Benchmark *ab initio* energy profiles for the gas-phase $S_N2$ reactions $Y^- + CH_3X \rightarrow CH_3Y + X^- \ (X,Y = F, Cl, Br)$.

Validation of hybrid DFT methods

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Abstract

The energetics of the gas-phase $S_N2$ reactions $Y^- + CH_3X \rightarrow CH_3Y + X^- \ (\text{where } X,Y = F, \text{ Cl, Br})$, were studied using (variants on) the recent W1 and W2 *ab initio* computational thermochemistry methods. These calculations involve CCSD and CCSD(T) coupled cluster methods, basis sets of up to $spdfgh$ quality, extrapolations to the one-particle basis set limit, and contributions of inner-shell correlation, scalar relativistic effects, and (where relevant) first-order spin-orbit coupling. Our computational predictions are in excellent agreement with experimental data where these have small error bars; in a number of other instances re-examination of the experimental data may be in order. Our computed benchmark data (including cases for which experimental data are unavailable altogether) are used to assess the quality of a number of semiempirical compound thermochemistry schemes such as G2 theory, G3 theory, and CBS-QB3, as well as a variety of density functional theory methods. Upon applying some modifications to the level of theory

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used for the reference geometry (adding diffuse functions, replacing B3LYP by the very recently proposed mPW1K functional [Lynch, B.J.; Fast, P.L.; Harris, M.; Truhlar, D.G. J. Phys. Chem. A 2000, 104, 4811]), the compound methods appear to perform well. Only the 'half-and-half' functionals BH&HLYP and mPWH&HPW91, and the empirical mPW1K functional, consistently find all required stationary points; the other functionals fail to find a transition state in the F/Br case. BH&HLYP and mPWH&HPW91 somewhat overcorrect for the tendency of B3LYP (and, to a somewhat lesser extent, mPW1PW91) to underestimate barrier heights. The Becke97 and Becke97-1 functionals perform similarly to B3LYP for the problem under study, while the HCTH and HCTH-120 functionals both appear to underestimate central barriers. HCTH underestimates complexation energies; this problem is resolved in HCTH-120. mPW1K appears to exhibit the best performance of the functionals considered, although its energetics are still inferior to the compound thermochemistry methods. mPW1K, however, appears to be very suitable for generating reference geometries for more elaborate thermochemical methods in kinetics applications.
I. INTRODUCTION

Due to the central importance of bimolecular nucleophilic substitution ($S_N2$) reactions in organic chemistry, the prototype $S_N2$ reactions

$$Y^- + CH_3X \rightarrow CH_3Y + X^- \quad (X,Y = F, Cl, \text{ and } Br)$$  \hspace{1cm} (1)

have aroused considerable interest in the past three decades. (Halomethanes have also received considerable attention in the area of atmospheric chemistry in connection with global warming and ozone layer destruction.) Both theoretical and experimental studies (see Refs. for reviews) indicate that the preferred gas phase reaction pathway involves a backside attack of the halide ion, $Y^-$, at the carbon atom followed by the familiar ‘Walden inversion’ of the CH$_3$ group. The resulting reaction profile (Figure 1) exhibits two local minima, i.e. entry and exit channel ion-molecule complexes $Y^-$···CH$_3$X and YCH$_3$···X$^-$, connected by a central transition state $[Y^-$···CH$_3$···X$^-]$, which has $D_{3h}$ and $C_{3v}$ symmetries in the identity ($X=Y$) and nonidentity ($X \neq Y$) cases, respectively. Although the qualitative form of this reaction pathway is widely accepted for substitution reactions in the gas phase, there is still considerable uncertainty about the exact energetics.

Böhme et al. and Brauman et al. were the first to investigate the gas-phase $S_N2$ reactions experimentally. Brauman and coworkers concluded that the measurements were best explained by a double-well potential with a central barrier. Subsequent experimental studies for a series of anionic nucleophiles with alkyl halides revealed that changes in the nucleophile, leaving group, and alkyl moiety leads to a wide variation of reaction rate constants; their observed variation was attributed to the central barrier height.

The double-well $S_N2$ potential energy surface also finds abundant theoretical support from ab initio calculations, which are currently one of the most useful tools for evaluating reaction potential energy profiles. For instance, Chandrasekhar et al. presented a comprehensive examination of Cl/Cl identity $S_N2$ reaction at the HF/6-31G* level, and Tucker and Truhlar examined the $S_N2$ reactions at the MP2/6-31G* level. Wladkowski et al. studied the F/F identity $S_N2$ reaction by large-scale coupled cluster theory involving single and double excitation operators with an a posteriori a quasiperturbative treatment of the effects of
connected triple substitutions (CCSD(T)) (see Refs.16,17 for reviews). Later, Radom, Pross and coworkers have carried out ab initio molecular orbital calculations at the G2(+) level of theory for the back-side identity18 and nonidentity19 S_N2 reactions. These authors have also investigated the identity front-side S_N2 reactions with retention of configuration20. The G2(+) theory is essentially G2 theory carried out from MP2/6-31+G* (rather than MP2/6-31G*) geometries and employing scaled HF/6-31+G* (rather than HF/6-31G*) zero-point energies. For the bromine and iodine containing systems, these authors employed Hay-Wadt relativistic effective core potentials (RECPs). Botschwina and coworkers examined the stationary points of the potential surface for the F/Cl nonidentity S_N2 reaction22 and for the Cl/Cl identity S_N2 reaction23 by means of large-scale CCSD(T) calculations. Finally, a referee brought a very recent large-scale coupled cluster study by Schmatz et al.24 to our attention.

Despite the well known successes (e.g.25,26) of the increasingly popular DFT (density functional theory) methods,27 their performance for transition state structures and reaction barrier heights leaves something to be desired. For instance, Durant28 found that the B3LYP, B3P86 and B3PW91 functionals all systematically underestimated barrier heights, while only the Becke half-and-half/Lee, Yang and Parr (BH&HLYP)29 functional predicted transition state barrier heights reasonably well — despite the fact that its performance for thermochemical and other properties is generally substantially poorer than that of B3LYP and B3PW91. Baker et al.30 arrived at a similar conclusion stating that the currently available density functionals are unable to provide a correct description of the transition states. For the prototype S_N2 reactions (Cl/Cl and Cl/Br) considered here, Radom and coworkers31 found that the popular B3LYP exchange-correlation functional significantly underestimated the overall and central barrier heights compared to the G2(+) and experimental results.

Nevertheless, the size of the systems involved in kinetic and mechanistic problems of organic and organometallic interest often makes DFT the only practical option. As a matter of fact, our group has recently reported DFT studies of the mechanism of competitive intramolecular C-C and C-H bond activation in rhodium(I) pincer complexes34 and of the
Aside from BH&HLYP, better performance for barrier heights has been claimed for a number of newer exchange-correlation functionals. For example, Adamo and Barone found that their mPW1PW91 (modified Perdew-Wang 1991 1-parameter hybrid exchange with Perdew-Wang 1991 correlation) at least correctly predicts a positive overall barrier for the Cl/Cl identity $S_N^2$ reaction, although it is still being underestimated. Very recently, Truhlar and coworkers proposed a new hybrid model called the modified Perdew-Wang 1-parameter model for kinetics (mPW1K). In this empirical functional, the coefficient $X$ for admixture of “exact” Hartree-Fock exchange

$$V_{XC} = XV_{X,HF} + (1 - X)V_{X,mPW91} + V_{C,PW91}$$

(2)

(where $X=1/4$ for standard mPW1PW91) was determined (using the fairly small 6-31+G* basis set) by minimizing the average deviation from a set of 40 barrier heights (20 forward, 20 reverse) obtained from a combination of experiment and theory (see Ref. for details). (Note that the Walden inversion, or for that matter cationic or anionic reactions of any kind, were not part of the parametrization set.) It was found that mPW1K reduced the mean unsigned error in reaction barrier heights by a factor of 2.4 over mPW1PW91 and by a factor of 3 over B3LYP.

Theoretical models such as Transition State Theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory were also employed to examine the $S_N^2$ reactions. Results from such studies (see and references therein) suggested that the assumption of statistical behavior in ion-molecule intermediate complexes is not valid. This “nonstatistical” behavior has been documented for several halide-methyl halide reactions and a thorough discussion is given by Hase. Classical trajectory simulations performed by Hase and coworkers questioned the basic assumptions of statistical theories and found that the trajectory calculations are very useful in interpreting the kinetics and dynamics of $S_N^2$ reactions.

Despite the enormous amount of work in the past, there are still significant gaps in the experimental data for the gas-phase $S_N^2$ reactions and, even where data are available, the results often possess large uncertainties. Recently, two computational thermochemistry
methods known as W1 and W2 (Weizmann-1 and Weizmann-2) theory\cite{32} have been developed in our laboratory. These are free of parameters derived from experiment and on average can claim ‘benchmark accuracy’ (defined in Ref.\cite{43} as a mean absolute error of 1 kJ/mol, or 0.25 kcal/mol) for molecular total atomization energies (TAEs) of first-and second-row compounds. The primary objective of the present study is to obtain high-quality energetic data for reaction (1) by means of W1 and W2 theory. Using these benchmark data, we shall then examine the performance of various DFT methods and \textit{ab initio} computational thermochemistry methods such as G1,\cite{44} G2,\cite{45} G3,\cite{46} and CBS-QB3\cite{47} theories.

\section*{II. COMPUTATIONAL METHODS}

All calculations were carried out on the 4-processor Compaq ES40 of our research group, and on the 12-CPU SGI Origin 2000 of the Faculty of Chemistry.

Energetics for the gas-phase stationary points for all six surfaces (i.e. F/F, Cl/Cl, Br/Br, F/Cl, F/Br, and Cl/Br) were obtained by means of the W1′ method described in Refs.\cite{43,48}. The W1′ method\cite{48} is a minor variation on W1 theory\cite{32} that exhibits improved accuracy for second-row systems at no additional computational cost. For a detailed description and theoretical and empirical arguments for each step, see Ref.\cite{43}; we shall merely summarize the main points here for the sake of clarity. The basis sets employed are mostly Dunning’s augmented correlation consistent \textit{n}-tuple zeta\cite{49,50} (aug-cc-p\textit{n}Z) basis sets; for second-row atoms high-exponent \textit{d} and \textit{f} functions were added (denoted ’+2d’ or ’+2d1f’) as recommended in Ref.\cite{52} for accommodating inner polarization. Since the standard aug-cc-p\textit{Vn}Z basis sets for bromine\cite{53} already contain quite high-exponent \textit{d} functions in order to describe the 3\textit{d} orbitals, no ‘inner polarization’ functions were deemed to be necessary on Br. We may distinguish the following six components in the ‘bottom-of-the-well’ TAE at the W1′ level:

- The SCF component of the TAE is obtained using the aug-cc-pVDZ+2d, aug-cc-pVTZ+2d, and aug-cc-pVQZ+2d1f basis sets, and extrapolated to the infinite-basis limit using the geometric expression\cite{54} \( A + B \cdot C^{-L} \), where the ‘cardinal number’
L=\{2,3,4\} for these three basis sets. (It is identical to the maximum angular momentum present for nonhydrogen atoms. Regular cc-pVnZ basis sets were used on hydrogen atoms throughout.)

- The CCSD (coupled cluster with all singles and doubles) valence correlation contribution to TAE is obtained using the aug-cc-pVTZ+2d and aug-cc-pVQZ+2d1f basis sets, then extrapolated to the infinite basis limit using the expression $A + B/L^{3.22}$.

- The (T) connected triple excitations component of TAE was computed using the aug-cc-pVDZ+2d and aug-cc-pVTZ+2d basis sets, and extrapolated to the infinite basis limit using the expression $A + B/L^{3.22}$.

- The inner-shell correlation contribution was computed as the difference between CCSD(T)/MTsmall values with and without constraining the inner-shell orbitals to be doubly occupied. The very deep-lying chlorine (1s) and bromine (1s,2s,2p) orbitals were doubly occupied throughout; the 'inner-shell correlation' thus represents carbon (1s), chlorine (2s,2p) and bromine (3s,3p,3d) correlation. (Basis set superposition error, BSSE, can be an issue for inner-shell correlation energies in heavier element systems; our experience suggests that BSSE in the W1/W2 inner shell correlation contributions largely cancels with basis set incompleteness.)

- The scalar relativistic contribution was computed as expectation values of the one-electron Darwin and mass-velocity (DMV) operators for the ACPF/MTsmall (averaged coupled pair functional) wave function, with all inner-shell electrons correlated except for chlorine (1s) and bromine (1s,2s,2p).

- The spin-orbit contribution to TAE, in the present case of all-closed-shell systems, is nothing more than the sum of the atomic fine structure corrections.

Where our computational hardware permitted (in practice, for F/F, Cl/Cl, and the Br/Br transition state), we also carried out even more demanding W2h calculations. In W2 theory, the same steps occur as above, except that the three valence basis sets are aug-cc-pVTZ+2d1f, aug-cc-pVQZ+2d1f, and aug-cc-pV5Z+2d1f (with L=3,4, and 5, respectively).
and that the extrapolation formula used for the CCSD and \((T)\) steps is simply \(A + B/L^3\). The W2h variant indicates, in this particular case, the use of unaugmented cc-pVnZ basis sets on carbon. The largest basis set CCSD step was carried out using the direct algorithm of Lindh, Schütz, and Werner. All these calculations were performed using MOLPRO 98.1 and a driver for the W1/W2 calculations written in MOLPRO’s scripting language. Reference geometries were obtained primarily using the B3LYP density functional method, which employs the Lee-Yang-Parr correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.

A number of lower-level procedures were validated against the W1′ and W2h results. These include the following set of DFT exchange-correlation functionals and basis sets: B3LYP/cc-pVTZ(\(+X\)), BH&HLYP/cc-pVTZ(\(+X\)), mPW1PW91/cc-pVTZ(\(+X\)), mPW1K/6-31+G*, mPW1K/cc-pVDZ(\(+X\)), mPW1K/cc-pVTZ(\(+X\)), where \((+X)\) indicates that diffuse functions are included only for halogens. BH&HLYP is essentially the B3LYP method, with the exception that the fraction of HF exchange is 50\% (H&H denotes ”half and half”). Analogous to BH&HLYP, we have also performed mPW\&HPW91. In addition, we carried out calculations using the standard G1, G2, G3, and CBS-QB3 model chemistries. The MP2/6-31G* and B3LYP/6-311G(2d,d,p) levels of theory (used for the reference geometries in G3 and CBS-QB3 respectively) fail to find stationary points for several of the ion-molecule complexes in the nonidentity cases (because of the absence of diffuse functions). Therefore, we have defined, by analogy with Radom and coworkers, G3(+) and CBS-QB3(+) model chemistries where MP2/6-31+G* and B3LYP/6-311+G(2d,d,p) reference geometries, respectively, are used. The G2(+) results quoted in the tables are taken from Radom and coworkers. All of these calculations were carried out using Gaussian 98 rev. A7 or trivial modifications thereof. Following the recommendations in Ref, larger grids than the default were used in the DFT calculations if necessary, specifically a pruned (99,590) grid for integration and gradients, and a pruned (50,194) grid for the solution of the coupled perturbed Kohn-Sham equations.

Finally, following very recent suggestions in the literature that some of these functionals may perform better for transition states, some calculations using the novel B97 (Becke-
and B97-1 (reparametrized Becke-1997), HCTH (Hamprecht-Cohen-Tozer-Handy), and HCTH-120 (reparametrization of HCTH including anions and weakly interacting systems) functionals were carried out by means of a slightly modified version of NWChem 3.3.1.

III. RESULTS AND DISCUSSION

A. Reference Geometries

Reference geometries for the W1' calculations were mostly obtained at the B3LYP/cc-pVTZ+1 level, where the ‘+1’ signifies the addition of a high-exponent $d$ function on second-row elements. (The Br basis set already includes high-exponent $d$ functions to cover the $(3d)$ orbital.) It was previously shown that B3LYP/cc-pVTZ geometries for stable molecules are generally within a few thousandths of an Å from experiment, as well that the use of B3LYP/cc-pVTZ+1 rather than much costlier CCSD(T)/cc-pVQZ+1 reference geometries insignificantly affects computed energies. (Modifications of popular computational thermochemistry methods that use DFT reference geometries include variants of G2 theory, G3//B3LYP, and CBS-QB3.) In some cases where B3LYP fails to locate the required stationary point, we used mPW1K/cc-pVTZ(+X) reference geometries. For the W2h calculations, CCSD(T)/cc-pVQZ+1 reference geometries were used. The geometries of all the structures involved in the present study calculated at various levels of theory are provided in the Supplementary Material.

B. Energetics

In order to assess the accuracy of W1' and W2h results, we consider first the total atomization energies (TAEs) of CH$_3$X and electron affinities (EAs) of X$^-$. A summary of our computed results and their components for the reactants/products of the S$_N$2 reactions is presented in Table 1. The final energies presented in the last column of the Table correspond to EAs of X (X = F, Cl and Br) and TAEs without zero-point vibrational energy (ZPVE).
of CH₃X. The inner-shell correlation contributions are all positive and the largest is 1.49 kcal/mol for CH₃Br. The core correlation contribution for TAE(CH₃X) is found to increase in the order F < Cl < Br, while for EA(X) it increases in the order Cl < F < Br. The importance of Darwin and mass-velocity corrections increases, as expected, with increasing atomic number (Z) of X and its contribution becomes substantial when X = Br.

It is perhaps more pertinent for our purposes to examine the relative energies (with respect to reactants) of the ion-molecule complexes and transition state structures. Table 2 presents W1′ and W2h results for identity reactions and only W1′ results for nonidentity reactions. W2h calculations for the nonidentity reactions are extremely expensive as the reaction intermediates are less symmetric. Moreover, the size of the bromine atoms prevents us from performing a W2h calculation on the identity Br⁻····CH₃Br ion-molecule complex. Likewise, we could not obtain the core correlation contributions for the Br⁻····CH₃Br ion-molecule complex at the W1′ level of theory. It was previously established that the inclusion of connected triple excitations in CCSD(T) is absolutely necessary for reliable core correlation contributions: the n³N⁴ CPU time dependence of the (T) step dominates the required CPU time for Cl and Br. Both the size of the halogen atoms and the reduced symmetry prevented us from performing core-correlation calculations for nonidentity S_N2 reactions, except for the F/Cl nonidentity case.

From Table 2, it can be seen that the final W1′ and W2h energy values for the identity reactions are very close to each other. Considering the very close agreement between W1′ and W2h results, the conclusion is warranted that the results from W1′ theory can be used as reference values to compare the results from other methods when W2h results are not available. As a general observation, the core contributions for the transition state structures are noticeably larger than for the ion-molecule complexes (see Table 2). Although the core-correlation contribution is small in absolute terms, its relative contribution to the likewise small overall barrier heights can be substantial. For example, it is 0.36 kcal/mol for [F····CH₃····F]^−, while the total energy is -0.37 kcal/mol. Likewise, the core correlation contributions for [Cl····CH₃····Cl]^− and [Br····CH₃····Br]^− are nearly 10% and 25% of the overall barrier (relative to reactants), respectively. At the W2h level, the core correlation
contribution to the total energy increases slightly. Scalar relativistic effects exhibit similar trends as those of core correlation, but the effects are fairly small. Only Cl$^-\cdot\cdot\cdot$CH$_3$Br, [Cl$\cdot\cdot\cdot$CH$_3$···Br]$^-$ and Br$^-\cdot\cdot\cdot$CH$_3$Cl exhibit noticeable scalar relativistic contributions, due to the presence of the heavy halogen Br.

Among the identity reactions only [F$\cdot\cdot\cdot$CH$_3$···F]$^-$ has a transition state below the reactants energy level. In the nonidentity case all the transition state structures lie below the reactants.

The computed final heats of formation ($\Delta H_f^\circ$) of CH$_3$X in kcal/mol are compared with experiment in Table 3. Both W1$'$ and W2h values are presented after accounting for ZPVEs and thermal corrections calculated at the B3LYP/cc-pVTZ+1 level. At this level the ZPVEs, after scaling by 0.985, are found to be 24.16, 23.26 and 22.89 kcal/mol, respectively, for CH$_3$F, CH$_3$Cl and CH$_3$Br. The corresponding thermal corrections are -1.92, -1.89 and -3.68 kcal/mol. The computed $\Delta H_f^\circ$ value for CH$_3$Cl lies within the experimental error bar: the experimental value for CH$_3$F is a crude estimate ($\pm 7$ kcal/mol) and our computed value is certainly more reliable. Our calculated value for CH$_3$Br is slightly outside the experimental error bar: some of the discrepancy could be due to the limitations of the scalar relativistic treatment. As shown by Bauschlicher, the simple DMV correction starts to exhibit minor deficiencies for third-row compounds; for first- and second-row compounds, it is in excellent agreement with more rigorous treatments.

Also included in Table 3 are calculated electron affinities of X (X = F, Cl and Br) in eV together with experimental results. Using a similar approach, but with even larger spd$g$hi basis sets as well as full CI corrections, we were able to reproduce the experimental EAs of the 1st- and 2nd-row atoms to within $\pm 0.001$ eV on average. The presently calculated W2h results of F and Cl EAs differ by only about 0.001 eV from these benchmark values (EA(F)=3.403 eV and EA(Cl)=3.611 eV), and the W2h results for F, Cl and Br are all within 0.003 eV of experiment. Although the W1$'$ values differ about 0.01 eV for F and Cl and 0.02 eV for Br, this is comparable to the W1/W2 target accuracy (0.25 kcal/mol on average). The performance of the W1$'$ and W2h methods for the reactants and products is obviously encouraging for the study of the problem at hand.
C. $S_N^2$ Reactions

The reaction mechanism with the double-well potential energy surface for the gas-phase $S_N^2$ reactions is shown in Figure 1. Obviously, the energy profile is symmetric for the identity reactions (Figure 1a), and asymmetric for the nonidentity reactions (Figure 1b). The complexation energy ($\Delta H_{\text{comp}}$), central barrier ($\Delta H_{\text{cent}}^\ddagger$), and overall activation barrier relative to the separated reactants ($\Delta H_{\text{ovr}}^\ddagger$) are defined in Figure 1. In the nonidentity case, the following additional quantities are defined in Figure 1b: overall enthalpy change for the reaction ($\Delta H_{\text{ovr}}$) and the central enthalpy difference $\Delta H_{\text{cent}}$ between product and reactant ion-molecule complexes, 3 and 1.

D. Identity Reactions

Complexation energies ($\Delta H_{\text{comp}}$), overall barrier heights ($\Delta H_{\text{ovr}}^\ddagger$) and central barriers ($\Delta H_{\text{cent}}^\ddagger$) obtained from W1’ and W2h methods are compared in Table 4 with DFT, Gn, and CBS-QB3 methods together with available experimental values.

It should be emphasized that the experimental data for the $S_N^2$ reactions are insufficient and the available data are subject to large uncertainties. Therefore, it would be appropriate to analyze the performance of various methods with respect to Wn methods. First of all, note that the mPW1K/6-31+G* $\Delta H_{\text{comp}}$ (13.55 kcal/mol) for the F/F case is very close to the W1’ and W2h results (13.66 and 13.72 kcal/mol, respectively). mPW1K/cc-pVDZ(+X) and mPW1K/cc-pVTZ(+X) methods however predict lower $\Delta H_{\text{comp}}$ values. In fact, the B3LYP, B97, HCTH-120, mPW1PW91, mPWH&HPW91 and mPW1K methods all predict roughly 1 kcal/mol lower complexation energies, while BH&HLYP and B97-1 agree well with W1’ and W2h. (The HCTH $\Delta H_{\text{comp}}$ is much lower than the others, vide infra.) G2 and CBS-QB3 values are close to the Wn results while the G3 method predicts higher complexation energy compared to the Wn methods. Inclusion of diffuse functions for the Gn and CBS-QB3 reference geometries (i.e. Gn(+) and CBS-QB3(+)) increases the $\Delta H_{\text{comp}}$ value by 0.4–0.6 kcal/mol.

A comparison of overall barrier heights is presented in the third column of Table 4. Both
W1’ (-0.37 kcal/mol) and W2h (-0.34 kcal/mol) theories predict negative barrier heights in the F/F case and the values are very close. The CBS-QB3(+) result is in excellent agreement therewith; all Gn theories predict barrier heights that are lower by 1 kcal/mol, with further lowering seen at the G2(+) and G3(+) levels. Among the DFT methods considered, only mPW1K/6-31+G* and HCTH/cc-pVDZ(+X) fortuitously predict overall barrier heights close to the Wn results: basis set extension for mPW1K leads to positive overall barrier heights, which are likewise found for the ”half and half” functionals. B3LYP, B97(-1) and HCTH-120 all significantly underestimate the barrier, mPW1PW91 to a lesser extent.

For the chlorine identity gas-phase S_N2 reactions, fairly accurate experimental values are available and are presented in Table 4. The experimental values reported by Li and coworkers\textsuperscript{11} correspond to the standard state. Hence, thermal corrections and ZPVEs are subtracted from experimental values in order to compare with the ”bottom of the well” calculated values. It is noteworthy that the W1’ (10.54 kcal/mol) and W2h (10.94 kcal/mol) complexation energies are in good agreement with the experimental value (10.53 kcal/mol). CBS-QB3 results are also in agreement with the Wn and experimental values, while those from DFT calculations are less satisfactory as they are about 1 kcal/mol lower. Also note that the G1 and G2 methods reproduce the complexation energy well, while G3 results are 0.5 kcal/mol higher than the Wn and experimental values.

The overall barrier height for the Cl/Cl reaction is found to be 3.07 and 2.67 kcal/mol at the W1’ and W2h levels of theory. Note first that the experimental value (2.90 kcal/mol) is very close and lies between the W1’ and W2h values. The $\Delta H_{\text{ovr}}$ value calculated at the mPW1K/6-31+G*, and CBS-QB3 levels of theory as well as the G2(+) value by Radom \textit{et al.}\textsuperscript{18} and the CCSD(T)/spdfg value by Botschwina\textsuperscript{23} agree well with the W2h result. The mPW1K exchange-correlation functional with the cc-pVDZ(+X) and cc-pVTZ(+X) basis sets predict somewhat higher $\Delta H_{\text{ovr}}$ values, while the G1, G2MP2 and G3(+) values are about 1 kcal/mol lower. B3LYP, B97, B97-1, and HCTH-120 all predict a negative overall barrier for the Cl/Cl system, in disagreement with all other methods considered and with experiment. BH&HLYP performs moderately well, while mPWH&HPW91 predicts a larger barrier height (4.50 kcal/mol) than Wn. The central barrier values presented in the last
column of the Table 4 reveal that the agreement between Wn theories (13.61 kcal/mol) and experiment (13.66 kcal/mol) is excellent. The G2MP2, G2(+) and CBS-QB3 methods also reproduce the central barriers very well. As expected from the overall barrier heights, the DFT results are less satisfactory, except for mPW1K/cc-pVDZ(+X) and mPW1K/cc-pVTZ(+X) which are in good agreement with the Wn values.

For the bromine identity S_n2 reaction, W1′ theory predicts 10.03 kcal/mol for ΔH_{comp}. Note that the G2(+) value is in close agreement with W1′ theory. The reported experimental value (11.34±0.4 kcal/mol) agrees fairly well. Most DFT levels of theory considered suggest a complexation energy about 1 kcal/mol lower than the W1′ value, except mPW1K/6-31+G** which is higher (12.78 kcal/mol, probably an artifact of the small basis set); B97 and B97-1 which closely bracket the W1′ value; HCTH-120 which is close to the W1′ value (see below); and HCTH which is 2.5 kcal/mol lower than the latter. The complexation energies for X^-···CH_3X are found to decrease in the order F > Cl > Br. This trend was noted previously by Radom and coworkers, who attributed it to the electronegativities of the halogens.

The overall barrier height for the Br/Br reaction is found to be 1.02 and 0.77 kcal/mol at the W1′ and W2h levels of theory. Of the various exchange-correlation functionals considered, only BH&HLYP, mPW&HPW91, and mPW1K find positive barriers (as do the G_n theories). It should be pointed out that the DFT results for this system display appreciable basis set sensitivity: for instance, the mPW1K/6-31+G* overall barrier has the wrong sign. It is interesting to note that the complexation energy derived from the experimental overall (1.73 kcal/mol) and central (11.68 kcal/mol) barrier heights is 9.95 kcal/mol while the reported experimental complexation energy (11.34 kcal/mol) is inconsistent with the derived value. In fact, the derived value is in excellent agreement with the W1′ value (10.03 kcal/mol). This clearly suggests that the experimental data should be re-examined.

The performance of both B97 and B97-1 for the identity reactions is quite similar to that of B3LYP. While the ‘pure DFT’ HCTH functional appears to yield markedly better overall barrier heights, this comes at the expense of significantly underestimated complexation energies (and severely overestimated ion-molecule distances, see Supplementary Material).
It was previously noted that HCTH severely underestimates interaction energies of H-bonded complexes; this was ascribed to the absence of anions and H-bonded dimers in the original HCTH parametrization set. A reparametrization against an enlarged sample of high-quality ab initio energies, denoted HCTH-120, eliminates this particular problem. For the identity S_N2 reactions, we find that complexation energies (and ion-molecule distances) are dramatically improved compared to HCTH: no corresponding improvement is however seen for the central barrier heights, and the overall barrier heights deteriorate accordingly.

Overall, the DFT methods are less satisfactory for barrier height calculations. Although the performance of mPW1K/6-31+G* method for F/F and Cl/Cl reactions was excellent, it is not the ultimate low cost method for barrier heights as it has predicted a negative barrier for the Br/Br system. This behavior illustrates the inadequacy of the 6-31+G* basis set for Br: the more extended correlation consistent basis sets with the mPW1K exchange-correlation functional do predict the sign correctly. In addition, Gn(+) and CBS-QB3(+) provide an acceptable account of reaction energetics.

E. Nonidentity Reactions

A comparison of computed and experimental complexation energies for the nonidentity S_N2 reactions is provided in Table 5. For the F⁻⋯·CH₃Cl ion-molecule complex we could find a stationary point neither at the MP2/6-31G* level of theory used for the G2 and G3 reference geometries nor at the B3LYP/6-311G(2d, d, p) level used for the CBS-QB3 reference geometries; at these levels of theory, the optimization leads to Cl⁻⋯·CH₃F even if the initial geometries were chosen to correspond to F⁻⋯·CH₃Cl. Addition of diffuse functions to the basis set for the reference geometry remedies the problem. Similarly, in the F/Br case only the Br⁻⋯·CH₃F complex is found as a stationary point at the MP2/6-31G* level of theory, and the transition state and second ion-molecule complex only appear when diffuse functions are added to the basis set. Furthermore, and regardless of the basis set employed, none of the DFT functionals except mPW1K, mPW91, and BH&HLYP find a transition state or a F⁻⋯·CH₃Br complex. (The CBS-QB3 method is not defined for Br and hence
no CBS-QB3 data are presented for the F/Br and Cl/Br ion-molecule complexes.) Table 5 also presents large-scale CCSD(T) energetics for the F/Cl and Cl/Br cases reported by Botschwina and coworkers. Available experimental values are presented at the end of the Table with uncertainties in parentheses.

Examination of Table 5 indicates that the $\Delta H_{\text{comp}}$ values strongly depend on the nucleophile ($Y^-$), decreasing in the order $F^- > Cl^- > Br^-$. They also depend on the leaving group ($X^-$), in the order $CH_3F < CH_3Cl < CH_3Br$. Similar observations were made earlier by Radom and coworkers.\(^5\)

Comparison of the complexation energies obtained from various methods with W1$'$ theory indicates that all DFT results for $Cl^- \cdots CH_3F$ are lower by 1 kcal/mol. The only available experimental value\(^8\) for $Cl^- \cdots CH_3F$ ($\Delta H^o = 11.41$ kcal/mol) has an uncertainty of 2.01 kcal/mol. Comparison of this value with the calculated values suggest that more accurate measurements are in order. For $Cl^- \cdots CH_3Br$ and $Br^- \cdots CH_3Cl$, rather more accurate high-pressure mass spectrometry data are available (12.54 and 11.01 kcal/mol). The W1$'$ values (11.91 and 10.32 kcal/mol) are very close to the experimental results, considering the experimental uncertainty of 0.4 kcal/mol. While the mPW1K/6-31+G* values for $Cl^- \cdots CH_3Br$ and $Br^- \cdots CH_3Cl$ are fortuitously within the experimental error bars, the other DFT methods predict lower values. Also note that G2(+) predicts complexation energies close to W1$'$ and experiment for $Cl^- \cdots CH_3Br$, while the $Br^- \cdots CH_3Cl$ value is small. A complete assessment of CBS-QB3 is not possible as it could not be applied to the bromine-containing systems.

Like for the identity reactions, complexation energies are significantly underestimated (and ion-molecule distances overestimated by up to 0.3 Å: see Supplementary Material) by HCTH, and this problem is mostly remedied by HCTH-120. B97 and especially B97-1 appear to represent an improvement over B3LYP for the complexation energies.

Calculated overall reaction enthalpies, central enthalpy differences between reactant and product ion-molecule complexes, overall barrier heights, and central barrier heights for the nonidentity $S_N2$ reactions are presented with available experimental results in Table 6. It needs to be reemphasized that all values are “bottom-of-the-well” (i.e, zero-point exclusive):
that is, the experimental values are presented after subtracting the ZPVEs (scaled by 0.985) and thermal corrections obtained using the B3LYP method.

The overall reaction enthalpies of the three nonidentity reactions, viz F/Cl, F/Br, and Cl/Br, calculated at the W1' level are -32.65, -41.43 and -8.56 kcal/mol, respectively. The corresponding experimental values are available and are presented in Table 6. The experimental value for the F/Cl reaction (-33.34 kcal/mol) is in close agreement with the W1' value. B3LYP, B97(-1), mPW1PW91, Gn, and CCSD(T)/spdzfg results are all in close agreement with the W1' value, but mPW1K, "half and half" and CBS-QB3 theories predict 3-5 kcal/mol higher exothermicity. For the F/Br reaction, the mPW1K/6-31+G* and mPW1PW91/cc-pVTZ(+X) methods yield overall reaction enthalpies which are quite close to the W1' result. The experimental result (-40.20 kcal/mol) is in good agreement with the best calculated values considering the uncertainty of 1 kcal/mol. The Gn theories predict exothermicities below, and mPW1K/cc-pVnZ(+X) above, the W1' value. Concerning the Cl/Br nonidentity reaction, the reported experimental value (-6.86 kcal/mol) differs from the W1' value by 2 kcal/mol. As expected, the very recent CCSD(T)/spdfgh results of Botschwina and coworkers are in close agreement with our predictions. Our results suggest that the Cl/Br experimental data may need to be reconsidered. Note the significant basis set dependence in the mPW1K results, which illustrates the inadequacy of the 6-31+G* basis set.

As a general observation, 50:50 admixture of HF exchange in the DFT theories increases the magnitude of the overall reaction enthalpy, and the increase is greater in BH&HLYP than in mPW&HPW91. Performance of B97 and B97-1 for the overall reaction enthalpies is similar to B3LYP, while HCTH and HCTH-120 represent underestimates in absolute value.

At the W1' level of theory, the calculated central barrier (ΔH\text{cent}) for the F/Cl system is 2.89 kcal/mol. Gn(+), CBS-QB3(+), BH&HLYP, mPW&HPW91, and mPW1K all reproduce the W1' value moderately well, while B3LYP, mPW1PW91, B97, B97-1, HCTH, and HCTH-120 all underestimate the central barriers. The experimental central barrier for the F/Cl system is nearly 4 kcal/mol higher than the calculated values. Judging from the performance of the various methods for the identity S_N2 reactions, it is almost certain that
the experimental F/Cl central barrier is in error and unambiguous new measurements are in order. For the F/Cl and Cl/Br systems, the B3LYP, mPW1PW91, B97, B97-1, HCTH, and HCTH-120 central barriers are all underestimated, while these exchange-correlation functionals find no barrier at all for the F/Br case. Like for the identity case, mPW1K/cc-pVTZ(+X) and BH&HLYP/cc-pVTZ(+X) central barriers agree well with the benchmark ab initio values, although the basis set sensitivity of particularly the Cl/Br results argues against using small basis sets like 6-31+G*.

Several studies have reported experimental overall barrier heights (Δ\(H_{\text{ovr}}^f\)), but only for the Cl/Br system, and the experimental data range from -0.61 to -1.83 kcal/mol. To our knowledge, no experimental data are available for the F/Cl and F/Br systems. For the Cl/Br system, the theoretical values span a range from -1.17 to -6.60 kcal/mol. Nevertheless, it is worth noting that the W1′ value (-1.82 kcal/mol) for the Cl/Br system is in excellent agreement with the experimental overall barrier height reported by Caldwell and coworkers (1.83 kcal/mol, after accounting for ZPVE and thermal corrections). Some caution should be exercised as the W1′ value does not include the core correlation contribution. Also note that G2 theory (-1.82 kcal/mol) reproduces the W1′ value very well. Except for mPW1K/cc-pVTZ(+X), mPW&HPW91/cc-pVTZ(+X), and BH&HLYP/cc-pVTZ(+X), all the DFT methods perform poorly, consistent with the preceding discussion.

IV. CONCLUSIONS

A benchmark study using the W1′ and W2h methods has been carried out for the potential surface of the gas-phase \(S_N2\) reactions \(Y^- + \text{CH}_3\text{X} \rightarrow \text{CH}_3\text{Y} + \text{X}^-\). A number of more approximate (and less expensive) methods — both compound models (like G2/G3 theory and CBS-QB3) and density functional methods — have been applied in an attempt to assess their performance for barrier heights in \(S_N2\) reactions. We arrive at the following conclusions.

(1) Our best calculations are in excellent agreement with experiment for the \(\Delta H_f^\circ\) values of the methyl halides (where available) and the electron affinities of the halogens. Where
accurate experimental data are available for the title reactions (e.g. for the Cl/Cl case), our best calculations agree with experiment to within overlapping uncertainties. Our calculations however suggest that more reliable experimental data are in order for most of the reactions considered.

(2) The nonidentity $S_N2$ reactions and F/F identity reaction possess transition state structures below the reactants energy while Cl/Cl and Br/Br transition structures are above the reactants energy. The complexation energies for identity $S_N2$ reactions are found to increase in the order $\text{Br} < \text{Cl} < \text{F}$ while the barrier heights follow the order $\text{F} \lesssim \text{Br} < \text{Cl}$. The complexation energies for the nonidentity $S_N2$ reactions indicate that the $\Delta H_{\text{comp}}$ strongly depend on the nucleophile and leaving group.

(3) The B3LYP, and to a lesser extent, mPW1PW91 exchange-correlation functionals systematically underestimate barrier heights and, in the F/Br case, are not even able to locate the correct stationary points on the potential surface. The latter problem is remedied by using the corresponding ‘half-and-half’ functionals BH&HLYP and mPWH&HPW91, which however appear to somewhat overcorrect the barrier height. The B97 and B97-1 functionals perform similarly to B3LYP for the problem under study. The ‘pure DFT’ HCTH and HCTH-120 functionals both underestimate central barrier heights; HCTH in addition underestimates complexation energies (and severely overestimates ion-molecule distances), which are however well reproduced by HCTH-120. Overall, the mPW1K functional appears to put in the best performance of all DFT methods considered, especially when using extended basis sets.

(4) The performance of G2(+), G3(+), and CBS-QB3(+) methods for the energetics still appears to be superior to the DFT methods. (The ‘(+)’ stands for the addition of diffuse functions to the basis set used in obtaining the reference geometries; this is mandatory to get transition states at all in the F/Br and Cl/Br cases.) The limitations for transition states of the B3LYP exchange-correlation functional suggest its replacement — at least for kinetics applications — by mPW1K in thermochemistry methods that employ DFT reference geometries, e.g. G3B3, CBS-QB3, and W1 theory. (In addition, larger basis sets than 6-31+G* should definitely be considered for the Br compounds.)
The present calculations illustrate the power of state-of-the-science theoretical methods in providing both qualitative and quantitative information regarding the reaction energetics. In the absence of accurate experimental data, our high quality results should be useful to future experimental and theoretical studies.

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Supporting Information Available: Calculated geometries of species involved in the $S_N2$ reactions are available on the World Wide Web at the Uniform Resource Locator (URL) [http://theochem.weizmann.ac.il/web/papers/sn2.html](http://theochem.weizmann.ac.il/web/papers/sn2.html). This material is also available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
REFERENCES

1 Shaik, S.S.; Schlegel, H.B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry: The S_N 2 Mechanism*; Wiley: New York, 1992.

2 Ingold, C.K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, 1969.

3 Wuebbles, D.J.; Edmonds, J. *Primer on Greenhouse Gases*; Lewis Publishers: Michigan, 1991.

4 WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 1998 (Global Ozone Research and Monitoring Project Report No. 44, WMO, Geneva, 1999).

5 Hase, W.L. *Science* **1994**, *266*, 998

6 Chabinyc, M.L.; Craig, S.L.; Regan, C.K.; Brauman, J.I. *Science* **1998**, *279*, 1882

7 (a) Böhme, D.K.; Young, L.B. *J. Am. Chem. Soc.* **1970**, *92*, 7354 (b) Tanaka, K.; Mackay, G.I.; Payzant, J.D.; Böhme, D.K. *Can. J. Chem.* **1976**, *54*, 1643 (c) Böhme, D.K.; Mackay, G.I.; Payzant, J.D. *J. Am. Chem. Soc.* **1974**, *96*, 4027

8 (a) Olmstead, W.N.; Brauman, J.I. *J. Am. Chem. Soc.* **1979**, *101*, 3715 (b) Brauman, J.I.; Olmstead, W.N.; Lieder, C.A. *J. Am. Chem. Soc.* **1974**, *96*, 4030 (c) Olmstead, W.N.; Brauman, J.I. *J. Am. Chem. Soc.* **1977**, *99*, 4219

9 Caldwell, G.; Magnera, T.F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959

10 (a) Barlow, S.E.; Van Doren, J.; Bierbaum, V.M. *J. Am. Chem. Soc.* **1988**, *110*, 7240 (b) DePuy, C.H.; Grovert, S.; Mullin, A.; Bierbaum, V.M. *J. Am. Chem. Soc.* **1990**, *112*, 8650

11 Li, C.; Ross, P.; Szulejko, J.E.; McMahon, T.B. *J. Am. Chem. Soc.* **1996**, *118*, 9360

12 De Turi, V.F.; Hintz, P.A.; Ervin, K.M. *J. Phys. Chem. A* **1997**, *101*, 5969

13 Chandrasekhar, J.; Smith, S.F.; Jorgensen, W.L. *J. Am. Chem. Soc.* **1985**, *107*, 154
14 Tucker, S.C.; Truhlar, D.G. *J. Phys. Chem.* **1989**, *93*, 8138

15 Wladkowski, B. D.; Allen, W. D.; Brauman, J. I.; *J. Phys. Chem.* **1994**, *98*, 13532

16 Lee, T.J.; Scuseria, G.E. in *Quantum mechanical electronic structure calculations with chemical accuracy*; Langhoff, S.R., Ed.; Kluwer: Dordrecht, The Netherlands, 1995; pp.47-108.

17 Bartlett, R.J. in *Modern Electronic Structure Theory. Vol 2*; Yarkony, D.R., Ed.; World Scientific: Singapore, 1995; pp.1047-1131.

18 Glukhovtsev, M.N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024

19 Glukhovtsev, M.N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 6273

20 Glukhovtsev, M.N.; Pross, A.; Schlegel, H.B.; Bach, R.D.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 11258

21 Wadt, W.R.; Hay, P.J. *J. Chem. Phys.* **1985**, *82*, 284

22 Botschwina, P.; Horn, M.; Seeger, S.; Oswald, R. *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 387

23 Botschwina, P. *Theor. Chem. Acc.* **1998**, *99*, 426

24 Schmatz, S.; Botschwina, P.; Stoll, H.; *Int. J. Mass Spectrom.* **2000**, *201*, 277

25 (a) Laming, G.J.; Handy, N.C.; Amos, R.D. *Mol. Phys.* **1993**, *80*, 1121 (b) Rienstra-Kiracofe, J.C.; Graham, D.E.; Schaefer III, H.F. *Mol. Phys.* **1998**, *94*, 767 (c) Altmann, J.A.; Handy, N.C.; and Ingamells, V.E. *Mol. Phys.* **1997**, *92*, 339 (d) De Proft, F.; Geerlings, P. *J. Chem. Phys.* **1997**, *106*, 3270 (e) De Proft, F.; Martin, J.M.L.; Geerlings, P. *Chem. Phys. Lett.* **1996**, *250*, 393

26 Martin, J.M.L.; El-Yazal, J.; François, J.P. *Mol. Phys.* **1995**, *86*, 1437

27 (a) Parr, R.G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: New York, 1989. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651 (c) Handy, N.C. in *Lecture notes in chemistry II*; Roos, B.O., Ed; Springer: Berlin, 1995. (d) Kohn, W.;
28 Durant, J.L. Chem. Phys. Lett. **1996**, *256*, 595

29 Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 1372

30 Baker, J.; Andzelm, J.; Muir, M.; Taylor, P.R. Chem. Phys. Lett. **1995**, *237*, 53

31 Glukhovtsev, M.N.; Bach, R.B.; Pross, A.; and Radom, L. Chem. Phys. Lett. **1996**, *260*, 558

32 Becke, A.; D. *J. Chem. Phys.* **1993**, *98*, 5648.

33 Lee, C.; Yang, W.; and Parr, R.; G. Phys. Rev. B **1988**, *37*, 785

34 Sundermann, A.; Uzan, O.; Milstein, D.; Martin, J.M.L. J. Am. Chem. Soc. **2000**, *122*, 7095

35 Sundermann, A.; Uzan, O.; Martin, J.M.L. Chem. Eur. J., accepted.

36 Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664

37 Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C.; Phys. Rev. B **1992**, *46*, 6671 and references therein

38 Lynch, B.J.; Fast, P.L.; Harris, M.; Truhlar, D.G. J. Phys. Chem. A **2000**, *104*, 4811

39 (a) Truhlar, D.G.; Garrett, B.C.; Klippenstein, S.J. J. Phys. Chem. **1996**, *100*, 12771 (b) Glasstone, S.; Laidler, K.J.; Eyring, H. in *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

40 (a) Gilbert, R.G.; Smith, S.C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific: Oxford, 1990. (b) Baer, T.; Hase, W.L. in *Unimolecular Reaction Dynamics-Theory and Experiments*; Oxford: New York, 1996.

41 Wang, H.; Zhu, L.; Hase, W.L. *J. Phys. Chem.* **1994**, *98*, 1608
42 (a) Mann, D.J.; Hase, W.L. J. Phys. Chem. A 1998, 102, 6208 (b) Su, T.; Wang, H.; Hase, W.L. J. Phys. Chem. A 1998, 102, 9819

43 Martin, J.M.L.; De Oliveira, G. J. Chem. Phys. 1999, 111, 1843

44 Curtiss, L. A.; Jones, C.; Trucks, G.W.; Raghavachari, K.; Pople, J. A. J. Chem. Phys. 1990, 93, 2537

45 Curtiss, L. A.; Raghavachari, K.; Trucks, G.W.; Pople, J. A. J. Chem. Phys. 1991, 94, 7221

46 Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. J. Chem. Phys. 1998, 109, 7764

47 Montgomery Jr., J.A.; Frisch, M.J.; Ochterski, J.W.; Petersson, G.A. J. Chem. Phys. 1999, 110, 2822

48 Martin, J.M.L. Chem. Phys. Lett. 1999, 310, 271

49 Dunning Jr., T. H.; J. Chem. Phys. 1989, 90, 1007

50 Kendall, R. A.; Dunning, T. H.; Harrison, R. J.; J. Chem. Phys. 1992, 96, 6796

51 Dunning Jr., T.H.; Peterson, K.A.; Woon, D.E.; "Correlation consistent basis sets for molecular calculations", in Encyclopedia of Computational Chemistry; Schleyer, P.v.R., Ed.; Wiley & Sons: Chichester, 1998.

52 Martin, J. M. L.; J. Chem. Phys. 1998, 108, 2791

53 Wilson, A.K.; Woon, D.E.; Peterson, K.A.; Dunning Jr., T.H.; J. Chem. Phys. 1999, 110, 7667

54 Feller, D.; J. Chem. Phys. 1992, 96, 6104

55 Purvis III, G. D.; Bartlett, R. J. J. Chem. Phys. 1982, 76, 1910

56 Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M.; Chem. Phys. Lett. 1989, 157, 479.
57 Bauschlicher Jr., C. W.; Ricca, A. J. Phys. Chem. A 1998, 102, 8044

58 Cowan, R.D.; Griffin, M. J. Opt. Soc. Am. 1976, 66, 1010

59 R.L. Martin J. Phys. Chem. 1983, 87, 750

60 Gdanitz, R. J.; Ahlrichs, R. Chem. Phys. Lett. 1988, 143, 413

61 Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K.; Chem. Phys. Lett. 1998, 286, 243

62 Parthiban, S.; Martin, J.M.L.; to be published.

63 M. Schütz, Lindh, R.; and H.-Werner, J. Mol. Phys. 1999, 96, 719

64 MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P.J.; with contributions from Almlöf, J.; Amos, R.D.; Berning, A.; Cooper, D.L.; Deegan, M.J.O.; Dobbyn, A.J.; Eckert, F.; Elbert, S.T.; Hampel, C.; Lindh, R.; Lloyd, A.W.; Meyer, W.; Nicklass, A.; Peterson, K.; Pitzer, R.; Stone, A.J.; Taylor, P.R.; Mura, M.E.; Pulay, P.; Schütz, M.; Stoll, H.; Thorsteinsson, T.

65 Martin, J. M. L.; Parthiban, S.; autoW1W2 (Weizmann Institute of Science, 2000). This driver is available on request from the authors.

66 The keywords used to carry out mPWH&HPW91 calculations with Gaussian98 are:

#mpw1pw91

IOp(5/45=10000500,5/46=05000500,5/47=10001000)

opt

67 Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery Jr., J.A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.;
Fo\textsc{x}, D. J.; Ke\textsc{ith}, T.; Al-Laham, M.A.; Peng, C. Y.; Nanayakkara, A.; Go\textsc{n}zalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Go\textsc{n}zalez, C.; Head-Gordon, M.; Replo\textsc{gle}, E. S.; and Pople, J. A.; \textit{Gaussian 98, Revision A.7} (Gaussian, Inc., Pittsburgh, PA, 1998).

68 Martin, J. M. L.; Bauschlicher Jr., C. W.; Ricca, A.; \textit{Comput. Phys. Commun.}, in press.

69 Preston, D. A.; Gilbert, B. A. \textit{Chem. Phys. Lett.} \textbf{2000}, 326, 537

70 Becke, A. D.; \textit{J. Chem. Phys.} \textbf{1997}, 107, 8554

71 Hampre\textsc{ch}t, F. A.; Cohen, A. J.; To\textsc{zer}, D. J.; Hand\textsc{y}, N. C.; \textit{J. Chem. Phys.} \textbf{1998}, 109, 6264

72 Boese, A. D.; Doltsinis, N. L.; Hand\textsc{y}, N. C.; Sprik, M.; \textit{J. Chem. Phys.} \textbf{2000}, 112, 1670

73 Anchell, J.; Apra, E.; Bern\textsc{hold}t, D.; Borowski, P.; By\textsc{laska}, E.; Clark, T.; Clere, D.; Dachsel, H.; de Jong, W.; Deegan, M.; Dupuis, M.; Dy\textsc{all}, K.; Elwood, D.; Fann, G.; Fr\textsc{\text{"{u}}rchtl}, H.; Glendening, E.; Gutowsk\textsc{i}, M.; Harr\textsc{ison}, R.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kendall, R.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nicholas, J.; Nieplo\textsc{cha}, J.; Rendall, A.; Rosing, M.; Sandrone, G.; Stave, M.; Straatsma, T.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wind\textsc{us}, T.; Wolinski, K.; Wong, A.; Zhang, Z.; "NWChem, A Computational Chemistry Package for Parallel Computers, Version 3.3.1" (1999), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA; see also Bern\textsc{hold}t, D. E.; Apra, E.; Fr\textsc{\text{"{u}}rchtl}, H. A.; Guest, M.F.; Harr\textsc{ison}, R. J.; Kendall, R. A.; Kutteh, R. A.; Long, X.; Nicholas, J. B.; Nichols, J. A.; Taylor, H. L.; Wong, A. T.; Fann, G. I.; Littlefield, R. J.; Nieplo\textsc{cha}, J.; \textit{Int. J. Quantum Chem. Symp.} \textbf{1995}, 29, 475

74 Martin, J. M. L.; Uzan, O. \textit{Chem. Phys. Lett.} \textbf{1998}, 282, 19

75 Mebel, A.M.; Morokuma, K.; Lin, M.C. \textit{J. Chem. Phys.} \textbf{1995}, 103, 7414

76 Bauschlicher Jr., C.W.; Partridge, H. \textit{J. Chem. Phys.} \textbf{1995}, 103, 1788; \textit{erratum J. Chem. Phys.} \textbf{1996}, 105, 4398
77 Baboul, A.G.; Curtiss, L.A.; Redfern, P.C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650

78 Martin, J.M.L.; Sundermann, A.; Fast, P.L.; Truhlar, D.G. *J. Chem. Phys.* **2000**, *122*, 7095

79 Bauschlicher Jr., C. W. *Theor. Chem. Acc.* **1999**, *101*, 421

80 Bauschlicher Jr., C. W. *J. Phys. Chem. A* **2000**, *104*, 2281

81 Bauschlicher Jr., C. W.; Martin, J. M. L.; Taylor, P.R. *J. Phys. Chem. A* **1999**, *103*, 7715

82 De Oliveira, G; Martin, J.M.L.; De Proft, F.; Geerlings, P. *Phys. Rev. A* **1999**, *60*, 1034

83 Wilbur, J.L.; Wladkowski, B.D.; Brauman J.I. *J. Am. Chem. Soc.* **1993**, *115*, 10823

84 Pellerite, M.J.; Brauman, J.I. *J. Am. Chem. Soc.* **1983**, *105*, 2672

85 Tuma, C.; Boese, A. D.; Handy, N. C.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 3939

86 Larson, J.W.; McMahon, T.B. *J. Am. Chem. Soc.* **1984**, *106*, 517 (b) Larson, J.W.; McMahon, T.B. *J. Am. Chem. Soc.* **1985**, *107*, 766

87 Chase, M.W.; Jr., Davies, C.A.; Downey, J.R.; Jr., Frurip, D.J.; McDonald, R.A.; and Syverud, A.N. *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* 14, supplement 1, 1985.

88 CRC Handbook of Chemistry and Physics, 78th ed. (Press, CRC; Boca Raton, FL, 1997)

89 Afeefy, H. Y.; Liebman, J. F.; and Stein, S. E. ”Neutral Thermochemical Data” in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. Mallard, W. G.; Linstrom, P. J.; November 1998, National Institute of Standards and Technology, Gaithersburg, MD, 20899 ([http://webbook.nist.gov/chemistry/](http://webbook.nist.gov/chemistry/)).

90 Wladkowski, B.D.; Brauman, J.I. *J. Phys. Chem.* **1993**, *97*, 13158

91 Lias, S.G.; Bartmess, J.E.; Liebman, J.F.; Holmes, J.L.; Levin, R.D.; and Mallard, W.J. *J. Phys. Chem. Ref. Data* 17, supplement 1, 1988.
92 Graul, S.T.; Bowers, M.T. *J. Am. Chem. Soc.* **1994**, *116*, 3875

93 Knighton, W.B.; Bognar, J.A.; O'Connor, P.M.; Grimsrud, E.P. *J. Am. Chem. Soc.* **1993**, *115*, 12079

94 Hu, W.-P.; Truhlar, D.G. *J. Am. Chem. Soc.* **1995**, *117*, 10726
TABLE 1. Components of computed electron affinities of X and total atomization energies (kcal mol\(^{-1}\)) of CH\(_3\)X (X = F, Cl and Br).

| Species | SCF limit | CCSD limit | (T) limit | Core corr. | Spin-Orbit splitting | Scalar Rel. effects | Final Energy |
|---------|-----------|------------|-----------|------------|----------------------|---------------------|--------------|
| W1'     |           |            |           |            |                      |                     |              |
| F\(^-\) | 30.21     | 44.76      | 4.17      | 0.17       | -0.39                | -0.26               | 78.66        |
| Cl\(^-\) | 58.35     | 24.16      | 2.28      | 0.02       | -0.84                | -0.34               | 83.63        |
| Br\(^-\) | 58.37     | 21.76      | 1.98      | 0.31       | -3.51                | -0.90               | 78.02        |
| CH\(_3\)F  | 319.57    | 97.39      | 5.41      | 1.12       | -0.47                | -0.37               | 422.65       |
| CH\(_3\)Cl | 303.73    | 86.14      | 5.27      | 1.19       | -0.93                | -0.42               | 394.98       |
| CH\(_3\)Br | 292.99    | 85.48      | 5.25      | 1.45       | -3.60                | -0.79               | 380.78       |
| W2h     |           |            |           |            |                      |                     |              |
| F\(^-\) | 30.08     | 44.71      | 4.15      | 0.17       | -0.39                | -0.26               | 78.46        |
| Cl\(^-\) | 58.33     | 23.82      | 2.26      | 0.02       | -0.84                | -0.34               | 83.25        |
| Br\(^-\) | 58.31     | 21.49      | 1.91      | 0.31       | -3.51                | -0.90               | 77.62        |
| CH\(_3\)F  | 319.82    | 96.89      | 5.34      | 1.14       | -0.47                | -0.37               | 422.34       |
| CH\(_3\)Cl | 303.90    | 86.03      | 5.28      | 1.21       | -0.93                | -0.42               | 395.07       |
| CH\(_3\)Br | 293.14    | 85.45      | 5.21      | 1.49       | -3.60                | -0.79               | 380.91       |
| Species         | SCF limit | CCSD limit | (T) limit | Core corr. | Scalar Rel. effects | Final Energy |
|-----------------|-----------|------------|-----------|------------|---------------------|--------------|
| W1′             |           |            |           |            |                     |              |
| F⁻⋯CH₃F        | -10.63    | -2.54      | -0.56     | 0.09       | -0.02               | -13.66       |
| [F⋯CH₃⋯F]⁻     | 8.23      | -6.23      | -2.65     | 0.36       | -0.08               | -0.37        |
| Cl⁻⋯CH₃Cl      | -8.08     | -1.93      | -0.62     | 0.08       | 0.01                | -10.54       |
| [Cl⋯CH₃⋯Cl]⁻   | 7.81      | -2.62      | -2.37     | 0.35       | -0.10               | 3.07         |
| Br⁻⋯CH₃Br      | -7.55     | -1.92      | -0.65     | 0.09       | -0.16               | -10.03a      |
| [Br⋯CH₃⋯Br]⁻   | 5.71      | -2.43      | -2.36     | 0.26       | -0.16               | 1.02         |
| W2h             |           |            |           |            |                     |              |
| F⁻⋯CH₃F        | -11.16    | -2.17      | -0.45     | 0.07       | -0.02               | -13.72       |
| [F⋯CH₃⋯F]⁻     | 8.58      | -6.61      | -2.58     | 0.35       | -0.08               | -0.34        |
| Cl⁻⋯CH₃Cl      | -8.01     | -2.39      | -0.65     | 0.10       | 0.01                | -10.94       |
| [Cl⋯CH₃⋯Cl]⁻   | 8.55      | -3.63      | -2.46     | 0.33       | -0.11               | 2.67         |
| [Br⋯CH₃⋯Br]⁻   | 6.57      | -3.41      | -2.38     | 0.21       | -0.21               | 0.77         |
| W1′             |           |            |           |            |                     |              |
| F⁻⋯CH₃Cl       | -13.67    | -1.16      | -0.76     | 0.18       | -0.02               | -15.43       |
| [F⋯CH₃⋯Cl]⁻    | -10.39    | -0.84      | -1.60     | 0.36       | -0.07               | -12.54       |
| Cl⁻⋯CH₃F       | -7.08     | -2.03      | -0.42     | 0.03       | 0.00                | -9.51        |
| F⁻⋯CH₃Br       | -15.08    | -1.24      | -0.72     | 0.03       | -17.01a             |              |
| [F⋯CH₃⋯Br]⁻    | -13.85    | -1.02      | -1.43     | 0.07       | -16.37a             |              |
| Br⁻⋯CH₃F       | -6.63     | -1.69      | -0.24     | 0.05       | -8.51a              |              |
| Cl⁻⋯CH₃Br      | -8.89     | -2.02      | -0.59     | -0.41      | -11.91a             |              |
| [Cl⋯CH₃⋯Br]⁻   | 2.24      | -2.69      | -2.28     | -0.57      | -3.30a              |              |
| Br⁻⋯CH₃Cl      | -7.38     | -2.03      | -0.45     | -0.46      | -10.32a             |              |

\(^a\) W1′ – Core Correlation
TABLE 3. Calculated and experimental heats of formation (kcal mol$^{-1}$) of CH$_3$X and electron affinities (eV) of X (X = F, Cl and Br)

| Species | W1$'$ | W2h  | Experiment | Species | W1$'$ | W2h  | Experiment |
|---------|-------|------|------------|---------|-------|------|------------|
| CH$_3$F | -57.06 | -56.75 | -56(7)    | F       | 3.411 | 3.402 | 3.401 190(4) |
| CH$_3$Cl | -20.14 | -20.23 | -20.00(50) | Cl      | 3.627 | 3.610 | 3.612 69(6) |
| CH$_3$Br | -8.50  | -8.63 | -8.20(19)  | Br      | 3.383 | 3.366 | 3.363 583(44) |
TABLE 4. Comparison of complexation energies ($\Delta H_{\text{comp}}$) of the ion-molecule complexes, overall barrier heights relative to reactants ($\Delta H_{\text{ovr}}^\ddagger$), and central barriers ($\Delta H_{\text{cent}}^\ddagger$) of identity $S_N2$ reactions, $X^- + CH_3X \rightarrow XCH_3 + X^-$, calculated at various levels of theory. All values in kcal/mol.

| X   | Method                        | $\Delta H_{\text{comp}}$ | $\Delta H_{\text{ovr}}^\ddagger$ | $\Delta H_{\text{cent}}^\ddagger$ |
|-----|-------------------------------|--------------------------|-----------------------------------|-----------------------------------|
| F   | W1'                           | 13.66                    | -0.37                             | 13.29                             |
|     | W2h                           | 13.72                    | -0.34                             | 13.38                             |
|     | B3LYP/cc-pVTZ(+X)             | 12.72                    | -2.58                             | 10.15                             |
|     | BH&HLYP/cc-pVTZ(+X)           | 13.22                    | 1.31                              | 14.53                             |
|     | mPW1PW91/cc-pVTZ(+X)          | 12.49                    | -0.95                             | 11.55                             |
|     | mPW1K/6-31+G*                 | 13.55                    | -0.30                             | 13.26                             |
|     | mPW1K/cc-pVDZ(+X)             | 12.63                    | -0.48                             | 13.00                             |
|     | mPW1K/cc-pVTZ(+X)             | 12.66                    | 1.23                              | 13.89                             |
|     | G1                             | 13.01                    | -1.37                             | 11.64                             |
|     | G2                             | 13.34                    | -1.15                             | 12.19                             |
|     | G2MP2                          | 13.41                    | -0.63                             | 12.78                             |
|     | G3                             | 14.23                    | -1.97                             | 12.26                             |
|     | CBS-QB3                        | 13.46                    | -0.85                             | 12.61                             |
|     | G3(+)                          | 14.59                    | -2.68                             | 11.90                             |
|     | CBS-QB3(+)                     | 14.15                    | -0.52                             | 13.63                             |
|     | G2(+)a                         | 13.81                    | -1.86                             | 11.95                             |
|     | CCSD(T)/spdf                   | 13.73                    | -0.92                             | 12.81                             |
| Cl  | W1'                           | 10.54                    | 3.07                              | 13.61                             |
|     | W2h                           | 10.94                    | 2.67                              | 13.61                             |
|     | B3LYP/cc-pVTZ(+X)             | 9.50                     | -0.48                             | 9.02                              |
|     | BH&HLYP/cc-pVTZ(+X)           | 9.67                     | 3.17                              | 12.84                             |
|     | mPW1PW91/cc-pVTZ(+X)          | 9.59                     | 1.23                              | 10.82                             |
|     | mPW1K/6-31+G*                 | 9.69                     | 4.50                              | 14.19                             |
|     | mPW1K/cc-pVDZ(+X)             | 10.10                    | -0.66                             | 9.44                              |
|     | mPW1K/cc-pVTZ(+X)             | 10.74                    | -1.46                             | 9.28                              |
|     | HCTH/cc-pVDZ(+X)              | 7.91                     | 1.45                              | 9.36                              |
|     | HCTH-120/cc-pVDZ(+X)          | 9.96                     | -1.93                             | 8.03                              |
|     | mPW1K/6-31+G*                 | 9.75                     | 3.20                              | 12.95                             |
|     | mPW1K/cc-pVDZ(+X)             | 9.65                     | 3.63                              | 13.28                             |
|     | mPW1K/cc-pVTZ(+X)             | 9.64                     | 3.66                              | 13.30                             |
|     | G1                             | 10.52                    | 1.79                              | 12.31                             |
|     | G2                             | 10.77                    | 3.06                              | 13.83                             |
| Method                        | E1  | E2    | E3   |
|-------------------------------|-----|-------|------|
| G2MP2                         | 10.89 | 2.74 | 13.63 |
| G3                            | 11.15 | 1.79 | 12.95 |
| CBS-QB3                       | 10.65 | 2.47 | 13.12 |
| G3(+)                         | 11.04 | 1.80 | 12.83 |
| CBS-QB3(+)                    | 10.69 | 2.40 | 13.09 |
| G2(+)                         | 10.71 | 3.01 | 13.72 |
| CCSD(T)/spdf                  | 10.53(40)_d  | 2.90_ e | 13.66(2.01)_f  |

| Method                        | E1  | E2    | E3   |
|-------------------------------|-----|-------|------|
| Br W1' − core                 | 10.03 | 1.02_ i | 10.79 |
| W2h                           | 0.77 |       |      |
| B3LYP/cc-pVTZ(+X)             | 9.06 | -2.42 | 6.64 |
| BH&HLYP/cc-pVTZ(+X)           | 9.04 | 1.25  | 10.29 |
| mPW1PW91/cc-pVTZ(+X)          | 9.21 | -1.03 | 8.18 |
| mPWH&HPW91/cc-pVTZ(+X)        | 9.19 | 2.22  | 11.40 |
| B97/cc-pVDZ(+X)               | 9.62 | -2.29 | 7.33 |
| B97-1/cc-pVDZ(+X)             | 10.24 | -3.02 | 7.22 |
| HCTH/cc-pVDZ(+X)              | 7.56 | -0.70 | 6.86 |
| HCTH-120/cc-pVDZ(+X)          | 9.73 | -4.06 | 5.68 |
| mPW1K/6-31+G*                 | 12.78 | -1.95 | 10.83 |
| mPW1K/cc-pVDZ(+X)             | 9.34 | 0.68  | 10.02 |
| mPW1K/cc-pVTZ(+X)             | 9.16 | 1.38  | 10.54 |
| G1                            | 9.68 | 1.11  | 10.78 |
| G2                            | 9.85 | 1.52  | 11.38 |
| G2MP2                         | 9.83 | 1.83  | 11.66 |
| G2(+) − ECP                   | 10.17 | 1.48  | 11.65 |
| Experiment                    | 11.34(40)_d  | 1.73_ g | 11.68_ h  |

_a G2(+) values are from Ref.18,  
b CCSD(T)/spdf values are from Ref.23,  
c Ref.15

Experimental values:  

\[d\text{From Ref.11, } e\text{ From Ref.8, } f\text{ From Ref.10, } g\text{ From Ref.83, } h\text{ From Ref.84}\]

_\text{i Core contribution included}_
TABLE 5. Comparison of complexation energies ($\Delta H_{\text{comp}}$, kcal/mol) of the ion-molecule complexes for the nonidentity $S_N2$ reactions, calculated at various levels of theory.

| Method | $\text{F}^-\cdots\text{CH}_3\text{Cl}$ | $\text{Cl}^-\cdots\text{CH}_3\text{F}$ | $\text{Br}^-\cdots\text{CH}_3\text{Cl}$ | $\text{Cl}^-\cdots\text{CH}_3\text{Br}$ | $\text{Br}^-\cdots\text{CH}_3\text{F}$ |
|--------|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| W1’ − core | 15.43$^a$ | 9.51$^a$ | 8.51 | 11.91 | 10.32 |
| B3LYP/cc-pVTZ(+X) | 15.37 | 8.09 | 7.18 | 10.24 | 8.42 |
| BH&HLYP/cc-pVTZ(+X) | 15.39 | 8.42 | 16.65 | 7.45 | 10.23 | 8.56 |
| mPW1PW91/cc-pVTZ(+X) | 15.06 | 8.13 | 7.27 | 10.32 | 8.54 |
| mPW1&HPW91/cc-pVTZ(+X) | 15.03 | 8.32 | 16.28 | 7.42 | 10.30 | 8.65 |
| B97/cc-pVDZ(+X) | 15.43 | 8.49 | 7.69 | 10.66 | 9.13 |
| B97-1/cc-pVDZ(+X) | 16.26 | 9.05 | 8.21 | 11.32 | 9.74 |
| HCTH/cc-pVDZ(+X) | 12.66 | 6.56 | 5.82 | 8.56 | 7.00 |
| HCTH-120/cc-pVDZ(+X) | 15.42 | 8.48 | 7.69 | 10.78 | 9.01 |
| mPW1K/6-31+G* | 15.32 | 8.79 | 17.63 | 9.12 | 12.97 | 10.56 |
| mPW1K/cc-pVDZ(+X) | 14.52 | 8.46 | 16.25 | 7.62 | 10.41 | 8.68 |
| mPW1K/cc-pVTZ(+X) | 14.97 | 8.25 | 16.30 | 7.37 | 10.27 | 8.60 |
| G1 | 9.58 | 8.35 | 11.17 | 9.10 |
| G2 | 9.68 | 8.42 | 11.35 | 9.36 |
| G2MP2 | 9.71 | 8.40 | 11.37 | 9.45 |
| G3 | 10.03 |
| CBS-QB3 | 9.33 |
| G3(+)$^c$ | 16.34 | 9.97 |
| CBS-QB3(+)$^c$ | 15.85 | 9.51 |
| G2(+)$^b$ | 15.62 | 9.64 | 16.74 | 8.56 | 11.47 | 9.64 |
| CCSD(T)/large$^c$ | 16.07 | 9.75 | 11.31 | 9.71 |
| Experiment. | 11.41(2.01)$^d$ | 12.54(40)$^e$ | 11.01 (40)$^e$ |

$^a$ Core contribution included

$^b$ G2(+) values are from Ref.$^3$.

$^c$ F/Cl: CCSD(T)/spdf $^g$ values from Ref.$^{22}$; Cl/Br: CCSD(T)/spdf $^g$ $^h$ values from Ref.$^{24}$.

Experimental values: $^d$From Ref.$^{86}$ $^e$ From Ref.$^{11}$
TABLE 6. Comparison of overall reaction enthalpies ($\Delta H_{ovr}$), central enthalpy differences between reactant and product ion-molecule complexes ($\Delta H_{cent}$), overall barrier heights ($\Delta H^\ddagger_{ovr}$) and central barrier heights ($\Delta H^\ddagger_{cent}$) for exothermic $Y^- + CH_3X \rightarrow YCH_3 + X^-$ reactions, calculated at various levels of theory. All values in kcal/mol.

| Y,X  | Method               | $\Delta H_{ovr}$ | $\Delta H_{cent}$ | $\Delta H^\ddagger_{ovr}$ | $\Delta H^\ddagger_{cent}$ |
|------|----------------------|------------------|-------------------|---------------------------|-----------------------------|
| F/Cl | W1'                  | -32.65           | -26.73            | -12.54                    | 2.89                        |
|      | B3LYP/cc-pVTZ(+X)    | -32.77           | -25.49            | -14.69                    | 0.67                        |
|      | BH&HLYP/cc-pVTZ(+X)  | -37.02           | -30.05            | -12.86                    | 2.53                        |
|      | mPW1PW91/cc-pVTZ(+X) | -33.08           | -26.15            | -13.43                    | 1.63                        |
|      | mPWH&HPW91/cc-pVTZ(+X)| -36.45         | -29.73            | -11.51                    | 3.52                        |
|      | B97/cc-pVDZ(+X)      | -32.90           | -25.95            | -14.70                    | 0.73                        |
|      | B97-1/cc-pVDZ(+X)    | -33.13           | -25.92            | -15.60                    | 0.66                        |
|      | HCTH/cc-pVDZ(+X)     | -30.77           | -24.67            | -11.95                    | 0.71                        |
|      | HCTH-120/cc-pVDZ(+X) | -30.58           | -23.64            | -15.14                    | 0.27                        |
|      | mPW1K/6-31+G*        | -36.59           | -30.07            | -13.02                    | 2.30                        |
|      | mPW1K/cc-pVDZ(+X)    | -34.74           | -28.68            | -11.95                    | 2.57                        |
|      | mPW1K/cc-pVTZ(+X)    | -35.50           | -28.78            | -11.97                    | 3.01                        |
|      | G1                   | -30.62           |                   |                           |                             |
|      | G2                   | -31.59           |                   |                           |                             |
|      | G2MP2                | -32.25           |                   |                           |                             |
|      | G3                   | -33.00           |                   |                           |                             |
|      | CBS-QB3              | -35.21           |                   |                           |                             |
|      | G3(+)                | -32.86           | -26.50            | -14.04                    | 2.30                        |
|      | CBS-QB3(+)           | -35.15           | -28.81            | -13.77                    | 2.07                        |
|      | G2(+)\(^a\)         | -31.44           | -25.46            | -12.63                    | 2.98                        |
|      | CCSD(T)/spdf\(^b\)  | -32.34           | -26.36            | -11.84                    | 3.89                        |
|      | Experiment           | -33.34(72)\(^c\)|                   |                           | 7.52(1.20)\(^d\)           |
| F/Br | W1' – core           | -41.43           | -32.93            | -16.37                    | 0.64                        |
|      | B3LYP/cc-pVTZ(+X)    | -40.78           |                   |                           |                             |
|      | BH&HLYP/cc-pVTZ(+X)  | -46.13           | -36.93            | -16.33                    | 0.32                        |
|      | mPW1PW91/cc-pVTZ(+X) | -41.65           |                   |                           |                             |
|      | mPWH&HPW91/cc-pVTZ(+X)| -45.90         | -37.05            | -15.42                    | 0.85                        |
|      | B97/cc-pVDZ(+X)      | -40.41           |                   |                           |                             |
|      | B97-1/cc-pVDZ(+X)    | -40.68           |                   |                           |                             |
|      | HCTH/cc-pVDZ(+X)     | -38.18           |                   |                           |                             |
|      | HCTH-120/cc-pVDZ(+X) | -37.96           |                   |                           |                             |
|      | mPW1K/6-31+G*        | -42.35           | -33.84            | -16.92                    | 0.71                        |
|      | mPW1K/cc-pVDZ(+X)    | -44.76           | -36.13            | -16.08                    | 0.18                        |
|      | mPW1K/cc-pVTZ(+X)    | -44.70           | -35.77            | -15.76                    | 0.54                        |
|      | G1                   | -40.87           |                   |                           |                             |
|      | G2                   | -40.02           |                   |                           |                             |
| Method                        | Cl/Br | W1' - core | B3LYP/cc-pVTZ(+X) | BH&HLYP/cc-pVTZ(+X) | mPW1PW91/cc-pVTZ(+X) | mPWH&HPW91/cc-pVTZ(+X) | B97/cc-pVDZ(+X) | B97-1/cc-pVDZ(+X) | HCTH/cc-pVDZ(+X) | HCTH-120/cc-pVDZ(+X) | mPW1K/6-31+G* | mPW1K/cc-pVDZ(+X) | mPW1K/cc-pVTZ(+X) | G1 | G2 | G2MP2 | G2(+)<sup>a</sup> | CCSD(T)/spdfg,gh<sup>b</sup> | Experiment<sup>c</sup> |
|-------------------------------|-------|------------|-------------------|----------------------|----------------------|------------------------|----------------|----------------|----------------|-----------------------|---------------|----------------|----------------------|---|---|---|---|--------------------|--------------------------|
| G2MP2                         | -40.35|            |                   |                      |                      |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| G2(+)<sup>a</sup>             | -39.47| -31.29     | -15.90            | 0.84                 |                      |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| Experiment                    |       |            |                   |                      |                      |                        |                |                |                |                       |                |                |                      |   |   |   |   | -6.86(72)<sup>c</sup> | -1.83(5)<sup>e</sup> |
| Cl/Br                         |       | -8.56      | -6.97             | -1.82                | 8.61                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  | -1.69(33)<sup>f</sup> |
| B3LYP/cc-pVTZ(+X)             |       | -8.01      | -6.19             | -5.25                | 4.99                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  | -1.52<sup>g</sup>      |
| BH&HLYP/cc-pVTZ(+X)           |       | -9.11      | -7.43             | -2.15                | 8.08                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  | -1.11<sup>h</sup>      |
| mPW1PW91/cc-pVTZ(+X)          |       | -8.57      | -6.79             | -3.99                | 6.33                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  | -0.61<sup>i</sup>      |
| mPWH&HPW91/cc-pVTZ(+X)        |       | -9.45      | -7.79             | -1.17                | 9.14                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| B97/cc-pVDZ(+X)               |       | -7.52      | -5.99             | -5.06                | 5.60                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| B97-1/cc-pVDZ(+X)             |       | -7.54      | -5.97             | -5.83                | 5.48                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| HCTH/cc-pVDZ(+X)              |       | -7.41      | -5.85             | -3.18                | 5.38                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| HCTH-120/cc-pVDZ(+X)          |       | -7.38      | -5.62             | -6.52                | 4.26                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| mPW1K/6-31+G*                 |       | -5.75      | -3.34             | -3.12                | 9.85                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| mPW1K/cc-pVDZ(+X)             |       | -10.02     | -8.30             | -6.60                | 3.81                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| mPW1K/cc-pVTZ(+X)             |       | -9.20      | -7.53             | -1.88                | 8.38                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| G1                            |       | -10.25     | -8.18             | -3.45                | 7.72                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| G2                            |       | -8.43      | -6.44             | -1.82                | 9.53                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| G2MP2                         |       | -8.11      | -6.18             | -1.67                | 9.70                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| G2(+)<sup>a</sup>             |       | -8.04      | -6.21             | -1.71                | 9.76                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| CCSD(T)/spdfg,gh<sup>b</sup>  |       | -8.53      | -6.93             | -2.33                | 8.98                 |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  |                          |
| Experiment                    |       |            |                   |                      |                      |                        |                |                |                |                       |                |                |                      |   |   |   |   |                  | -1.83(5)<sup>e</sup>   |

<sup>a</sup> G2(+) values are from Ref.<sup>19</sup>

<sup>b</sup> Ref.<sup>22</sup> (F/Cl) and Ref.<sup>24</sup> (Cl/Br)

<sup>b'</sup> Table 2 of Ref.<sup>24</sup>

Experimental values: <sup>c</sup>From Ref.<sup>91</sup>, <sup>d</sup>From Ref.<sup>84</sup>, <sup>e</sup>From Ref.<sup>9</sup>, <sup>f</sup>From Ref.<sup>92</sup>, <sup>g</sup>From Ref.<sup>93</sup>, <sup>h</sup>From Ref.<sup>90</sup>, <sup>i</sup>From Ref.<sup>94</sup>
FIGURES

FIG. 1. Schematic representation of potential energy surface for the (a) identity and (b) non-identity $S_N^2$ reactions
Benchmark *ab initio* energy profiles for the gas-phase $S_N2$
reactions $Y^- + CH_3X \rightarrow CH_3Y + X^- (X,Y = F,Cl,Br)$.

Validation of hybrid DFT methods

Supplementary Data

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## TABLE I. Calculated and experimental geometries (Å, degree) of CH₃X (X=F, Cl, and Br).

| Species   | Method/Basis Set            | r(C–X)  | r(C–H)  | ∠XCH  |
|-----------|----------------------------|---------|---------|-------|
| CH₃F      | CCSD(T)/cc-pVQZ+1           | 1.382   | 1.089   | 108.9 |
|           | B3LYP/cc-pVTZ(+X)           | 1.392   | 1.090   | 108.7 |
|           | BH&HLYP/cc-pVTZ(+X)         | 1.372   | 1.082   | 108.8 |
|           | mPW1PW91/cc-pVTZ(+X)        | 1.380   | 1.090   | 108.9 |
|           | mPWH&HPW91/cc-pVTZ(+X)      | 1.362   | 1.083   | 109.1 |
|           | B97/cc-pVDZ(+X)             | 1.399   | 1.102   | 108.7 |
|           | B97-1/cc-pVDZ(+X)           | 1.398   | 1.102   | 108.7 |
|           | HCTH/cc-pVDZ(+X)            | 1.400   | 1.103   | 108.8 |
|           | HCTH-120/cc-pVDZ(+X)        | 1.402   | 1.104   | 108.7 |
|           | mPW1K/6-31+G*               | 1.374   | 1.087   | 108.7 |
|           | mPW1K/cc-pVDZ(+X)           | 1.378   | 1.093   | 108.8 |
|           | mPW1K/cc-pVTZ(+X)           | 1.367   | 1.085   | 109.0 |
|           | MP2/6-31G*                  | 1.390   | 1.092   | 109.1 |
|           | MP2/6-31+G***               | 1.407   | 1.090   | 108.0 |
|           | B3LYP/6-311G(2d,d,p)        | 1.388   | 1.093   | 109.2 |
|           | B3LYP/6-311+G(2d,d,p)       | 1.396   | 1.091   | 108.6 |
|           | Expt.                      | 1.383   | 1.086   | 108.8 |
| CH₃Cl     | CCSD(T)/cc-pVQZ+1           | 1.783   | 1.085   | 108.4 |
|           | B3LYP/cc-pVTZ(+X)           | 1.796   | 1.085   | 108.3 |
|           | BH&HLYP/cc-pVTZ(+X)         | 1.779   | 1.077   | 108.4 |
|           | mPW1PW91/cc-pVTZ(+X)        | 1.766   | 1.085   | 108.5 |
|           | mPWH&HPW91/cc-pVTZ(+X)      | 1.761   | 1.079   | 108.6 |
|           | B97/cc-pVDZ(+X)             | 1.808   | 1.097   | 108.1 |
|           | B97-1/cc-pVDZ(+X)           | 1.808   | 1.097   | 108.0 |
|           | HCTH/cc-pVDZ(+X)            | 1.793   | 1.098   | 108.4 |
|           | HCTH-120/cc-pVDZ(+X)        | 1.796   | 1.098   | 108.4 |
|           | mPW1K/6-31+G*               | 1.772   | 1.084   | 108.8 |
|           | mPW1K/cc-pVDZ(+X)           | 1.768   | 1.090   | 108.5 |
|           | mPW1K/cc-pVTZ(+X)           | 1.765   | 1.081   | 108.6 |
|           | MP2/6-31G*                  | 1.777   | 1.088   | 108.9 |
|           | MP2/6-31+G***               | 1.780   | 1.089   | 108.9 |
|           | B3LYP/6-311G(2d,d,p)        | 1.803   | 1.087   | 108.2 |
|           | B3LYP/6-311+G(2d,d,p)       | 1.803   | 1.087   | 108.2 |
|           | Expt.                      | 1.776   | 1.085   | 108.6 |
| CH₃Br     | CCSD(T)/cc-pVQZ+1           | 1.944   | 1.084   | 107.8 |
|           | B3LYP/cc-pVTZ(+X)           | 1.957   | 1.083   | 107.6 |
|           | BH&HLYP/cc-pVTZ(+X)         | 1.938   | 1.076   | 107.8 |
|           | mPW1PW91/cc-pVTZ(+X)        | 1.936   | 1.084   | 107.9 |
|           | mPWH&HPW91/cc-pVTZ(+X)      | 1.917   | 1.078   | 108.0 |
|           | B97/cc-pVDZ(+X)             | 1.959   | 1.097   | 107.6 |
| Method                  | R (Å) | E (°) | X (Å) |
|------------------------|-------|-------|-------|
| B97-1/cc-pVDZ(+X)       | 1.959 | 1.097 | 107.6 |
| HCTH/cc-pVDZ(+X)        | 1.952 | 1.097 | 107.9 |
| HCTH-120/cc-pVDZ(+X)    | 1.956 | 1.097 | 107.8 |
| mPW1K/6-31+G*           | 1.925 | 1.083 | 108.2 |
| mPW1K/cc-pVDZ(+X)       | 1.927 | 1.089 | 107.9 |
| mPW1K/cc-pVTZ(+X)       | 1.922 | 1.079 | 108.0 |
| MP2/6-31G*              | 1.947 | 1.086 | 107.9 |
| MP2/6-31+G**            | 1.954 | 1.088 | 108.0 |
| Expt.                   | 1.934 | 1.082 | 107.7 |

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a From Glukhovtsev, M.N.; Pross, A.; Radom, L.; *J. Am. Chem. Soc.* **1995**, *117*, 2024.

Experimental values:

b From Egawa, T.; Yamamoto, S.; Nakata, M.; Kuchitsu, K.; *J. Mol. Struct.* **1987**, *156*, 213.

c From Jensen, T.; Brodersen, S.; Guelachvili, G.; *J. Mol. Spectrosc.* **1981**, *88*, 378.

d From Graner, G.; *J. Mol. Spectrosc.* **1981**, *90*, 394.
TABLE II. Geometries (Å, degree) of ion-molecule complexes X⋯CH$_3$X (X=F, Cl, and Br) of the SN$_2$ identity reactions.

| Species | Method/Basis Set          | r(X⋯C)  | r(C−X)  | r(C−H)  | θ HCX  |
|---------|---------------------------|---------|---------|---------|--------|
| X=F     | CCSD(T)/cc-pVQZ+1         | 2.494   | 1.432   | 1.082   | 109.1  |
|         | B3LYP/cc-pVTZ(+X)         | 2.588   | 1.447   | 1.082   | 108.4  |
|         | BH&HLYP/cc-pVTZ(+X)       | 2.581   | 1.418   | 1.075   | 108.8  |
|         | mPW1PW91/cc-pVTZ(+X)      | 2.575   | 1.428   | 1.083   | 108.9  |
|         | mPWH&HPW91/cc-pVTZ(+X)    | 2.567   | 1.404   | 1.077   | 109.2  |
|         | B97/cc-pVDZ(+X)           | 2.643   | 1.453   | 1.095   | 108.3  |
|         | B97-1/cc-pVDZ(+X)         | 2.613   | 1.453   | 1.095   | 108.3  |
|         | HCTH/cc-pVDZ(+X)          | 2.794   | 1.453   | 1.096   | 108.4  |
|         | HCTH-120/cc-pVDZ(+X)      | 2.668   | 1.462   | 1.096   | 108.2  |
|         | mPW1K/6-31+G*             | 2.572   | 1.421   | 1.080   | 108.5  |
|         | mPW1K/cc-pVDZ(+X)         | 2.579   | 1.425   | 1.087   | 108.8  |
|         | mPW1K/cc-pVTZ(+X)         | 2.571   | 1.411   | 1.079   | 109.1  |
|         | MP2/6-31G*                | 2.426   | 1.439   | 1.083   | 109.5  |
|         | MP2/6-31+G**              | 2.628   | 1.456   | 1.084   | 107.7  |
|         | B3LYP/6-311G(2d,d,p)      | 2.420   | 1.453   | 1.084   | 110.0  |
|         | B3LYP/6-311+G(2d,d,p)     | 2.565   | 1.455   | 1.084   | 108.2  |
| X=Cl    | CCSD(T)/cc-pVQZ+1         | 3.123   | 1.860   | 1.080   | 107.8  |
|         | B3LYP/cc-pVTZ(+X)         | 3.191   | 1.846   | 1.080   | 107.9  |
|         | BH&HLYP/cc-pVTZ(+X)       | 3.203   | 1.818   | 1.073   | 108.2  |
|         | mPW1PW91/cc-pVTZ(+X)      | 3.163   | 1.817   | 1.081   | 108.5  |
|         | mPWH&HPW91/cc-pVTZ(+X)    | 3.166   | 1.796   | 1.075   | 108.7  |
|         | B97/cc-pVDZ(+X)           | 3.198   | 1.855   | 1.094   | 107.7  |
|         | B97-1/cc-pVDZ(+X)         | 3.168   | 1.857   | 1.093   | 107.6  |
|         | HCTH/cc-pVDZ(+X)          | 3.375   | 1.838   | 1.094   | 108.1  |
|         | HCTH-120/cc-pVDZ(+X)      | 3.241   | 1.848   | 1.095   | 107.9  |
|         | mPW1K/6-31+G*             | 3.181   | 1.809   | 1.080   | 108.7  |
|         | mPW1K/cc-pVDZ(+X)         | 3.182   | 1.804   | 1.086   | 108.6  |
|         | mPW1K/cc-pVTZ(+X)         | 3.167   | 1.801   | 1.077   | 108.7  |
|         | MP2/6-31G*                | 3.158   | 1.812   | 1.084   | 109.0  |
|         | MP2/6-31+G**              | 3.270   | 1.810   | 1.085   | 108.8  |
|         | B3LYP/6-311G(2d,d,p)      | 3.146   | 1.861   | 1.082   | 107.6  |
|         | B3LYP/6-311+G(2d,d,p)     | 3.187   | 1.854   | 1.083   | 107.8  |
| X=Br    | CCSD(T)/cc-pVQZ+1         | 3.277   | 2.023   | 1.079   | 106.9  |
|         | B3LYP/cc-pVTZ(+X)         | 3.321   | 2.016   | 1.079   | 106.9  |
|         | BH&HLYP/cc-pVTZ(+X)       | 3.301   | 1.980   | 1.072   | 107.4  |
|         | mPW1PW91/cc-pVTZ(+X)      | 3.290   | 1.982   | 1.080   | 107.5  |
|         | mPWH&HPW91/cc-pVTZ(+X)    | 3.313   | 1.953   | 1.074   | 107.9  |
|         | B97/cc-pVDZ(+X)           | 3.320   | 2.013   | 1.093   | 107.0  |
|         | B97-1/cc-pVDZ(+X)         | 3.281   | 2.014   | 1.093   | 106.9  |
|         | HCTH/cc-pVDZ(+X)          | 3.471   | 2.007   | 1.094   | 107.2  |
|         | HCTH-120/cc-pVDZ(+X)      | 3.332   | 2.022   | 1.094   | 106.9  |
| Method                     | r (Å) | r_2 (Å) | r_3 (Å) | Angle (°) |
|----------------------------|-------|---------|---------|-----------|
| mPW1K/6-31+G*              | 3.215 | 1.960   | 1.079   | 108.0     |
| mPW1K/cc-pVDZ(+X)          | 3.304 | 1.968   | 1.086   | 107.6     |
| mPW1K/cc-pVTZ(+X)          | 3.312 | 1.960   | 1.076   | 107.8     |
| MP2/6-31G*                 | 3.196 | 1.992   | 1.083   | 107.7     |
| MP2/6-31+G**               | 3.395 | 1.988   | 1.084   | 107.8     |

*a From Glukhovtsev, M.N.; Pross, A.; Radom, L.; *J. Am. Chem. Soc.* **1995**, *117*, 2024.
TABLE III. Geometries (Å, degree) of ion-molecule complexes, Y−⋯CH₃X, of the SN₂ non-Identity reactions (complex 1).

| Y/X | Method/Basis Set | r(Y−⋯C) | r(C−X) | r(C−H) | ΔH CX |
|-----|-----------------|---------|--------|--------|-------|
| F/Cl | B3LYP/cc-pVTZ(+X) | 2.443 | 1.908 | 1.076 | 106.1 |
|     | BH&HLYP/cc-pVTZ(+X) | 2.494 | 1.853 | 1.070 | 107.4 |
|     | mPW1PW91/cc-pVTZ(+X) | 2.462 | 1.861 | 1.078 | 107.3 |
|     | mPW1PW91/cc-pVTZ(+X) | 2.489 | 1.825 | 1.072 | 108.1 |
|     | B97/cc-pVDZ(+X) | 2.467 | 1.913 | 1.090 | 106.0 |
|     | B97-1/cc-pVDZ(+X) | 2.445 | 1.916 | 1.090 | 105.9 |
|     | HCTH/cc-pVDZ(+X) | 2.565 | 1.903 | 1.091 | 106.5 |
|     | HCTH-120/cc-pVDZ(+X) | 2.459 | 1.931 | 1.090 | 105.6 |
|     | mPW1K/6-31+G* | 2.487 | 1.846 | 1.077 | 107.8 |
|     | mPW1K/cc-pVTZ(+X) | 2.486 | 1.833 | 1.074 | 108.0 |
|     | MP2/6-31+G* | 2.616 | 1.832 | 1.083 | 108.5 |
|     | MP2/6-31+G* | 2.528 | 1.853 | 1.080 | 107.6 |

| F/Br | BH&HLYP/cc-pVTZ(+X) | 2.392 | 2.052 | 1.068 | 105.2 |
|      | mPW1PW91/cc-pVTZ(+X) | 2.404 | 2.007 | 1.070 | 106.4 |
|      | mPW1K/6-31+G* | 2.411 | 2.022 | 1.075 | 106.2 |
|      | mPW1K/cc-pVDZ(+X) | 2.360 | 2.045 | 1.081 | 105.2 |
|      | mPW1K/cc-pVTZ(+X) | 2.389 | 2.022 | 1.072 | 106.0 |
|      | MP2/6-31+G* | 2.528 | 2.028 | 1.081 | 106.8 |

| Cl/Br | B3LYP/cc-pVTZ(+X) | 3.112 | 2.024 | 1.079 | 106.7 |
|       | BH&HLYP/cc-pVTZ(+X) | 3.149 | 1.986 | 1.072 | 107.3 |
|       | mPW1PW91/cc-pVTZ(+X) | 3.088 | 1.989 | 1.080 | 107.4 |
|       | mPW1PW91/cc-pVTZ(+X) | 3.113 | 1.958 | 1.074 | 107.8 |
|       | B97/cc-pVDZ(+X) | 3.134 | 2.021 | 1.093 | 106.8 |
|       | B97-1/cc-pVDZ(+X) | 3.098 | 2.022 | 1.093 | 106.8 |
|       | HCTH/cc-pVDZ(+X) | 3.269 | 2.012 | 1.094 | 107.1 |
|       | HCTH-120/cc-pVDZ(+X) | 3.132 | 2.031 | 1.093 | 106.8 |
|       | mPW1K/6-31+G* | 3.070 | 1.966 | 1.079 | 107.9 |
|       | mPW1K/cc-pVDZ(+X) | 3.114 | 1.974 | 1.085 | 107.5 |
|       | mPW1K/cc-pVTZ(+X) | 3.109 | 1.966 | 1.076 | 107.8 |
|       | MP2/6-31G* | 3.092 | 1.992 | 1.082 | 107.6 |
|       | MP2/6-31+G* | 3.199 | 1.992 | 1.084 | 107.7 |
|       | CCSD(T)/spdf | 3.095 | 1.986 | 1.082 | 107.5 |

a From Glukhovtsev, M.N.; Pross, A.; Radom, L.; J. Am. Chem. Soc. 1996, 118, 6273.

b From Schmatz, S.; Botschwina, P.; Stoll, H.; Int. J. Mass Spectrom. 2000, 201, 277.

c From Botschwina, P.; Horn, M.; Seeger, S.; Oswald, R.; Ber. Bunsenges. Phys. Chem. 1997, 101, 387.
TABLE IV. Geometries (Å, degree) of ion-molecule complexes, YCH$_3$····X$^-$, of the SN$_2$ non-identity reactions (complex 3).

| Y/X       | Method/Basis Set            | r(X···C) | r(C–Y) | r(C–H) | $\angle$HCY |
|-----------|-----------------------------|----------|--------|--------|-------------|
| F/Cl      | B3LYP/cc-pVTZ+(+X)          | 3.286    | 1.425  | 1.085  | 108.8       |
|           | BH&HLYP/cc-pVTZ+(+X)        | 3.268    | 1.401  | 1.077  | 109.0       |
|           | mPW1PW91/cc-pVTZ+(+X)       | 3.246    | 1.409  | 1.085  | 109.2       |
|           | mPWH&HPW91/cc-pVTZ+(+X)     | 3.230    | 1.389  | 1.079  | 109.4       |
|           | B97/cc-pVDZ(+X)             | 3.320    | 1.432  | 1.098  | 108.7       |
|           | B97-1/cc-pVDZ(+X)           | 3.268    | 1.432  | 1.098  | 108.7       |
|           | HCTH/cc-pVDZ(+X)            | 3.528    | 1.431  | 1.099  | 108.7       |
|           | HCTH-120/cc-pVDZ(+X)        | 3.358    | 1.436  | 1.099  | 108.7       |
|           | mPW1K/6-31+G*               | 3.241    | 1.403  | 1.083  | 108.8       |
|           | mPW1K/cc-pVDZ(+X)           | 3.252    | 1.407  | 1.089  | 109.0       |
|           | mPW1K/cc-pVTZ(+X)           | 3.235    | 1.394  | 1.081  | 109.3       |
|           | MP2/6-31G*                  | 3.227    | 1.415  | 1.087  | 109.4       |
|           | MP2/6-31+G**                 | 3.255    | 1.438  | 1.086  | 108.0       |
|           | B3LYP/6-31G(2d,d,p)         | 3.299    | 1.418  | 1.089  | 109.4       |
|           | B3LYP/6-311+G(2d,d,p)       | 3.271    | 1.430  | 1.087  | 108.7       |
|           | CCSD(T)/spdf$^b$            | 3.188    | 1.418  | 1.086  | 108.9       |
| F/Br      | B3LYP/cc-pVTZ+(+X)          | 3.497    | 1.421  | 1.085  | 108.8       |
|           | BH&HLYP/cc-pVTZ+(+X)        | 3.482    | 1.398  | 1.078  | 109.0       |
|           | mPW1PW91/cc-pVTZ+(+X)       | 3.451    | 1.406  | 1.086  | 109.2       |
|           | mPWH&HPW91/cc-pVTZ+(+X)     | 3.433    | 1.386  | 1.080  | 109.3       |
|           | B97/cc-pVDZ(+X)             | 3.518    | 1.428  | 1.098  | 108.7       |
|           | B97-1/cc-pVDZ(+X)           | 3.458    | 1.428  | 1.098  | 108.7       |
|           | HCTH/cc-pVDZ(+X)            | 3.746    | 1.428  | 1.099  | 108.8       |
|           | HCTH-120/cc-pVDZ(+X)        | 3.565    | 1.433  | 1.100  | 108.7       |
|           | mPW1K/6-31+G*               | 3.367    | 1.401  | 1.083  | 108.8       |
|           | mPW1K/cc-pVDZ(+X)           | 3.445    | 1.404  | 1.090  | 109.0       |
|           | mPW1K/cc-pVTZ(+X)           | 3.443    | 1.391  | 1.081  | 109.3       |
|           | MP2/6-31G*                  | 3.315    | 1.414  | 1.088  | 109.5       |
|           | MP2/6-31+G**                 | 3.457    | 1.435  | 1.087  | 108.0       |
| Cl/Br     | B3LYP/cc-pVTZ+(+X)          | 3.405    | 1.839  | 1.081  | 108.0       |
|           | BH&HLYP/cc-pVTZ+(+X)        | 3.416    | 1.813  | 1.074  | 108.3       |
|           | mPW1PW91/cc-pVTZ+(+X)       | 3.368    | 1.812  | 1.082  | 108.5       |
|           | mPWH&HPW91/cc-pVTZ+(+X)     | 3.369    | 1.791  | 1.076  | 108.7       |
|           | B97/cc-pVDZ(+X)             | 3.396    | 1.850  | 1.094  | 107.8       |
|           | B97-1/cc-pVDZ(+X)           | 3.354    | 1.851  | 1.094  | 107.7       |
|           | HCTH/cc-pVDZ(+X)            | 3.588    | 1.832  | 1.095  | 108.2       |
|           | HCTH-120/cc-pVDZ(+X)        | 3.440    | 1.842  | 1.095  | 108.0       |
|           | mPW1K/6-31+G*               | 3.274    | 1.809  | 1.080  | 108.6       |
|           | mPW1K/cc-pVDZ(+X)           | 3.381    | 1.800  | 1.087  | 108.6       |
|           | mPW1K/cc-pVTZ(+X)           | 3.371    | 1.797  | 1.077  | 108.7       |
|           | MP2/6-31G*                  | 3.257    | 1.812  | 1.084  | 109.1       |
| Method          | C  | H  | C-H  | Angle |
|-----------------|----|----|------|-------|
| MP2/6-31+G**a   | 3.457 | 1.807 | 1.085 | 108.9 |
| CCSD(T)/spdfc   | 3.318 | 1.820 | 1.083 | 108.2 |

*a* From Glukhovtsev, M.N.; Pross, A.; Radom, L.; *J. Am. Chem. Soc.* **1996**, *118*, 6273.

*b* From Schmatz, S.; Botschwina, P.; Stoll, H.; *Int. J. Mass Spectrom.* **2000**, *201*, 277.

*c* From Botschwina, P.; Horn, M.; Seeger, S.; Oswald, R.; *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 387.
TABLE V. Geometries (Å, degree) of the XCH$_3$X$^-$ transition structures, (X=F, Cl, and Br) of the SN$_2$ identity reactions (complex 2).

| Species | Method/Basis Set | r(X···C) | r(C−H) |
|---------|-----------------|---------|--------|
| X=F     | CCSD(T)/cc-pVQZ+1 | 1.808   | 1.071  |
|         | B3LYP/cc-pVTZ(+X) | 1.854   | 1.070  |
|         | BH&HLYP/cc-pVTZ(+X) | 1.823   | 1.062  |
|         | mPW1PW91/cc-pVTZ(+X) | 1.824   | 1.071  |
|         | mPW1K/6-31+G* | 1.807   | 1.070  |
|         | mPW1K/cc-pVDZ(+X) | 1.810   | 1.077  |
|         | mPW1K/cc-pVTZ(+X) | 1.804   | 1.066  |
|         | MP2/6-31G* | 1.778   | 1.076  |
|         | MP2/6-31+G** | 1.837   | 1.074  |
|         | B3LYP/6-311G(2d,d,p) | 1.830   | 1.074  |
|         | B3LYP/6-311+G(2d,d,p) | 1.862   | 1.073  |
| X=Cl    | CCSD(T)/cc-pVQZ+1 | 2.305   | 1.070  |
|         | B3LYP/cc-pVTZ(+X) | 2.355   | 1.069  |
|         | BH&HLYP/cc-pVTZ(+X) | 2.332   | 1.061  |
|         | mPW1PW91/cc-pVTZ(+X) | 2.310   | 1.070  |
|         | mPW1K/6-31+G* | 2.313   | 1.069  |
|         | mPW1K/cc-pVDZ(+X) | 2.303   | 1.076  |
|         | mPW1K/cc-pVTZ(+X) | 2.295   | 1.065  |
|         | MP2/6-31G* | 2.308   | 1.072  |
|         | MP2/6-31+G** | 2.317   | 1.073  |
|         | B3LYP/6-311G(2d,d,p) | 2.366   | 1.072  |
|         | B3LYP/6-311+G(2d,d,p) | 2.364   | 1.072  |
| X=Br    | CCSD(T)/cc-pVQZ+1 | 2.461   | 1.071  |
|         | B3LYP/cc-pVTZ(+X) | 2.511   | 1.069  |
|         | BH&HLYP/cc-pVTZ(+X) | 2.488   | 1.062  |
|         | mPW1PW91/cc-pVTZ(+X) | 2.464   | 1.070  |
|         | mPW1K/6-31+G* | 2.502   | 1.084  |
|         | mPW1K/cc-pVDZ(+X) | 2.496   | 1.084  |
|         | mPW1K/cc-pVTZ(+X) | 2.533   | 1.085  |
|         | CCSD(T)/cc-pVQZ+1 | 2.530   | 1.085  |
| Method                     | R  | θ  |
|----------------------------|----|----|
| mPW1K/6-31+G*              | 2.430 | 1.069 |
| mPW1K/cc-pVDZ(+X)          | 2.459 | 1.076 |
| mPW1K/cc-pVTZ(+X)          | 2.447 | 1.066 |
| MP2/6-31G*                 | 2.444 | 1.073 |
| MP2/6-31+G**               | 2.480 | 1.074 |

<sup>a</sup> From Glukhovtsev, M.N.; Pross, A.; Radom, L.; *J. Am. Chem. Soc.* 1995, 117, 2024.
TABLE VI. Geometries (Å, degree) of the YCH$_3$X$^-$ transition structures, of the SN$_2$ non-identity reactions (complex 2).

| Y/X | Method/Basis Set | r(Y···C) | r(C···X) | r(C·H) | $\angle$HCX |
|-----|-----------------|---------|---------|-------|------------|
| F/Cl | B3LYP/cc-pVTZ(+X) | 2.143 | 2.091 | 1.070 | 99.0 |
|      | BH&HLYP/cc-pVTZ(+X) | 2.065 | 2.107 | 1.062 | 97.2 |
|      | mPW1PW91/cc-pVTZ(+X) | 2.072 | 2.086 | 1.071 | 97.8 |
|      | mPW1KHPW91/cc-pVTZ(+X) | 2.016 | 2.088 | 1.064 | 96.7 |
|      | B07/cc-pVDZ(+X) | 2.143 | 2.091 | 1.085 | 98.8 |
|      | B07-1/cc-pVDZ(+X) | 2.139 | 2.086 | 1.085 | 98.8 |
|      | HCTH/cc-pVDZ(+X) | 2.190 | 2.098 | 1.086 | 99.2 |
|      | HCTH-120/cc-pVDZ(+X) | 2.208 | 2.077 | 1.086 | 100.0 |
|      | mPW1K/6-31+G* | 2.063 | 2.080 | 1.070 | 98.0 |
|      | mPW1K/cc-pVTZ(+X) | 2.047 | 2.083 | 1.076 | 97.4 |
|      | mPW1K/cc-pVTZ(+X) | 2.029 | 2.089 | 1.066 | 97.0 |
|      | MP2/6-31+G** | 2.016 | 2.142 | 1.073 | 95.6 |
|      | B3LYP/6-311+G(2d,d,p) | 2.173 | 2.080 | 1.074 | 99.7 |
|      | CCSD(T)/spdf | 2.030 | 2.121 | 1.072 | 96.3 |
| F/Br | BH&HLYP/cc-pVTZ(+X) | 2.174 | 2.181 | 1.063 | 100.0 |
|      | mPW1KHPW91/cc-pVTZ(+X) | 2.105 | 2.175 | 1.065 | 99.2 |
|      | mPW1K/6-31+G* | 2.114 | 2.181 | 1.070 | 99.2 |
|      | mPW1K/cc-pVDZ(+X) | 2.179 | 2.145 | 1.078 | 100.9 |
|      | mPW1K/cc-pVTZ(+X) | 2.129 | 2.168 | 1.067 | 99.7 |
|      | MP2/6-31+G** | 2.108 | 2.242 | 1.075 | 97.9 |
| Cl/Br | B3LYP/cc-pVTZ(+X) | 2.416 | 2.451 | 1.069 | 91.8 |
|      | BH&HLYP/cc-pVTZ(+X) | 2.388 | 2.433 | 1.062 | 91.6 |
|      | mPW1PW91/cc-pVTZ(+X) | 2.369 | 2.409 | 1.070 | 91.7 |
|      | mPW1KHPW91/cc-pVTZ(+X) | 2.342 | 2.391 | 1.064 | 91.5 |
|      | B07/cc-pVDZ(+X) | 2.408 | 2.445 | 1.084 | 91.7 |
|      | B07-1/cc-pVDZ(+X) | 2.403 | 2.439 | 1.084 | 91.7 |
|      | HCTH/cc-pVDZ(+X) | 2.488 | 2.467 | 1.085 | 91.3 |
|      | HCTH-120/cc-pVDZ(+X) | 2.435 | 2.469 | 1.085 | 91.8 |
|      | mPW1K/6-31+G* | 2.313 | 2.421 | 1.069 | 90.1 |
|      | mPW1K/cc-pVDZ(+X) | 2.363 | 2.401 | 1.076 | 91.8 |
|      | mPW1K/cc-pVTZ(+X) | 2.349 | 2.396 | 1.065 | 91.6 |
|      | MP2/6-31G* | 2.336 | 2.419 | 1.072 | 90.5 |
|      | MP2/6-31+G** | 2.371 | 2.430 | 1.073 | 91.4 |
|      | CCSD(T)/spdf | 2.354 | 2.422 | 1.072 | 91.2 |

$^a$ From Glukhovtsev, M.N.; Pross, A.; Radom, L.; J. Am. Chem. Soc. 1996, 118, 6273.

$^b$ From Schmatz, S.; Botschwina, P.; Stoll, H.; Int. J. Mass Spectrom. 2000, 201, 277.

$^c$ From Botschwina, P.; Horn, M.; Seeger, S.; Oswald, R.; Ber. Bunsenges. Phys. Chem. 1997, 101, 387.