

## EFFECT OF ELECTRON CORRELATION ON $S_N2$ ACTIVATION BARRIERS. FOURTH-ORDER MBPT CALCULATIONS

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*Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday. It has been a great pleasure for us to work with Dr R. Zahradnik on many common projects in chemical reactivity.*

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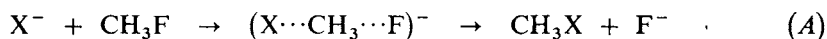
The activation barriers for a series of model gas-phase nucleophilic displacement reactions have been calculated at the MBPT(4)/DZ + P + D level. Electron correlation significantly reduces the barrier height, in most cases by about 50%. The role of individual contributions up to the fourth order MBPT is analyzed in detail showing the vital importance of single and triple excitations.

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Nucleophilic  $S_N2$  displacement reactions have attracted much attention of both experimentalists and theoreticians for many years. Two recent reviews on this class of reactions<sup>1,2</sup> can be mentioned as the typical representatives of both experimental and theoretical approach to this topic. The impact of  $S_N2$  reactions on various branches of organic chemistry is remarkable (structure-reactivity relations, stereochemistry, solvent effects, steric and polar effects, correlation diagrams, intrinsic reactivity indices<sup>1-5</sup>). Their exceptional role can be further illustrated by Brauman's quotation<sup>4</sup>: "... the nucleophilic displacement reaction is also among the best understood chemical reactions and this reaction occupies a critical place in the pedagogy of elementary organic reactions. Nevertheless, the area still has major conceptual problems associated with it...".

In order to explain why the pertinent reaction is fast or slow the rigorous prediction of the potential energy hypersurface is needed, in particular — the stationary points on it. In this context,  $S_N2$  reactions are of special importance for quantum chemists, since they represent ideal candidates for the gas-phase reactivity studies. Moreover, they may serve as suitable model for testing of the new methods for the correlation energy evaluation which is of vital importance in chemical reactivity. Since the extremely short-lived complexes which correspond to stationary points on energy hypersurfaces are often not directly amenable to experiment, quantum chemistry represents an alternative tool for their investigation, providing information about their structure and energetics.

This contribution deals with the results of our continuing research on model  $S_N2$  reactions of alkylhalides<sup>6-9</sup>. The primary focus of our interest is the analysis of the correlation energy contributions to activation barrier within the many-body perturbation theory framework. The role of correlation energy in the  $S_N2$  activation process has been the subject of controversy during the last decade. The first systematic survey on  $S_N2$  activation barriers was published in 1976 by Keil and Ahlrichs<sup>10</sup>. They found that the absolute magnitude of the correlation contribution calculated by CEPA method is quite large, being as much as 30 kJ/mole. However, no obvious systematic pattern concerning the sign of the correlation correction followed from their study. Various recent reactivity investigations on different types of reactions<sup>11-15</sup> support the notion that the correlation contribution to activation barrier is negative<sup>16</sup>. Only a few exceptions exist for  $S_N2$  reactions<sup>10,17</sup> and we shall postpone the analysis of this problem to the discussion. Preliminary experience with MBPT computations suggest that the order-by-order contributions alter as the sign concerns and that the second-order doubles and fourth-order singles and triples are mainly responsible for the significant barrier lowering. In order to confirm whether this trend is general we have selected a series of various nucleophiles attacking the substrate  $CH_3F$  in model  $S_N2$  reaction:



### THEORETICAL

The overall energy barrier  $\Delta E_{XF}^b$  is of central interest in this study. For the calculations of  $\Delta E_{XF}^b$ , i.e. the difference between the energy of the transition state and reactant energies:

$$\Delta E_{XF}^b = E[XCH_3F]^- - E[X]^- - E[CH_3F], \quad (1)$$

we used the fourth-order many-body perturbation theory including effects from single, double, triple and quadruple excitations. The theoretical background and details of computational implementation of this approach are described in several recent papers and monographs<sup>16,18-23</sup>. Here we recapitulate only the notation of the energy terms used in subsequent sections. The individual energy contributions at the  $n$ -th order of MBPT corresponding to singly-, doubly-, triply-, and quadruply-excited configurations are denoted as  $S(n)$ ,  $D(n)$ ,  $T(n)$ , and  $Q(n)$ , the latter includes also the renormalization term. Thus, the cumulative correlation energy contributions at the pertinent order of MBPT are written as

$$E_{MBPT(2)} = D(2) \quad (2a)$$

$$E_{MBPT(3)} = D(2) + D(3) \quad (2b)$$

$$E_{\text{MBPT}(4)} = D(2) + D(3) + S(4) + D(4) + T(4) + Q(4). \quad (2c)$$

The geometries of all polyatomic species required for the evaluation of  $\Delta E_{\text{XF}}^{\text{b}}$  are depicted in Fig. 1. Note that the data for the reactions with hydride and fluoride anion (energies and geometries) were taken from our previous studies<sup>7,9</sup>. The remaining transition state structures refer to SCF gradient-optimized 4-31G geometries<sup>1</sup> and the geometries of polyatomic anions and CH<sub>3</sub>F were taken from refs<sup>24,25</sup>. Of course this choice is not fully optimal, because the electron correlation may influence the geometry, especially in the case of long axial bonds C··X, C··F. However, the correlated gradient optimization of any transition structure included here is beyond our computational capabilities at present. The recent MBPT(2)/6-311G(*d, p*) optimization of the simplest H··CH<sub>3</sub>··F<sup>-</sup> structure was done by Havlas and coworkers<sup>26</sup>. This optimization was based on numerically determined gradient of the energy. According to their results the inclusion of second-order MBPT energy together with the 6-311G(*d, p*) polarized basis set leads to moderate shortening of the axial bonds in the transition structure by  $0.12 \cdot 10^{-10}$  m (5%) with respect to the SCF value from<sup>10</sup>. They also tested the corresponding change of the barrier at MBPT(2)/6-311G(*d, p*) level using these two geometries and arrived to the decrease of 15.7 kJ/mol when going from SCF to MBPT(2) geometry. It should be stressed, however, that their 6-311G(*d, p*) basis set does not include diffuse *p*-functions which, on the contrary, were present in Keil and Ahlrichs calculation<sup>10</sup>. Our selection of SCF geometries of almost the same quality was motivated by the aim to investigate the trends of correlation contributions within a series of nucleophiles.

The basis set used for the evaluation of MBPT energies may be regarded as the so-called "minimum correlated basis", the notation we advocated recently<sup>16</sup>. Dunning's contraction<sup>27</sup> of Huzinaga's (9s5p/4s) primitive set<sup>28</sup> to [4s2p/2s] was used as a starting point in its construction. This underlying basis was augmented by polarization *p*-, *d*-, and diffuse *p*-functions. The resulting basis set (hereafter denoted as DZ + P + D) is of the same quality as in ref.<sup>9</sup>, i.e. [4s3p1*d*] for C, N, O, F atoms, [4s2p1*d*] for the carbon atom of the CH<sub>3</sub>-group and [2s1*p*] for hydrogen atoms. The details of the basis set construction for each species are collected in Table I. We note that for reactions with CN<sup>-</sup> the polarization *p*-functions on hydrogen atoms of the CH<sub>3</sub>-group were omitted. This choice was dictated by economical reasons. As we have learned previously<sup>7</sup> this omission has only slight effect on the barrier height.

## RESULTS AND DISCUSSION

Table II contains the electronic energies of individual systems. Four calculations were performed for CH<sub>3</sub>F in order to evaluate the barrier within a given reaction from consistent energies and geometries. A summary of various contributions to

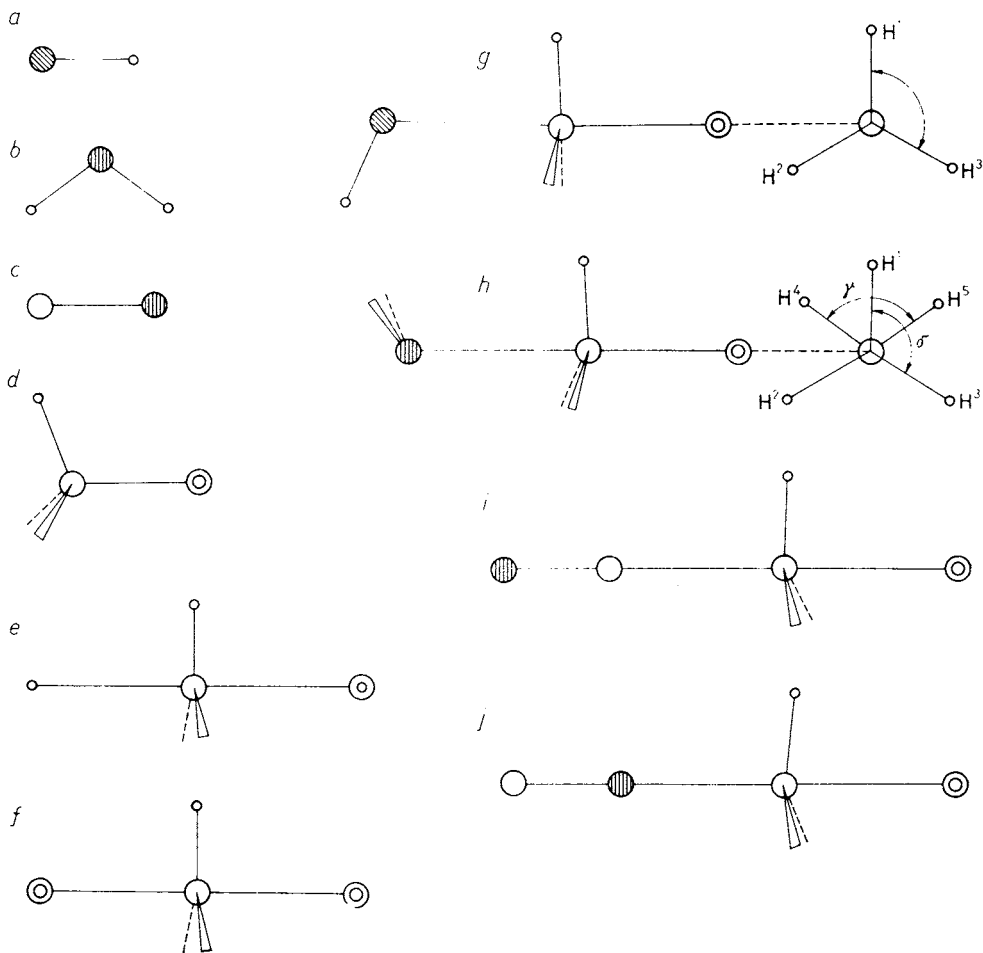
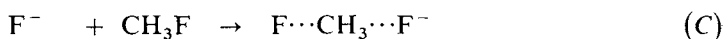
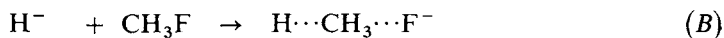


FIG. 1

Definition of internal coordinates for the structures included in this study. Lengths  $r$  are in  $10^{-10}$  m, angles  $\omega$  in deg: **a**  $\text{OH}^-$ ,  $C_{\infty v}$ ,  $r(\text{OH}) = 0.985$ ; **b**  $\text{NH}_2^-$ ,  $C_{2v}$ ,  $r(\text{NH}) = 1.043$ ,  $\omega(\text{HNH}) = 101.10$ ; **c**  $\text{CN}^-$ ,  $C_{\infty v}$ ,  $r(\text{CN}) = 1.17$ ; **d**  $\text{CH}_3\text{F}$ ,  $C_{3v}$ ,  $r(\text{CF}) = 1.418$ ,  $r(\text{CH}) = 1.079$ ,  $\omega(\text{HCF}) = 110.43$ ; **e**  $\text{HCH}_3\text{F}^-$ ,  $C_{3v}$ ,  $r(\text{CF}) = 1.958$ ,  $r(\text{CH}_{\text{eq}}) = 1.064$ ,  $r(\text{CH}_{\text{ax}}) = 1.937$ ; **f**  $\text{FCH}_3\text{F}^-$ ,  $D_{3h}$ ,  $r(\text{CF}) = 1.804$ ,  $r(\text{CH}) = 1.064$ ; **g**  $\text{HOCH}_3\text{F}^-$ ,  $C_s$ ,  $r(\text{CF}) = 1.775$ ,  $r(\text{CO}) = 1.973$ ,  $r(\text{CH}) = 1.059$ ,  $r(\text{OH}) = 0.965$ ,  $\omega(\text{FCH}_1) = 93.2$ ,  $\omega(\text{FCH}_2) = 92.1$ ,  $\omega(\text{OCH}_1) = 85.0$ ,  $\omega(\text{HOC}) = 111.2$ ,  $\delta = 119.7$ ; **h**  $\text{H}_2\text{NCH}_3\text{F}^-$ ,  $C_s$ ,  $r(\text{CF}) = 1.728$ ,  $r(\text{CN}) = 2.138$ ,  $r(\text{CH}) = 1.06$ ,  $r(\text{NH}) = 1.024$ ,  $\omega(\text{FCH}_1) = 94.1$ ,  $\omega(\text{FCH}_2) = 95.3$ ,  $\omega(\text{FCN}) = 181.2$ ,  $\gamma = 104.48$ ,  $\omega(\text{H}_4\text{NC}) = 126.3$ ,  $\delta = 120.4$ ; **i**  $\text{NCCH}_3\text{F}^-$ ,  $C_{3v}$ ,  $r(\text{CF}) = 1.902$ ,  $r(\text{CC}) = 2.008$ ,  $r(\text{CN}) = 1.158$ ,  $r(\text{CH}) = 1.05$ ,  $\omega(\text{FCH}) = 87.2$ ; **j**  $\text{CNCH}_3\text{F}^-$ ,  $C_{3v}$ ,  $r(\text{CF}) = 1.973$ ,  $r(\text{NC}) = 1.849$ ,  $r(\text{CN}) = 1.166$ ,  $r(\text{CH}) = 1.058$ ,  $\omega(\text{FCH}) = 84.8$

activation barriers is in Table III. Data in Table III refer to the following reactions.



The correlation between SCF 4-31G and DZ + P + D activation barriers will be discussed first (Fig. 2). The agreement is rather poor (the 4-31G barriers being systematically too low) but the correlation is quite good. The exception is the hydride anion for which the 4-31G barrier is extraordinarily negative. We have compared our SCF value for this nucleophile (+53 kJ/mol) with various SCF/DZ + P + D results of Havlas and coworkers<sup>26</sup>, optimized at the higher computational levels,

TABLE I

Orbital exponents of polarization and diffuse functions used in the construction of the DZ + P + D basis set

Atom	Group	Orbital	
		<i>d</i>	<i>p</i>
H	H <sup>-</sup> <sup>a,b</sup>	—	0.3
	—CH <sub>3</sub>	—	0.75
C	—CH <sub>3</sub>	0.7	—
	—C≡N	0.62	0.034
N	NH <sub>2</sub> <sup>-</sup>	0.83	0.048
	—NH <sub>2</sub>	0.92	0.048
	—C≡N	0.91	0.048
O	OH <sup>-</sup>	1.14	0.059
	—OH	1.17	0.059
F	F <sup>-</sup> <sup>c</sup>	1.2	0.09
	CH <sub>3</sub> F	1.6	0.09

<sup>a</sup> Exponent for *s*-orbital is 0.04; <sup>b</sup> used also for axial hydrogen atom in HCH<sub>3</sub>F<sup>-</sup>; <sup>c</sup> used also for FCH<sub>3</sub>F<sup>-</sup>.

TABLE II

Valence shell correlation energies. SCF values in  $E/E_h$ , correlation contributions in  $0.001 E/E_h$  ( $E_h = 2625.5$  kJ/mol), values for  $H^-$ ,  $F^-$ ,  $CH_3F^a$ ,  $CH_3F^b$  taken from ref.<sup>7</sup>, values for  $OH^-$ ,  $HOCH_3F^-$ , from ref.<sup>9</sup>

Reaction component	$-E_{SCF}$	$-E_{MBPT(4)}$	$-D(2)$	$-D(3)$	$-S(4)$	$-D(4)$	$-T(4)$	$-Q(4)$
$H^-$	0.486 810	31.814	22.104	7.215	0.122	2.730	0.000	0.357
$F^-$	99.443 298	213.990	207.197	-8.341	4.962	4.248	6.135	0.211
$OH^-$	75.400 409	229.961	220.132	-7.371	4.172	6.126	7.555	1.193
$CN^-$	92.316 002	294.720	276.610	-1.402	3.702	8.390	13.128	5.707
$NH_2^-$	55.536 767	219.990	204.655	2.914	2.660	5.447	6.854	2.541
$CH_3F^a$	139.075 919	363.584	334.326	14.588	3.351	7.240	7.757	3.678
$CH_3F^b$	139.071 944	340.252	313.969	12.312	3.039	6.892	7.003	2.963
$CH_3F^c$	139.077 420	362.829	333.648	14.655	3.307	7.188	7.675	3.644
$CH_3F^d$	139.073 520	339.797	313.353	12.360	3.266	6.827	6.927	2.935
$HCH_3F^-$	139.538 584	388.806	349.972	11.115	8.928	10.641	11.611	3.460
$FCH_3F^-$	238.510 085	584.899	545.902	1.329	12.353	12.493	17.320	4.499
$HOCH_3F^-$	214.471 133	599.479	558.095	3.134	11.553	13.858	18.471	5.634
$H_2NCH_3F^-$	194.606 747	591.947	545.293	12.437	9.682	13.325	18.167	6.957
$CNCH_3F^-d$	231.357 090	654.429	603.930	5.067	11.915	17.429	24.717	8.629
$NCCH_3F^-d$	231.362 239	657.272	607.811	4.357	11.907	17.125	25.194	9.123

<sup>a</sup> Geometry from ref.<sup>10</sup>; <sup>b</sup> geometry from ref.<sup>10</sup>, polarization function on hydrogen atoms omitted; <sup>c</sup> geometry from ref.<sup>2,5</sup>; <sup>d</sup> geometry from ref.<sup>2,5</sup>, polarization functions on hydrogen atoms omitted.

TABLE III  
Contributions to the activation barrier (in kJ/mol)

Contribution	Nucleophile					
	H <sup>-</sup>	F <sup>-</sup>	NH <sub>2</sub> <sup>-</sup>	OH <sup>-</sup>	CN <sup>-</sup>	CN <sup>-</sup>
$E_{\text{SCF}}$	52.96	23.98	19.53	17.58	71.63	85.15
$E_{\text{MBPT}(2)} = D(2)$	-36.49	-11.50	-18.35	-11.33	-46.86	-36.67
$D(3)$	22.09	12.91	13.47	10.90	17.33	15.47
$S(4)$	-15.14	-10.61	-9.75	-9.28	-12.97	-12.99
$D(4)$	-2.68	-2.64	-1.81	-1.43	-5.01	-5.81
$T(4)$	-12.10	-9.00	-9.55	-8.51	-13.49	-12.24
$Q(4)$	0.37	1.60	2.03	2.09	1.26	-0.03
$E_{\text{MBPT}(3)}$	-14.41	1.42	-4.88	-0.43	-29.53	-21.20
$E_{\text{MBPT}(4)}$	-43.95	-19.23	-23.97	-17.56	-59.74	-52.28
$E_{\text{SCF}} + E_{\text{MBPT}(2)}$	-16.46	-12.48	-1.18	6.25	24.77	48.48
$E_{\text{SCF}} + E_{\text{MBPT}(3)}$	38.55	25.39	14.66	17.15	42.10	63.95
$E_{\text{SCF}} + E_{\text{MBPT}(4)}$	9.01	4.74	-4.43	0.02	11.89	32.87

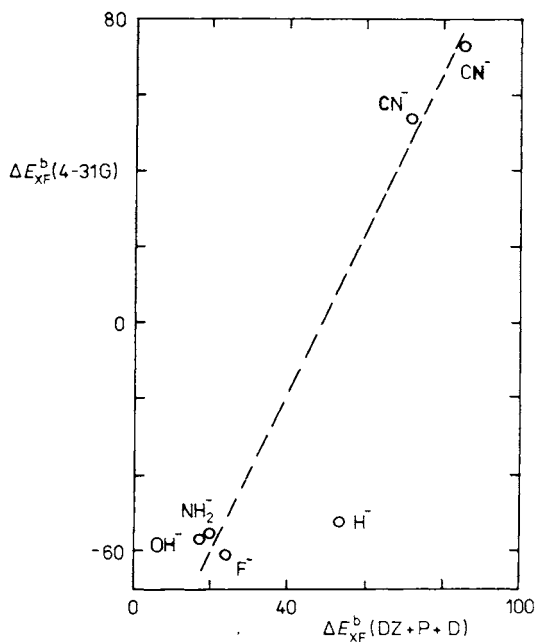


FIG. 2

Correlation between SCF/4-31G and SCF/DZ + P + D barriers. Values in kJ/mol. CN<sup>-</sup> and CN<sup>-</sup> refer to C-side and N-side attack of cyanide anion, respectively

and they consistently lie in the range 50–60 kJ/mol. The deviation of hydride anion from the correlation in Fig. 2 can be explained by the very poor 4-31G representation of this ion. Thus, at the SCF/4-31G level, the  $S_N2$  reaction with  $H^-$  might suffer from the larger basis set superposition error than the other reactions do. The correlation in Fig. 2 serves also as the further check of the 4-31G geometries for the reactions with  $NH_2^-$ ,  $OH^-$ ,  $CN^-$ , the respective points lie almost on the straight line.

We now turn our attention to the effect of electron correlation on the activation barriers. Inclusion of the simplest second-order correction gives the qualitatively same trend in barriers as is found for the complete fourth-order calculation. If we analyze the latter in detail we can see that the individual contributions possess different energy patterns (Fig. 3). While the  $D(2)$  and  $D(3)$  values exhibit opposite trends, i.e. tend to cancel out, the fourth-order components for a series of nucleophiles are quite similar. However, there are extraordinary differences in absolute values of these quantities. The  $D(2)$ ,  $D(3)$ ,  $S(4)$ , and  $T(4)$  are dominant contributions, while  $D(4)$  and  $Q(4)$  have only marginal effects on activation barrier. It is interesting that the patterns for  $D(4)$  and  $Q(4)$  as well as for  $S(4)$  and  $T(4)$  are very similar, almost identical in the latter case. Fig. 3 immediately shows the main outcome of the preceding analysis – namely, the quantities  $D(2)$ ,  $S(4)$ ,  $T(4)$  are responsible for the negative correlation contribution to the activation barrier,

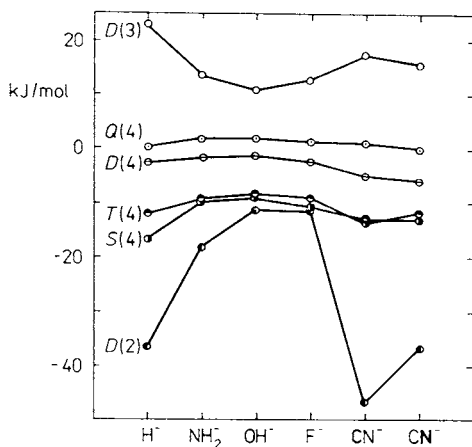


FIG. 3

Patterns of individual correlation energy contributions (in kJ/mol) within the fourth-order of MBPT for the set of six nucleophiles

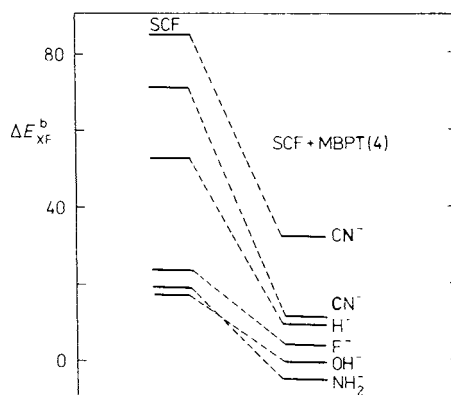


FIG. 4

Lowering of the activation barrier (in kJ/mol) due to the electron correlation for the set of six nucleophiles



It should be stressed that this complicated interplay of various positive and negative terms is often left unanalysed and attention is paid only to cumulative order-by-order contributions. For instance, in Table III we may see a large range (of about 40 kJ/mol) of cumulative contributions MBPT(2), compared to a 15 kJ/mol range of cumulative contributions MBPT(3) and MBPT(4). However, such a comparison gives no explanation why  $D(3)$  and the sum  $S(4) + D(4) + T(4) + Q(4)$  are of opposite sign.

The total lowering of the activation barrier caused by the electron correlation is depicted in Fig. 4. The uniform drop of the barrier height is really significant and emphasizes the importance of correlation effects in the S<sub>N</sub>2 activation process. The order of the nucleophiles corresponds to their classification proposed by Tanaka and coworkers<sup>29</sup>. According to their flowing afterglow measurements NH<sub>2</sub><sup>-</sup>, OH<sup>-</sup>, F<sup>-</sup>, and H<sup>-</sup> belong to anions of high nucleophilicity, while CN<sup>-</sup> is distinctively less reactive. This concerns especially the N-side attack of CN<sup>-</sup>. The activation barrier for the ambident CN<sup>-</sup> ion is lower if the methyl fluoride is attacked by the C-side of CN<sup>-</sup>. This lowering is caused mainly by the negative  $D(2)$  contribution, incidentally the most negative second-order term among the  $D(2)$  contributions calculated in this study.

The above analysis can be utilized also in explaining the discrepancy between our MBPT(4) calculations and previous S<sub>N</sub>2 studies<sup>10,17</sup> which indicated that the electron correlation may have the destabilizing effect on the S<sub>N</sub>2 transition states. Both cited papers used methods which did not include the important  $S(4)$  and  $T(4)$  contributions to the activation barrier. The discrepancy between our MBPT(4) and CEPA results of Keil and Ahlrichs<sup>10</sup> can be explained by the omission of these two terms and approximate treatment of  $Q(4)$ . In the work of Evanseck et al.<sup>17</sup> only the second and third order of MBPT using split-valence polarized 6-31G(*d*) basis set was employed. Thus, in addition to the lower level of the theory also the basis set without the diffuse *p*-functions was used. As known, these functions are necessary for the proper description of negative ions, so we can suspect that their positive correlation contribution to  $\Delta E^b$  is the basis set effect at the correlated level.

We shall make no direct comparison with experimental data, since the necessary vibrational analysis and the statistical thermodynamical treatment of present reactions will be published in a separate paper. Here we only repeat that our activation barriers correlate quite well with the apparent Arrhenius activation energies of Tanaka et al.<sup>29</sup>. This notion was also supported by the comparisons made in our preceding papers<sup>6-9</sup>.

## CONCLUSION

The MBPT(4) calculations of activation barriers for the set of model gas-phase S<sub>N</sub>2 reactions between simple negative ions and the methyl fluoride have revealed

vital importance of the correlation effects on the barrier height. For all reactions the correlation contribution lowers  $\Delta E_{XF}^b$ , single and triple excitations contribute extraordinarily to this lowering, while the double excitation terms at the second and third order tend to compensate each other, similar compensation is observed in the remaining MBPT(4) components,  $D(4)$  and  $Q(4)$ . The exceptional role of single and triple excitations (which occur for the first time at the fourth order and may be overestimated<sup>16,30</sup>) should be further examined, e.g. by the coupled cluster approach. This goal, together with the investigation of the basis set effects and the improvement of the transition state geometry will be subject of our future work.

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