$ the work term. The last three terms are usually estimated in classical approximation giving together $-5RT/2$, i.e., −1.48 kcal/mol for T = 298 K, in the present cases. The vibrational contributions are calculated from the frequencies in Table III: the ZPE terms are 0.2 and 0.1 kcal/mol for X = F and Cl, respectively, and the temperature dependent terms are 1.3 and 1.5 kcal/mol so that, for the total corrections in equation 3, very small values are obtained: nearly 0 for X = F and +0.1 kcal/mol for X = Cl. This is not unexpected considering the results for similar systems $OH^-\cdots CH_3F$[4e] and $OH^-\cdots CH_3Cl$.[4g]

It should be noticed that our vibrational frequencies show a close agreement with the values of Ryaboy[5d] (X = F, 4-31G basis set) and of Luke et al.[4f] (X = Cl, 3-21G basis set); the deviations from experiment for CH_3X (see Table III) are in the typical range.

For the chlorine and bromine complexes, enthalpies of association have been obtained from high-pressure mass spectrometry (HPMS) measurements by Dougherty and Roberts;[26] they find −8.6 ± 0.2 kcal/mol for X = Cl and −9.2 ± 0.5 kcal/mol for X = Br in reasonably good agreement with our calculated results. Recently Larson and McMahon[27] determined for the enthalpy of formation of the chlorine complex a value of −12.2 ± 2 kcal/mol from an investigation of halide exchange equilibria with ion cyclotron resonance (ICR). Considering the relatively large uncertainty estimated by these authors, the deviation from our result should not be overemphasized.

Finally we point out that there is a distinct jump in the ΔE^{IDC} values when going from the fluorine to the higher row halogen complexes. This can be qualitatively understood as a consequence of the pronounced differences of the ionic radii and corresponding distances (see Table II).

Transition Configurations. A. Geometric Structure. For the three systems the transition configuration was determined at the AE and PP Hartree–Fock SCF levels to have a trigonal-bipyramidal structure of D_{3h} symmetry; the fully optimized geometrical parameters are given in Table V. The simple saddle point character (one imaginary normal frequency) was checked for X = F and Cl in AE Hartree–Fock SCF calculations with DZ basis sets.

As could be expected from previous studies,[3i,t] the equatorial bond lengths C–H$_{eq}$ are only slightly different from the C–H bond lengths in CH_3X (Table II) whereas the axial interatomic distances C–X$_{ax}$ are considerably enlarged (by about 30%) compared to the C–X bond lengths in the corresponding CH_3X. We note again that the PP approach simulates very well the AE results.

B. Energy. In the past, simple prototype S_N2 reactions 1 have been frequently considered as being of a quasi-closed-shell type (i.e., the formal closed-shell electronic structure of the whole system is maintained during the rearrangement) so that the correlation part of the electronic energy should not significantly change when going along the reaction path from reactants to products. Accordingly, most of the previous work was restricted to the Hartree–Fock SCF level, showing mainly the strong influence of the basis set quality (see, e.g., refs 3i,t). Several more recent studies,[4b–l,5b] however, revealed the assumption of zero correlation energy contribution to the reaction profile, particularly to the activation barrier height, to be not justified for these systems. This is certainly due to substantial electronic charge redistribution and the formation of a formally five-bonded carbon atom at the transition configuration.[4e] The calculated values for the barrier heights turned out to depend strongly on the quantum chemical method used to describe the electronic correlation and on the basis set so that no reliable quantitative information is available so far, even for the most extensively studied system $H^- + CH_3F$.[4h–l] In Table VI pertinent data for the reactions 2 from previous calculations are presented together with our results.

The earlier work on $F^- + CH_3F$ cited in Table VI illustrates the diversity of findings concerning the role of electron correlation: from the first rather crude CI treatment with an unbalanced basis set of Dedieu and Veillard,[4a] leading to a negligible correlation contribution, to the CEPA study of Keil and Ahlrichs[4b] who obtained a positive correlation part of the barrier doubling the SCF value, to the fourth-order perturbation theoretical calculation of Urban, Černušák, and Kellö,[4c] which gives a negative contribution of the correlation energy to the barrier height. The situation is, by the way, analogous in the case of the reaction $H^- + CH_3F$.[4h–l] For reactions 2 with heavier halogens much less theoretical data beyond Hartree–Fock SCF are available: for $Cl^- + CH_3Cl$ only two studies[4b,f] of that level have been published so far, and for $Br^- + CH_3Br$ nonempirical calculations are missing altogether.

Our results in Tables VI and VII show larger differences between the AE and PP values for the barrier heights than for the complex stabilization energies (compare Table IV), increasing from F to Cl to Br and being less pronounced when electron correlation is taken into account. This fact reflects certainly the complicated electronic structure reorganization in forming the transition configuration, which cannot be described in a sufficiently complete way by a frozen-core approximation. We do not analyze further this problem but assume that the general effects and trends to be discussed are appropriately given by the PP approach.

The main observations from the data collected in Table VI are as follows: (1) The CI(SD) results confirm that for the fluorine reaction the energy contribution from electronic correlation to the barrier is negative; i.e., the magnitude of electronic correlation energy is larger in the transition configuration than in the reactants. With the Davidson correction included, the correlation part agrees also quantitatively well with the value of Urban et al.[4c] A reasonable estimate of the "true" ΔE^B barrier should be 1–3 kcal/mol. A negative correlation contribution to the barrier was obtained also for other S_N2 reactions, which involve only first-row atoms and H ($H^- + CH_3F$[4c,h–l], $OH^- + CH_3F$[4e]). (2) For the systems with the higher row halogens (X = Cl, Br) the portion of correlation energy in the barrier height is calculated to be positive (for X = Cl in agreement with the two previous studies[4b,f] mentioned above), i.e., the magnitude of electronic correlation energy is smaller in the transition region than in the reactants. (3) Largely as a consequence of the different behavior of the correlation energy contribution, the monotonous (decreasing) trend of the barrier heights when going from F to Cl to Br, as obtained at the Hartree–Fock SCF level, is lost by inclusion of electron correlation.

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(26) Dougherty, R. C.; Roberts, J. D. *Org. Mass Spectrom.* **1974**, *8*, 81.
(27) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

Table VII. Calculated "Intrinsic" Barriers ΔE^{IB} (kcal/mol) of Symmetrical S_N2 Reactions $X^- + CH_3X$[a,b]

	ΔE^{IB}							
	F			Cl			Br	
method	AE(C)[c]	AE[d]	PP[d]	AE(C)[c]	AE[d]	PP[d]	AE[d,e]	PP[d]
SCF	20.0	19.3	18.0	15.7	15.4	13.4	12.7	9.7
CI(SD)	17.1	16.0	15.3	18.1	18.1	16.5		11.6
	(15.5)	(14.1)	(13.5)	(17.5)	(17.4)	(15.9)		(10.9)

[a] See Figure 1. [b] Hartree–Fock SCF and CI(SD) results with DZDP basis for the geometries of Tables II and V. Values in parentheses obtained with the Davidson correction. [c] Completely optimized geometry parameters; see Table V and footnote *h* of Table II. [d] Only X^-–C distance of the complexes optimized; see Table II. [e] Without p polarization functions on hydrogen.

The accuracy of the barrier heights obtained in our calculations is difficult to assess. There is a number of approximations in the treatment leading to uncertainties. Minor changes in the geometrical parameters modify the barrier heights only slightly as we realized from a test calculation for $F^- + CH_3F$ using the geometry optimized with the DZ basis (changing interatomic distances by about 0.1 Å and less), which led to about 1 kcal/mol smaller values at the SCF level. Applying the CI(SD) approach, the differences were even less significant. The consequence of CI(SD) truncation was partly tested by comparing results for different selection thresholds (t = 5 and 10 μH) to be ≥0.6 kcal/mol. The influence of other factors like multiple excitations in the CI (quadruple excitations are approximately taken into account by a Davidson correction) and, particularly, basis set extension can hardly be estimated without tremendous computational expenditure, which we are not able to bestow on.

The predicted ordering of the barrier heights ΔE^B, according to Table VI, is $\Delta E^B(Cl) > \Delta E^B(Br) \gtrsim \Delta E^B(F)$. If we calculate from the data of Tables IV and VI the intrinsic barriers, $\Delta E^{IB} = \Delta E^B + |\Delta E^{IDC}|$ (compare Figure 1), we obtain $\Delta E^{IB}(Cl) > \Delta E^{IB}(F) > \Delta E^{IB}(Br)$ (see Table VII). These trends contradict earlier semiempirical findings[7] and appear somewhat unexpected: Why should the $Cl^- + CH_3Cl$ reaction be much more hindered than the others? That more accurate calculations will modify the sequence is rather unlikely since this would imply that the improvement of the barrier height must be much larger, by several kilocalories per mole, for X = Cl than for X = F and Br. From the theoretical point of view, the barrier comes about by an involved interplay of different electronic effects as can be seen from the complicated nature of the wave function in advanced calculations. A simple qualitative explanation of the nonmonotonous trend of the barrier height can be given on the basis of a refined valence bond (VB) analysis such as recently published by Hiberty et al.[28a,b] for the analogous system $H^- + CH_4$. The interaction of the two basic VB structures of $(XCH_3X)^-$ leads to a monotonous decrease of the barrier height;[7] inclusion of ionic structures, however, stabilizes the F system much more than the Cl and Br systems so that the nonmonotonous ordering of barrier heights results as obtained in our calculations.[28c] Furthermore, if we make use of even more qualitative concepts, for the identity reactions 2 we have in the sequence F^-–Cl^-–Br^- decreasing nucleophilicity and increasing leaving group ability. Because of these two counteracting tendencies, there is no reason why a monotonous trend in reactivity should result.

For comparison with experimental data we calculated the correction terms that convert the barrier height, ΔE^B, to the activation enthalpy, ΔH^B_T, according to eq 3. The zero-point contributions ΔE^0_v were obtained as −0.2 and −0.5 kcal/mol for X = F and Cl, respectively, the total corrections amounted to −1.0 kcal/mol for both cases.[29]

Information on activation barrier heights can be extracted from experimental rate constant data only on the basis of some theoretical model. Therefore, in addition to the uncertainties of the measurement, there are always errors introduced by the model assumptions for which it is usually not possible to give a quantitative estimation. Concerning the experimental conditions, the reactions under consideration should be very slow, probably at the present detection limit or below[2i] so that it is not surprising that only two experimental rate constant measurements have been published so far by Brauman et al.[2f] and very recently by Barlow et al.,[2m] both for $Cl^- + CH_3Cl$. In the latter investigation the authors took advantage of the high sensitivity of their new flowing afterglow shift-drift apparatus; they obtained a rate constant of 3.5×10^{-14} cm^3 s^{-1} at 300 K, 2 orders of magnitude smaller than Brauman's value of 1974. Considering this finding it is understandable that repeated attempts of Brauman et al.[2k] to measure the rate of $Cl^- + CH_3Cl$ and $Br^- + CH_3Br$ S_N2 rearrangement were not successful because of the higher detection limit of their ICR technique.

Various model concepts have been applied to deduce information on barrier heights from experimental data or to make predictions on an empirical footing:

(i) Based on an Arrhenius-like expression and assuming a unimodal potential profile, Bohme et al.[2d] tried to estimate an "experimental" activation barrier ΔE^B from the data of Brauman et al.[2f] for $Cl^- + CH_3Cl$; the result was 3.4 kcal/mol. Taking the new (and probably more reliable) value of Barlow et al.[2m] and using the same procedure we obtained a barrier height of 6.4 kcal/mol, in close agreement with our theoretical predictions (see Table VI).

(ii) From empirical correlations established for three groups of anions in an extensive flowing afterglow study, Bohme et al.[2d] were able to conclude that the activation barriers ΔE^B for $F^- + CH_3F$ and $Cl^- + CH_3Cl$ should be ~3 kcal/mol and ≳4.5 kcal/mol, respectively. These values are in qualitative accordance with our calculated barriers.

(iii) Another approach has been chosen by Brauman et al.[2g-k] Supposing a double-well potential profile (as in Figure 1) and using RRKM theory with empirical input data, for $Cl^- + CH_3Cl$ an activation barrier ΔE^B of 1.2 kcal/mol was obtained and for $Br^- + CH_3Br$ the barrier was inferred to be of about the same magnitude[2h,k] thus contradicting our results. However, also using a simplified RRKM approach, Barlow et al.[2m] obtained an "experimental" barrier of 1 ± 1 kcal/mol for $Cl^- + CH_3Cl$, approximately the same value as determined by Brauman et al.[2h,k] but based on a rate constant 2 orders of magnitude smaller.

(iv) Employing the rate–equilibrium relationship developed by Marcus for electron- and proton-transfer reactions, which enables one to connect the intrinsic barriers ΔE^{IB} (see Figure 1) of unsymmetrical and symmetrical reactions 1 and 2, respectively, Brauman et al.[2h,i,k] deduced for $F^- + CH_3F$ a barrier height ΔE^B of 17.2 kcal/mol and an intrinsic barrier ΔE^{IB} of 26.2 kcal/mol (assuming a well depth of 9 kcal/mol); these values do not agree with ours.

(v) Finally we mention again the study of Shaik and Pross[7] who gave a model estimate of intrinsic barriers ΔE^{IB} for reactions 2 based on rate constant measurements of Bohme et al. and of Brauman et al. for various S_N2 reactions 1 leading to values of 19.5 ± 1.0 kcal/mol for X = F, 11.6 ± 1.8 kcal/mol for X = Cl, and 9.7 ± 1.9 kcal/mol for X = Br, rather different from our theoretical data in Table VII. Somewhat closer to our results are the intrinsic barriers obtained by Shaik:[8] 18.7, 14.4, and 10.6

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(28) (a) Sini, G.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G.; Hiberty, P. C. *J. Phys. Chem.* **1989**, *93*, 5661. (b) Sini, G.; Hiberty, P. C.; Shaik, S. S. *J. Chem. Soc., Chem. Commun.* **1989**, 772. (c) Hiberty, P. C. Personal communication.

(29) We note that Urban et al.[4c] obtained a much larger ZPE correction of +2.2 kcal/mol for the $F^- + CH_3F$ barrier. This discrepancy is due to substantial differences of some of their vibrational frequencies for the transition configuration,[6a] compared to ours (Table III) and to those of Ryaboy.[5d]

kcal/mol for X = F, Cl, and Br, respectively; the simple curve crossing model, however, is certainly a rather crude approximation (see the above-mentioned VB analysis[28]).

This discussion shows that it is not possible at present to verify our predictions quantitatively by comparison with experimental information, except for the finding that all three reactions should have positive barriers ΔE^{B} of a few kilocalories per mole.

IV. Conclusions

From the present study the following main findings should be accentuated:

(1) The inclusion of electronic correlation effects is a prerequisite for a reliable description of the potential energy profile for S_N2 rearrangements in the systems $(XCH_3X)^-$ with X = F, Cl, and Br. For the potential well depths the correlation contributions are very small (a few tenths of a kilocalorie per mole) whereas for the activation barriers they amount to several kilocalories per mole. To determine the latter quantities accurately, advanced methods beyond the Hartree–Fock level and extended basis sets of at least DZDP quality are necessary.

(2) The geometrical parameters of the ion–dipole complexes correspond to a face-centered structure with C_{3v} symmetry.

(3) The ion–dipole complex stabilities are rather reliably obtained to lie in the ranges 11–13 kcal/mol for X = F and 8–9 kcal/mol for X = Cl and Br, for the latter in good accordance with experimental (HPMS) data.

(4) The geometrical structure of the transition configuration is trigonal-bipyramidal (D_{3h} symmetry).

(5) The uncertainties of the calculated barrier heights are much larger; cautious estimates should be 1–3 kcal/mol for X = F, 6–8 kcal/mol for X = Cl, and 2–4 kcal/mol for X = Br (relative to the reactants).

The correlation part is negative for X = F but positive for X = Cl and Br. Thus in the sequence F–Cl–Br a nonmonotonous change is obtained: $\Delta E^{\mathrm{B}}(\mathrm{Cl}) > \Delta E^{\mathrm{B}}(\mathrm{Br}) \gtrsim \Delta E^{\mathrm{B}}(\mathrm{F})$ for the barriers, $\Delta E^{\mathrm{IB}}(\mathrm{Cl}) > \Delta E^{\mathrm{IB}}(\mathrm{F}) > \Delta E^{\mathrm{IB}}(\mathrm{Br})$ for the intrinsic barriers, in the latter case with somewhat smaller gradation between Cl and F systems.

At present, no conclusive comparison with experimental data is possible.

(6) For X = F and Cl at the Hartree–Fock SCF and CI levels, as well as for X = Br at the Hartree–Fock SCF level, the pseudo-potential results agree reasonably well with all-electron results. For the ion–dipole complex stabilities the correspondence is almost perfect; for the barrier heights, there are increasing differences in the sequence F–Cl–Br but retaining the trend.

Summarizing, the results of the present study should stimulate further experimental work to provide more complete and reliable data on rate constants and complex stabilities but also theoretical investigations for analyzing measured quantities, as well as predicting more accurate potential energy characteristics and possibly kinetic parameters.

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Note Added in Proof. After submission of the manuscript, two recent theoretical papers came to our knowledge in which, at the Hartree–Fock and MP2 levels with basis sets not too different in quality from ours, ion–dipole complexes and transition configurations of S_N2 systems, eqs 1 and 2, are investigated. Z. Shi and R. J. Boyd (*J. Am. Chem. Soc.* **1989**, *111*, 1575) report mainly on geometrical and charge distribution characteristics of an extended series of systems; the structural parameters obtained for $F^- + CH_3F$ and $Cl^- + CH_3Cl$ in Hartree–Fock approximation are in close agreement with our results. Geometries, energies, and vibrational frequencies for the $Cl^- + CH_3Cl$ system are calculated by S. C. Tucker and D. G. Truhlar (*J. Phys. Chem.* **1989**, *93*, 8138). These authors conclude that electron correlation (MP2 level) has a noticeable effect on the optimized geometries and on vibrational frequencies; nevertheless their data are still qualitatively in accordance with ours. The complex stabilization energy is somewhat larger compared with our values; the barrier height, however, is significantly smaller ("best" result ~4.5 kcal/mol), not unexpected for the MP2 approximation.

Registry No. CH_3F, 593-53-3; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; $(FCH_3F)^-$, 56448-24-9; $(ClCH_3Cl)^-$, 127182-89-2; $(BrCH_3Br)^-$, 127182-90-5.

On the Determination of Redox Potentials of Highly Reactive Aromatic Mono- and Multications

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Abstract: Thermodynamic redox potentials of reactive mono- and multiple charged cations of aromatic systems can be accurately determined by cyclic voltammetry by using solvents such as SO_2 or CH_2Cl_2, a sophisticated sample preparation technique, low temperatures, and an appropriate time scale in the experiment. These conditions allow inter alia the measurement, for the first time, of the redox potentials (vs Ag/AgCl) of the reversible mono-, dication (tri- or tetracation) formation of naphthalene (1.67 V), fluoranthene (1.46 V), triphenylene ([di] 2.49 V), α,α-binaphthyl ([mono] 1.58 V, [di] 1.86 V), benzo[*c*]benzo-[3,4]cinnolino[1,2-*a*]cinnoline ([tri] 2.75 V), hexamethoxytriphenylene ([tetra] 2.27 V), 5,5′-dimethyl-2,2′-bithienyl ([mono] 1.08 V, [di] 1.68 V), and 3,3′-dimethoxy-2,2′-bithienyl (0.79 V).

The thermodynamic oxidation potentials of many aromatic systems, obtained either by polarographic or by voltammetric techniques, have been reported several times in the literature.[1] In recent years new exciting fields of research have been de-