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On the Choice of the Ab Initio Level of Theory for Potential Energy Surface Developments

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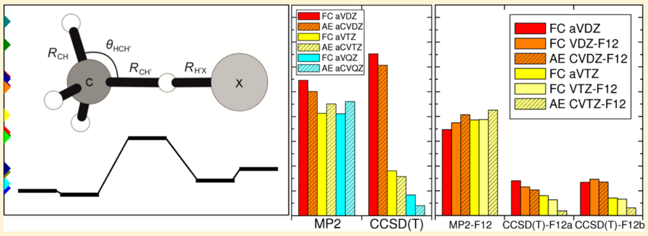
Ⓢ *Supporting Information*



ABSTRACT: We test the accuracy of various standard, explicitly correlated F12, and composite ab initio methods with different correlation consistent basis sets for high-dimensional potential energy surface (PES) developments, thereby providing a practical guidance for reaction dynamics studies. Relative potential energies are computed at 15 geometries covering the energy range and configuration space of chemical importance for each of the six prototypical polyatomic reactions, X + CH_4 → HX + CH_3 [X = F, O, Cl] and X^- + CH_3Y → Y^- + CH_3X [X/Y = F/F, OH/F, F/Cl]. The average accuracies of the Hartree−Fock and MP2 methods are 1500−8000 and 400−1000 cm^{-1}, respectively. The standard CCSD(T) method provides errors of 900−1400 and 250−450 cm^{-1} with aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. The explicitly correlated CCSD(T)-F12 method reduces the corresponding errors to about 200 and 100 cm^{-1}; thus, we recommend using the F12 methods for PES developments. For F12 computations, the cc-pV*n*Z-F12 [*n* = D and T] basis sets usually, but not always, perform better than the corresponding aug-cc-pV*n*Z bases. We do not find clear preference between the F12a and F12b methods for PES developments. Composite methods are advocated instead of standard CCSD(T) because for example, one can obtain CCSD(T)/aug-cc-pV*n*Z quality results on the expense of MP2/aug-cc-pV*n*Z [*n* = T and Q] computations. The post-CCSD(T), the core correlation, and the scalar relativistic effects are found to be ~100, 80−130, and 10−50 cm^{-1}, respectively. The all-electron CCSD(T)/aug-cc-pCV*n*Z relative energies differ from the complete-basis-set limit by about 1000, 300, 100, and 50 cm^{-1} for *n* = D, T, Q, and 5, respectively.

I. INTRODUCTION

Potential energy surfaces (PESs) govern the motion of the atoms in chemical reactions; thus, PESs play a central role in many fields of chemistry, especially in reaction dynamics. In the recent years, there has been a great progress toward representing PESs of polyatomic reactions by analytical functions by fitting a few tens of thousands of ab initio energy points.[1−7] The accuracy of the PESs determines the accuracy of the dynamics computations. Many computational studies proved that theory can reproduce most of the available experimental findings if an accurate PES is used for the dynamical simulations.[8−11] The accuracy of the PES depends on (1) the accuracy of the fit and (2) the accuracy of the ab initio energy points. The former is always checked by looking at the root-mean-square (RMS) error of the fit. This RMS error shows how the analytical function reproduces the ab initio data used for the fitting. The latter is sometimes examined at the most important stationary points, that is, saddle points (transition states) and minima (products, reactants, complexes, and intermediates). However, little is known about the performance of the various ab initio levels of theory away from the stationary points of the multidimensional PESs of polyatomic chemical reactions.

The goal of the present study is to investigate the accuracy, relative to highly accurate reference data, of different ab initio methods and basis sets at several geometries covering the energy range and configuration space of chemical importance. We perform computations for six representative polyatomic systems, involving six to seven atoms, such as the F, O(^{3}P), and Cl + CH_4 abstraction and F^-, OH^- + CH_3F, and F^- + CH_3Cl substitution reactions.[8−10,12,13] We test the standard correlation methods, MP2 and CCSD(T),[14,15] the novel explicitly correlated MP2-F12 and CCSD(T)-F12 methods,[16,17] and several composite methods with different correlation consistent basis sets. The effects of the post-CCSD(T) electron correlation, core−core and core−valence electron correlation, scalar relativity, and extrapolation to the complete basis set (CBS) limit are also investigated. Therefore, this study provides the estimated accuracy of the ab initio data points relative to the "exact" relativistic all-electron full-configuration-interaction CBS limits. On the basis of the present results and the RMS errors of the fits, one can really estimate the accuracy of the analytical PESs. Furthermore, the present study provides useful guidance for direct dynamics simulations as well, where the fitting error does not exist, but the affordable ab initio level of theory may be less accurate as shown in this study.

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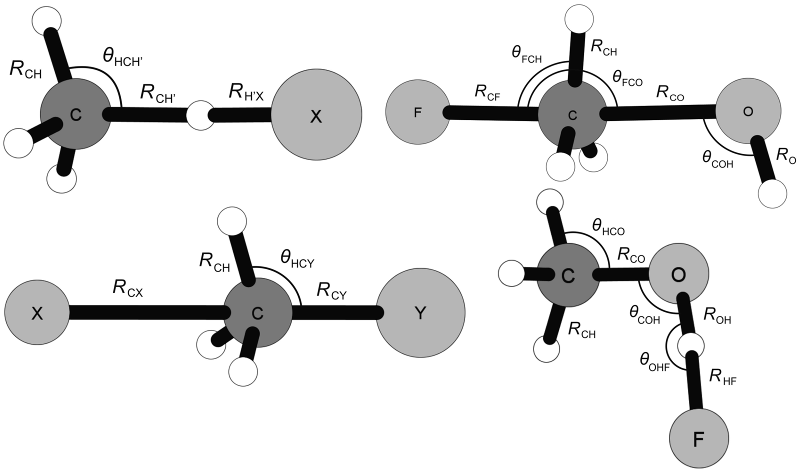

Figure 1. Selected structures for the X + CH_4 [X = F, O(^{3}P), and Cl] and X^- + CH_3Y [X/Y = F/F, OH/F, and F/Cl] reactions showing the definition of the internal coordinates. The structures on the left and right have C_{3v} and C_s point-group symmetry, respectively. The actual values of the internal coordinates are given in the SI.

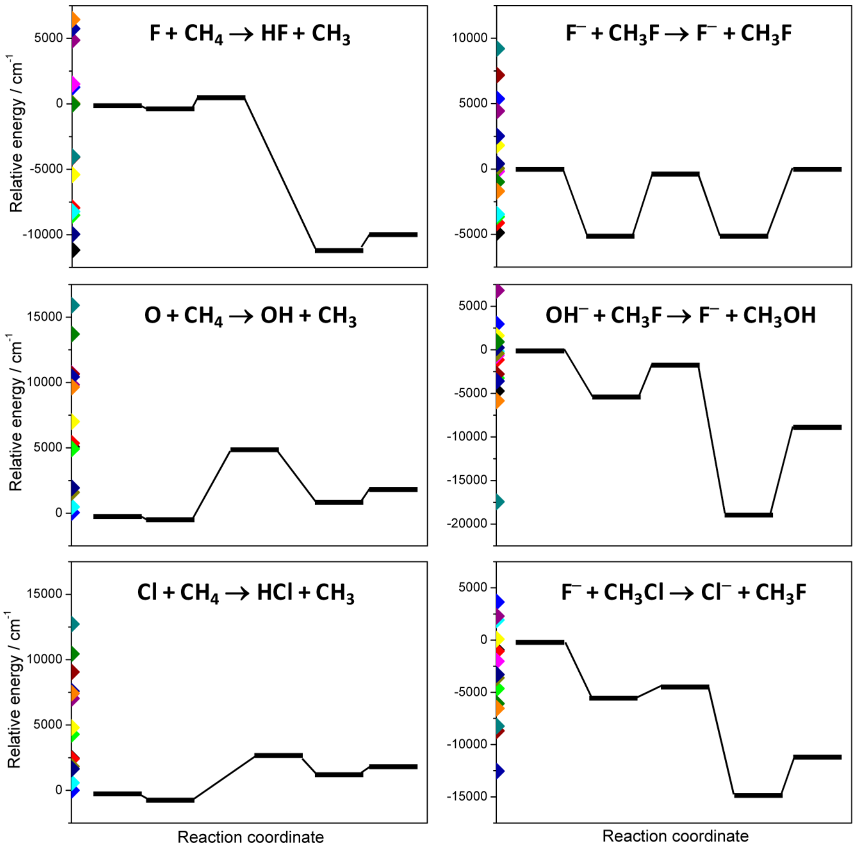

Figure 2. Schematics of the potential energy surfaces of the F, O(^{3}P), and Cl + CH_4 abstraction and F^-, OH^- + CH_3F, and F^- + CH_3Cl substitution reactions showing the stationary points. The energies of the 15 configurations selected for testing the different ab initio methods and bases are indicated along the relative energy axes. (See Figure 1 and the SI for the corresponding structures.)

II. COMPUTATIONAL DETAILS

A. Selection of the Structures. We have selected 15 representative structures for each reaction covering the energy range and configuration space of chemical significance. As shown in Figure 1, the geometries are obtained by varying all of the independent internal coordinates while the point-group symmetries of C_{3v} and C_s are maintained for the six- and seven-atom systems, respectively. The actual values of the internal coordinates and the corresponding energies are given in Tables S1−S6 in the Supporting Information (SI). The distributions of the energy points and the stationary points of the PESs of the F, O(^{3}P), and Cl + CH_4 and F^-, OH^- + CH_3F, and F^- + CH_3Cl reactions are shown in Figure 2. As seen in Figure 2, the PESs of the six reactions represent different shapes and energetics. The F + CH_4, OH^- + CH_3F, and F^- + CH_3Cl reactions are highly exothermic, the O(^{3}P) and Cl + CH_4 reactions are slightly endothermic, and the F^- + CH_3F reaction is isoenergetic. All reactions have pre- and postreactive

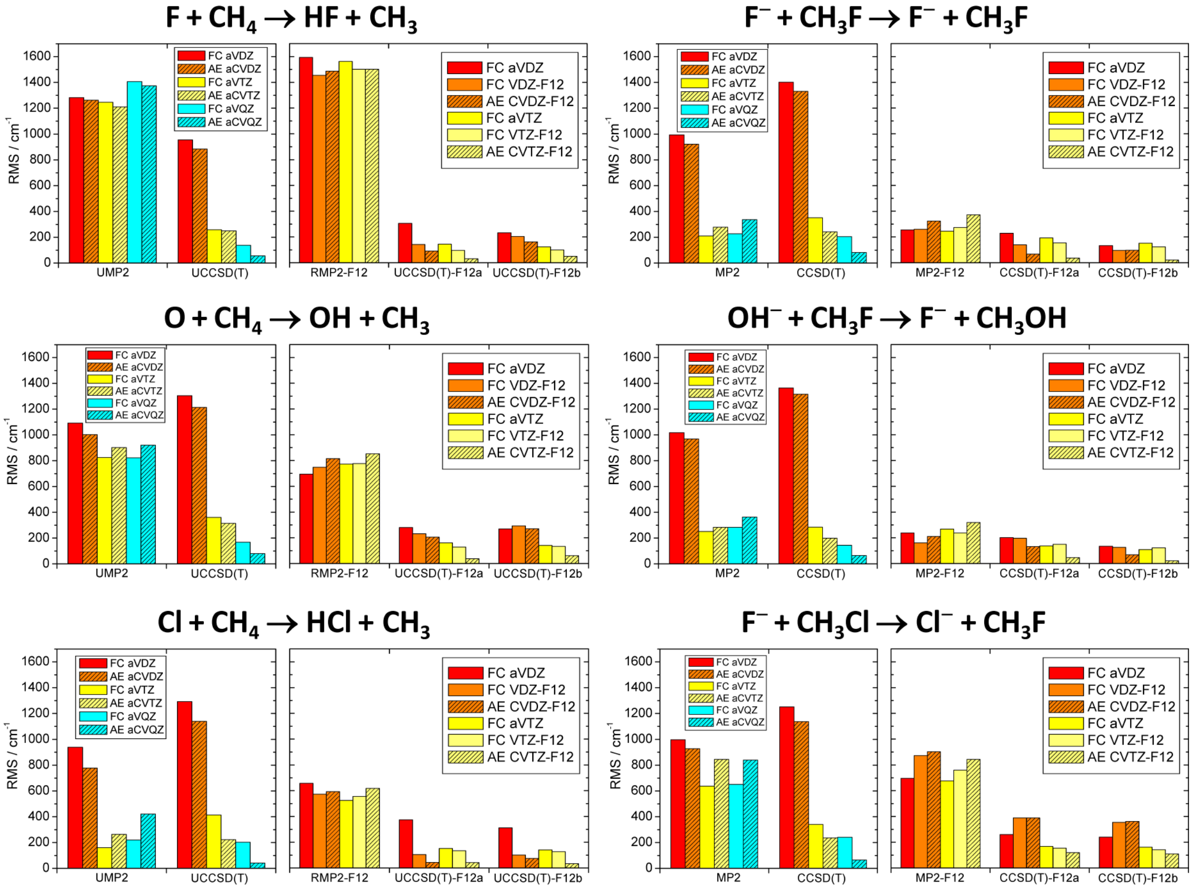

Figure 3. RMS errors of different standard and explicitly correlated F12 ab initio levels of theory for the F, O(^{3}P), and Cl + CH_4 abstraction and F^-, OH^- + CH_3F, and F^- + CH_3Cl substitution reactions. The RMS errors are based on 15 energy points, shown in Figure 2, and are relative to all-electron CCSD(T)-F12b/cc-pCVQZ-F12 reference data. FC and AE denote frozen core and all electron computations, respectively. The 15 energies and the corresponding geometries for each reaction at the various levels of theory are given in Tables S1–S6 in the SI.

complexes in the entrance and exit channels, respectively. As expected, these pre- and postreactive wells are much deeper for the substitution reactions due to relatively strong ion-dipole interactions. As Figure 2 also shows, some of the selected points are well above the minimum energy paths, thereby representing regions of the PESs that are rarely examined by electronic structure studies.

At the above-described 15 configurations, we have performed all-electron CCSD(T)-F12b/cc-pCVQZ-F12 computations for each reaction. This level of theory agrees with the corresponding CBS limit within 35 cm^{-1} (0.1 kcal mol^{-1}) or even better, as we show in Section III.E. We use these 15 high-quality energies relative to the reactant asymptote as reference data when we test the accuracy of the various ab initio methods and bases.

B. Standard Electron Correlation Computations. We use the standard second-order Møller–Plesset perturbation theory (MP2)[14] and the coupled cluster method with single, double, and perturbative triple excitations [CCSD(T)][15] based on single-configuration Hartree–Fock (HF) orbitals. For the open-shell abstraction reactions, the unrestricted MP2 (UMP2) and restricted open-shell HF (ROHF)-based unrestricted CCSD(T), denoted as UCCSD(T), are employed. We perform frozen-core (FC) computations, where only the valence electrons are correlated, as well as all-electron (AE) computations, where all the valence and outer core, that is, $1s^2$ for C, O, and F and $2s^22p^6$ for Cl, electrons are correlated.

For FC computations, the correlation-consistent polarized valence *n*-ζ basis sets augmented with diffuse functions, aug-cc-pV*n*Z [*n* = D, T, Q],[18] are used. We employ the aug-cc-pCV*n*Z [*n* = D, T, Q][19] basis sets, where C denotes tight functions designed for the description of the core electron correlation, for the AE computations. All standard MP2 and CCSD(T) computations are performed by the ab initio program package MOLPRO.[20]

C. Explicitly Correlated Computations. We perform explicitly correlated F12 computations using the MP2-F12, CCSD(T)-F12a, and CCSD(T)-F12b methods,[16,17] as implemented in MOLPRO. Note that for CCSD(T)-F12a/b, the F12 refers only to the CCSD energy, whereas the (T) correction is added by the standard way. For open-shell systems, the restricted MP2-F12 (RMP2-F12) and the ROHF-UCCSD(T)-F12a/b methods,[21] denoted simply as UCCSD(T)-F12a/b, are employed.

We use both the aug-cc-pV*n*Z [*n* = D and T][18] and the cc-pV*n*Z-F12 [*n* = D and T][22] basis sets for the FC F12 computations. Note that the latter basis sets are optimized for F12 computations. For AE F12 computations, the cc-pCV*n*Z-F12 [*n* = D and T][23] basis sets are employed. For the auxiliary basis sets, required for F12 computations, the default settings of MOLPRO are used.

D. Composite Methods. Following the ideas of the focal point analysis approach,[24,25] we test the performance of various

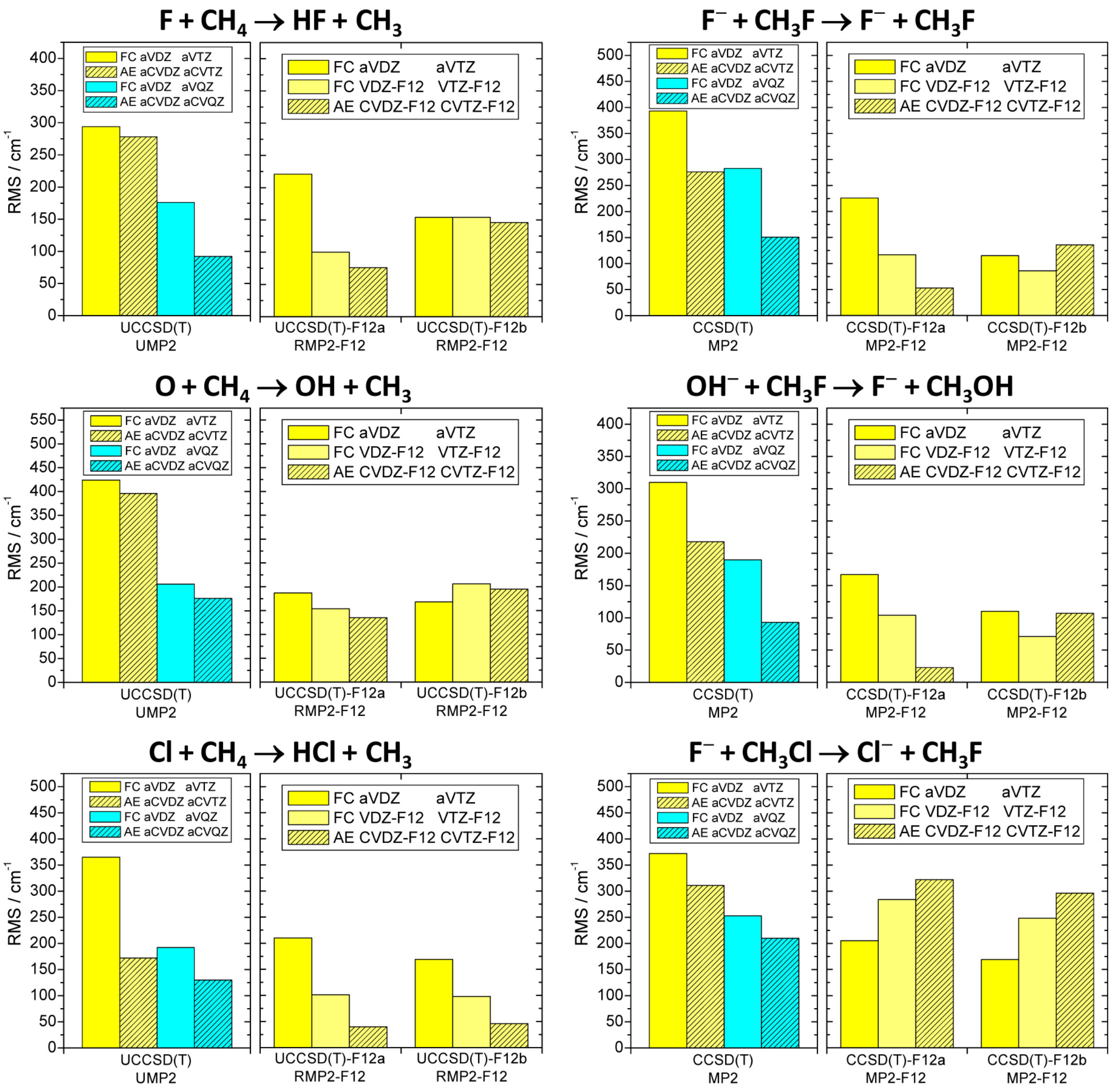

Figure 4. RMS errors of different composite ab initio methods for the F, O(^{3}P), and Cl + CH$_4$ abstraction and F$^-$, OH$^-$ + CH$_3$F, and F$^-$ + CH$_3$Cl substitution reactions. The RMS errors are based on 15 energy points, shown in Figure 2, and are relative to all-electron CCSD(T)-F12b/cc-pCVQZ-F12 reference data. The composite energies are obtained as A/small + B/large − B/small, where methods A and B are given below the columns and the bases small and large are indicated by different colors as shown in the panels. FC and AE denote frozen core and all electron computations, respectively.

composite methods. We consider composite energies obtained as

$$\text{A/small} + \text{B/large} - \text{B/small} \qquad (1)$$

where A and B are a more expensive and a cheaper ab initio method, respectively, and small and large denote the size of two different basis sets. Equation 1 is expected to provide A/large-quality results without actually performing the very expensive A/large computations.

In the present study, we consider FC/AE-CCSD(T) and FC/AE-CCSD(T)-F12a/b as method A and FC/AE-MP2 and FC/AE-MP2-F12 as method B. The small basis set is aug-cc-pVDZ, aug-cc-pCVDZ, cc-pVDZ-F12, or cc-pCVDZ-F12 and the large basis set is aug-cc-pV*n*Z [*n* = T and Q], aug-cc-pCV*n*Z [*n* = T and Q], cc-pVTZ-F12, or cc-pCVTZ-F12.

E. Auxiliary Corrections and CBS Extrapolation. Core correlation effects are estimated as difference between AE and FC CCSD(T) energies obtained with the same aug-cc-pCVQZ basis. The scalar relativistic effects are computed as the difference between second-order Douglas–Kroll[26] AE-CCSD(T)/aug-cc-pCVQZ and nonrelativistic AE-CCSD(T)/aug-cc-pCVQZ energies.

For the F and O + CH$_4$ reactions, we compute post-CCSD(T) correlation effects by performing frozen-core UHF-UCCSD(T), UHF-UCCSDT, and UHF-UCCSDT(Q) computations with the aug-cc-pVDZ basis set using the MRCC[27] code interfaced to MOLPRO. For these two reactions, we also compute the AE-UCCSD(T)/CBS limits using the extrapolation formulas[28,29]

$$E_n^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + a(n+1)\text{e}^{-9\sqrt{n}} \qquad (2)$$

$$E_n^{\text{corr.}} = E_{\text{CBS}}^{\text{corr.}} + bn^{-3} \qquad (3)$$

where the ROHF energies and their CBS limit are denoted as E_n^{HF} and $E_{\text{CBS}}^{\text{HF}}$, respectively, and the correlation energy increments and their CBS limit are $E_n^{\text{corr.}}$ and $E_{\text{CBS}}^{\text{corr.}}$, respectively.

We extrapolate using the aug-cc-pCV*n*Z bases with [$n = 3$ and 4] and [$n = 4$ and 5], and the corresponding CBS limits are denoted as CBS(T,Q) and CBS(Q,5), respectively.

III. RESULTS AND DISCUSSION

The performance of the different standard and F12 methods and basis sets for the X + CH_4 [X = F, O(^{3}P), and Cl] and X^- + CH_3Y [X/Y = F/F, OH/F, and F/Cl] reactions are shown in Figure 3. The accuracy of a given method/basis is characterized by the RMS error defined as

$$\left(\frac{1}{15}\sum_{i=1}^{15}[E_i(\text{method/basis}) - E_i(\text{AE-CCSD(T)-F12b/cc-pCVQZ-F12})]^2\right)^{1/2} \quad (4)$$

where each E_i is relative to a reference energy of a reactant-like structure obtained at the corresponding level of theory. The 15 energies and their errors obtained by the different ab initio levels are given in Tables S1−S6 in the SI. The accuracy of the various composite methods is also investigated based on eq 4, where the first E_i values are the composite energies as given in eq 1.

A. Standard Electron Correlation Computations. As Figure 3 shows, the standard MP2 method with the aug-cc-pVDZ basis usually gives RMS errors of ~1000 cm^{-1} (3 kcal mol^{-1}). For Cl + CH_4, F^- + CH_3F, and OH^- + CH_3F, these RMS errors drop to ~300 cm^{-1} when the aug-cc-pVTZ or aug-cc-pVQZ basis is used. However, for F, O + CH_4, and F^- + CH_3Cl, significant improvement of the MP2 energy is not seen when we increase the size of the basis set. It is somewhat interesting to find that CCSD(T)/aug-cc-pVDZ has the worst accuracy (RMS is usually larger than 1200 cm^{-1}) for all reactions except F + CH_4. For F + CH_4, CCSD(T)/aug-cc-pVDZ has an RMS error of 955 cm^{-1}, whereas MP2/aug-cc-pVDZ is even worse, 1282 cm^{-1}, but for the other five systems, MP2 performs better than CCSD(T)/aug-cc-pVDZ. Therefore, it is clear that CCSD(T)/aug-cc-pVDZ is not recommended for PES developments. The first level of theory that can provide chemical accuracy, defined as 1 kcal mol^{-1} (350 cm^{-1}), is CCSD(T)/aug-cc-pVTZ. On the basis of the present tests, one can be confident that CCSD(T)/aug-cc-pVTZ gives an accuracy of 350 ± 100 cm^{-1}. The worst performance of CCSD(T)/aug-cc-pVTZ is found for Cl + CH_4, where the RMS error is 414 cm^{-1}. For this reaction, AE-CCSD(T)/aug-cc-pCVTZ gives significantly smaller error of 223 cm^{-1}. Note that for F^- + CH_3Cl, which has the most core electrons, AE-CCSD(T)/aug-cc-pCVTZ slightly outperforms even the FC-CCSD(T)/aug-cc-pVQZ level (RMS errors of 236 and 241 cm^{-1}, respectively), and for Cl + CH_4, these two levels give similar accuracy (RMS errors of 223 and 203 cm^{-1}).

B. Explicitly Correlated Computations. Figure 3 shows that the explicitly correlated F12 methods converge much faster than the standard ones. It is usually true that the double-ζ basis sets provide triple-ζ quality results or even better when we compare with the standard computations. Therefore, the large RMS errors (~1200 cm^{-1}) of the standard CCSD(T)/aug-cc-pVDZ level of theory reduce to ~200 cm^{-1} when CCSD(T)-F12 computations are performed with aug-cc-pVDZ or cc-pVDZ-F12. The CCSD(T)-F12 computations with aug-cc-pVTZ or cc-pVTZ-F12 give only ~100 cm^{-1} RMS deviations. The cc-pV*n*Z-F12 basis sets were developed for F12 computations; thus, we can expect better performance of these basis sets when we compare with the corresponding aug-cc-pV*n*Z bases. Indeed, in many cases, CCSD(T)-F12/cc-pVDZ-F12 energies are more accurate than the CCSD(T)-F12/aug-cc-pVDZ results. The difference is especially pronounced for Cl + CH_4, where the former gives an RMS error of ~100 cm^{-1}, whereas the latter gives an RMS error of ~350 cm^{-1}. For F^- + CH_3Cl, the aug-cc-pVDZ basis, with an RMS error of ~250 cm^{-1}, is better because cc-pVDZ-F12 gives an RMS deviation of >350 cm^{-1}.

It was demonstrated in previous studies that the F12a method overestimates the correlation energy, whereas the F12b method underestimates it.[30] Therefore, with double-ζ and triple-ζ basis sets, F12a is recommended, whereas F12b converges better with large basis sets, for example, quadruple-ζ or even larger. The present test computations for six reactions do not show a clear preference between the F12a and F12b methods. As Figure 3 shows, the two F12 approaches usually provide very similar results when the same basis set is used.

C. Composite Methods. The accuracy of different composite methods is shown in Figure 4. As an example, let us consider the CCSD(T)/aug-cc-pVDZ + MP2/aug-cc-pVTZ − MP2/aug-cc-pVDZ composite expression, which should provide CCSD(T)/aug-cc-pVTZ quality results with a much less computational cost. Indeed, the RMS errors of this composite method are 221(259), 424(361), 365(414), 393(351), 310(285), and 372(341) cm^{-1} for F + CH_4, O + CH_4, Cl + CH_4, F^- + CH_3F, OH^- + CH_3F, and F^- + CH_3Cl, respectively, in good agreement with the RMS errors of CCSD(T)/aug-cc-pVTZ, as shown in parentheses. It is worth noting the corresponding RMS errors of CCSD(T)/aug-cc-pVDZ, 955, 1305, 1293, 1402, 1364, and 1252 cm^{-1}, which boost the advantage of the composite method. We can further improve the accuracy by using the CCSD(T)/aug-cc-pVDZ + MP2/aug-cc-pVQZ − MP2/aug-cc-pVDZ composite method, which gives RMS deviations, for the above reactions in order, of 176(138), 206(168), 192(203), 283(205), 190(145), and 253(241) cm^{-1}, where the agreement with CCSD(T)/aug-cc-pVQZ is shown in parentheses. Note that we get CCSD(T)/aug-cc-pVQZ-quality results on the expense of MP2/aug-cc-pVQZ computations. On the basis of these composite tests, we can conclude that the composite approaches greatly improve the efficiency of the standard ab initio methods. Therefore, we recommend the use of the composite energy expressions instead of standard CCSD(T) results, especially if one does not have access to program packages in which explicitly correlated methods are available.

We have also tested the performance of the composite expressions with the F12 methods. Here the utility of the composite methods is less impressive. Figure 4 shows the accuracy of different composite methods based on either CCSD(T)-F12a or CCSD(T)-F12b combined with MP2-F12 with aug-cc-pV*n*Z, cc-pV*n*Z-F12, and cc-pCV*n*Z-F12 [*n* = D and T] basis sets. Considering the composite energy formula CCSD(T)-F12a/cc-pVDZ-F12 + MP2-F12/cc-pVTZ-F12 − MP2-F12/cc-pVDZ-F12, we get RMS errors of 100(96), 154(128), 101(134), 117(154), 104(149), and 284(154) cm^{-1} for F + CH_4, O + CH_4, Cl + CH_4, F^- + CH_3F, OH^- + CH_3F, and F^- + CH_3Cl, respectively, where the agreement with the RMS errors of CCSD(T)-F12a/cc-pVTZ-F12 is shown in parentheses. As seen, this composite method provides CCSD(T)-F12a/cc-pVTZ-F12-quality or even better results,

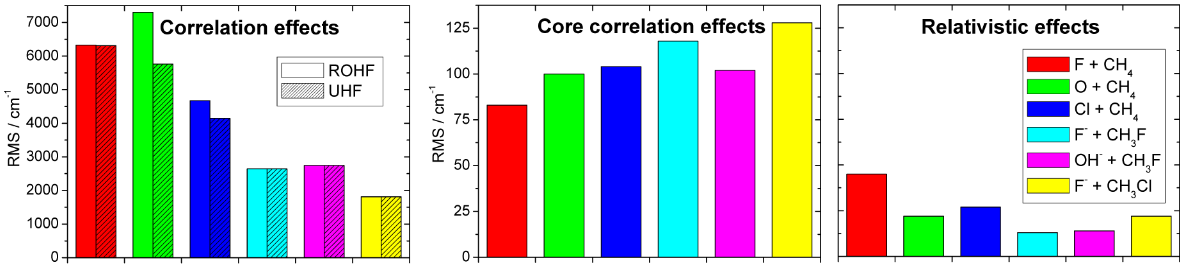

Figure 5. RMS deviations of 15 Hartree–Fock/aug-cc-pCVQZ (left), frozen-core CCSD(T)/aug-cc-pCVQZ (middle), and Douglas–Kroll all-electron CCSD(T)/aug-cc-pCVQZ (right) energies relative to all-electron CCSD(T)/aug-cc-pCVQZ energy points for the F, O(^{3}P), and Cl + CH$_4$ abstraction and F$^-$, OH$^-$ + CH$_3$F, and F$^-$ + CH$_3$Cl substitution reactions.

except for F$^-$ + CH$_3$Cl. Furthermore, the composite method always improves the accuracy of CCSD(T)-F12a/cc-pVDZ-F12 because the latter has RMS errors of 142, 232, 104, 140, 197, and 389 cm^{-1}, respectively. Therefore, composite methods should also be considered for F12 computations; however, here we recommend a more careful test of the method before one computes tens of thousands of energies for PES developments. Because the CCSD(T)-F12a/b methods almost always give chemical accuracy even with a double-ζ basis, one may just perform CCSD(T)-F12a/b computations with aug-cc-pVDZ or cc-pVDZ-F12 for large systems when the use of a triple-ζ basis is not affordable.

D. Accuracy of the HF Method. Figure 5 shows the accuracy of the HF method for the six reactions based on the RMS deviations between HF/aug-cc-pCVQZ and AE-CCSD(T)/aug-cc-pCVQZ. As seen, electron correlation plays a major role in all six reactions because the RMS errors of the HF method are as large as 4000–8000 cm^{-1} for the abstraction reactions and 1500–3000 cm^{-1} for the substitution reactions. For the open-shell abstraction reactions, ROHF and UHF give different results. The largest deviations between the ROHF and UHF energies are found for O(^{3}P) + CH$_4$, where ROHF gives an RMS error of 7302 cm^{-1}, whereas the RMS error of UHF is 5765 cm^{-1}. For F(^{2}P) + CH$_4$ and Cl(^{2}P) + CH$_4$, the RMS errors of ROHF/UHF are 6323/6311 and 4673/4147 cm^{-1}, respectively. The fact that the difference between ROHF and UHF is the largest for O(^{3}P) + CH$_4$ may be explained by the higher multiplicity relative to the halogen reactions. It is important to note that the difference between the ROHF and UHF-based correlation methods tends to diminish as we increase the level of the correlation treatment. Thus, at the CCSD(T) level, the relative energies are the same within a few inverse centimeters if we use either ROHF or UHF orbitals. We also note that the present tests warrant caution when one is to use the HF method for direct dynamics simulations because we can expect errors larger than 10 kcal mol^{-1}.

E. Auxiliary Corrections and CBS Extrapolation. We have investigated the core correlation and the scalar relativistic effects on the relative energies, as shown in Figure 5. The core correlation effects, which involve the correlation of the core–core and core–valence electrons, are in the range of 80–130 cm^{-1} for all reactions investigated in this study. Thus, correlation of the core electrons can be neglected if we aim for chemical accuracy (an average error of ~350 cm^{-1}), but one should consider this effect if really high accuracy is required or the system involves heavy atoms such as Br, I, and so on, as discussed for Br + CH$_4$ in ref 31. As expected, the scalar relativistic effects are smaller than the core correlation effects because the former effects are in the range of only 10–50 cm^{-1} for the six reactions. Therefore, one can neglect the scalar relativistic effects for PES developments for polyatomic reactions involving first and second row atoms only. Of course, as computers and methodologies improve, we may consider these effects in future high-quality PES studies.

We have computed the post-CCSD(T) correlation effects for the F and O + CH$_4$ reactions up to CCSDT(Q). Figure 6 shows the effects for the 15 relative energies for each reaction. As seen, both the d[CCSDT] and d[CCSDT(Q)] correlation energy increments, relative to the preceding level of coupled-

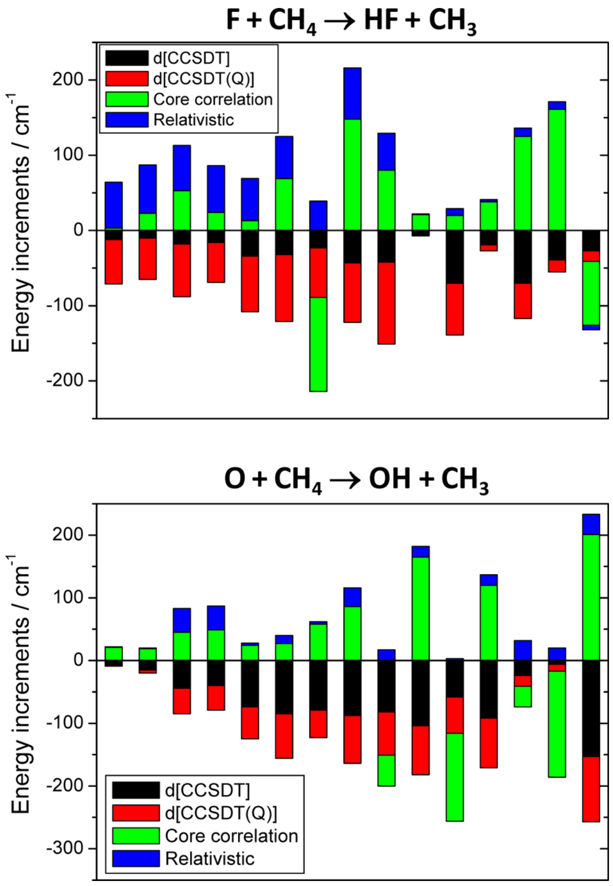

Figure 6. Post-CCSD(T) correlation effects, d[CCSDT] = CCSDT − CCSD(T) and d[CCSDT(Q)] = CCSDT(Q) − CCSDT, obtained with aug-cc-pVDZ; core correlation effects, AE-CCSD(T) − FC-CCSD(T) with aug-cc-pCVQZ; and scalar relativistic effects, DK-AE-CCSD(T) − AE-CCSD(T) with aug-cc-pCVQZ for the F and O(^{3}P) + CH$_4$ reactions. The results are shown for the 15 energy points for each reaction with increasing energy order from left to right. (The energy distributions of the points are shown in Figure 2.)

cluster theory, give negative contributions to the relative energies at all geometries considered in this study. The RMSs of {d[CCSDT] and d[CCCSDT(Q)]} are {36 and 62} and {75 and 58} in cm^{-1}, for F + CH_4 and O + CH_4, respectively. The total RMS CCSDT(Q) correlation effects relative to CCSD(T) are 94 and 132 cm^{-1} for the F and O + CH_4 reactions, respectively. The correlation effects beyond CCSDT(Q) are expected to be an order of magnitude smaller, thus negligible. Chemical accuracy can be achieved without the above post-CCSD(T) correlation effect, whose computations are quite expensive even if a small basis is used. It is worth knowing that electron correlation beyond CCSD(T) can result in an uncertainty of the PES of ~0.3 kcal mol^{-1}. If we consider both the post-CCSD(T) correlation and the scalar relativistic effect, as seen in Figure 6, we can expect some error cancellation, because the d[CCSDT] and d[CCSDT(Q)] corrections are always negative, whereas the scalar relativistic effects are almost always positive. The RMSs of the sum of the above small correction terms are 62 and 117 cm^{-1}, that is, less than the corresponding post-CCSD(T) effects of 94 and 132 cm^{-1}, for the F and O + CH_4 reactions, respectively.

For the F and O + CH_4 reactions, we have performed AE-CCSD(T)/aug-cc-pCV*n*Z computations up to $n = 5$ and determined the CBS(T,Q) and CBS(Q,5) limits using eqs 2 and 3. The basis set incompleteness errors of CBS(T,Q), aug-cc-pCVQZ, aug-cc-pCV5Z, and cc-pCVQZ-F12 relative to CBS(Q,5) are shown in Figure 7. The RMS errors for the {aCVQZ, aCV5Z} results are {77 and 43} and {115 and 59} in cm^{-1}, for F + CH_4 and O + CH_4, respectively. Thus, the uncertainty of the CBS(Q,5) limit is expected to be <30 cm^{-1} (less than the half of the aCV5Z − CBS(Q,5) difference). The AE-CCSD(T)-F12b/cc-pCVQZ-F12 computations outperform AE-CCSD(T)/aug-cc-pCV5Z and provide almost CBS quality results because the RMS deviations from CBS(Q,5) are only 26 and 35 cm^{-1} for F + CH_4 and O + CH_4, respectively. This is the reason why we have used AE-CCSD(T)-F12b/cc-pCVQZ-F12 as reference to test the accuracy of the different ab initio levels of theory. It is useful to note that the CBS(T,Q) extrapolation performs very poorly (see Figure 7) because the RMS deviations between CBS(T,Q) and CBS(Q,5) are 110 cm^{-1} (F + CH_4) and 81 cm^{-1} (O + CH_4). Thus, for example, in the case of the F + CH_4 reaction, CBS(T,Q) extrapolation does not improve the aug-cc-pCVQZ results.

The T_1 diagnostics[32] of the AE-CCSD/aug-cc-pCVQZ computations for all six reactions are given in Figure 8. As seen, at most of the geometries the T_1 values are well below 0.02, indicating that single-reference correlation methods are sufficient for PES developments for the reactions investigated in the present study. Considering the two outliers found for the F and O + CH_4 reactions, where the T_1 diagnostics show large values of 0.033 and 0.031, respectively, we find that the d[CCSDT(Q)] correlation effects are −69 and −78 cm^{-1}, whose absolute values are not much larger than the corresponding RMSs of d[CCSDT(Q)], that is, 62 and 58 cm^{-1}.

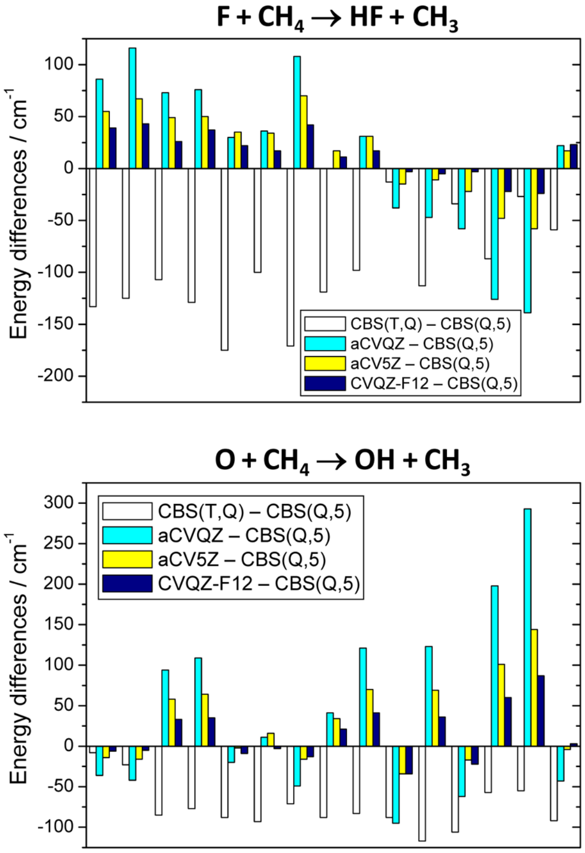

Figure 7. Basis set incompleteness errors of AE-CCSD(T)/CBS-(T,Q), AE-CCSD(T)/aug-cc-pCVQZ, AE-CCSD(T)/aug-cc-pCV5Z, and AE-CCSD(T)-F12b/cc-pCVQZ-F12 relative to AE-CCSD(T)/CBS(Q,5) for the F and $O(^3P)$ + CH_4 reactions. CBS(T,Q) and CBS(Q,5) mean extrapolations to the complete basis set limit using aug-cc-pCV*n*Z [*n* = T, Q] and [*n* = Q, 5] bases, respectively. The results are shown for the 15 energy points for each reaction with increasing energy order from left to right. (The energy distributions of the points are shown in Figure 2.)

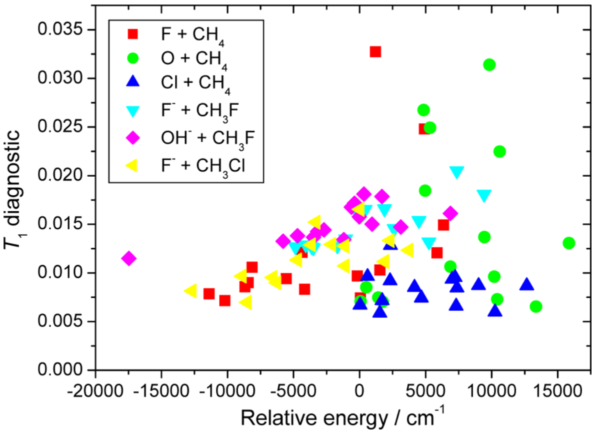

Figure 8. T_1 diagnostics of AE-CCSD/aug-cc-pCVQZ at the 15 geometries as a function of the relative potential energies (see Figures 1 and 2 and the SI) for the F, $O(^3P)$, and Cl + CH_4 abstraction and F^-, OH^- + CH_3F, and F^- + CH_3Cl substitution reactions.

Finally, we mention that the spin−orbit (SO) effects should be considered for the open-shell abstraction reactions, especially for Cl + CH_4 from the six systems investigated in this study, where the SO effect is in the range of 0−294 cm^{-1}. The SO effects are usually only significant in a certain region of the PES, for example, in the entrance channel of the halogen + CH_4 reactions. Following the strategy employed for Cl and Br + CH_4,[9,31] one can select the relevant configurations from the total data set based on geometrical conditions, where the SO corrections can be computed with multireference configuration interaction (MRCI) method using the interacting states approach.[33] Then, one can use the energy differences between the SO ground and non-SO MRCI results as additive corrections to the non-SO CCSD(T)-based energy points. Using the above strategy, we can get the SO correction with a few inverse centimeters accuracy, and thus the uncertainty of the SO effects does not compromise the accuracy of the PESs.

IV. SUMMARY AND CONCLUSIONS

Electronic structure methods and basis sets are usually tested for equilibrium and saddle-point properties, such as geometries, harmonic frequencies, reaction enthalpies, atomization energies, and barrier heights, and for potential energy curves of diatomic molecules. Dynamical simulations of polyatomic chemical reactions, however, require the knowledge of the electronic energies far away from the stationary points. Therefore, we have tested the accuracy of various standard, explicitly correlated, and composite methods at 6 × 15 geometries covering the energy range and configuration space of chemical importance for the X + CH_4 [X = F, $O(^3P)$, and Cl] and X^- + CH_3Y [X/Y = F/F, OH/F, and F/Cl] reactions. The present study provides practical guidance for choosing the most efficient ab initio level of theory for high-dimensional PES developments. Our findings and recommendations can be summarized as follows:

(1) The dynamical electron correlation plays an important role in the accurate computation of the potential energies because the HF method has extremely large average errors of 4000−8000 and 1500−3000 cm^{-1} for the X + CH_4 and X^- + CH_3Y reactions, respectively. Thus, the use of the HF method for direct dynamics simulations is not recommended.

(2) The average error of the MP2/aug-cc-pVDZ level of theory, which is one of the highest ab initio levels of theory that can be afforded for direct dynamics calculations, is ∼1000 cm^{-1} (3 kcal mol^{-1}) for all six reactions investigated. Increasing the size of the basis set, the accuracy of the MP2 method improves for Cl + CH_4, F^- + CH_3F, and OH^- + CH_3F, whereas no improvement is found for F, O + CH_4, and F^- + CH_3Cl. For the former three reactions, MP2/aug-cc-pVTZ gives quite accurate results with an average error close to 200 cm^{-1} due to favorable error cancellations. The overall accuracy of the MP2 method, based on the comparison of AE-MP2 and AE-CCSD(T) with the same aug-cc-pCVQZ basis, is around 400 and 1000 cm^{-1} for Cl + CH_4, F^-, OH^- + CH_3F and F, O + CH_4, and F^- + CH_3Cl, respectively.

(3) The standard CCSD(T)/aug-cc-pVDZ level of theory performs surprisingly poorly providing average errors of ∼1000 cm^{-1} or larger for all six reactions. The CCSD(T)/aug-cc-pVTZ level usually gives chemical accuracy because the average error of this level is in the range of 250−450 cm^{-1}.

(4) The explicitly correlated CCSD(T)-F12 method is strongly recommended for PES developments because CCSD(T)-F12 gives RMS errors of ∼200 and ∼100 cm^{-1} with double- and triple-ζ basis sets, respectively. We do not find a clear preference between the aug-cc-pV*n*Z and cc-pV*n*Z-F12 basis sets and the F12a and F12b methods. We recommend testing the performance of these methods and basis sets for the system of interest. The test can be especially useful in the case of a double-ζ basis because the performance of aug-cc-pVDZ and cc-pVDZ-F12 can be significantly different. In most cases, but not always, cc-pVDZ-F12 provides better accuracy.

(5) The use of composite methods is recommended instead of standard CCSD(T) computations because, for example, one can get CCSD(T)/aug-cc-pV*n*Z quality results on the expense of MP2/aug-cc-pV*n*Z [*n* = T and Q] computations. Composite methods can be useful for F12 computations as well, but here some preliminary tests are recommended.

(6) Core correlation and scalar relativistic effects are found in the ranges of 80−130 and 10−50 cm^{-1}, respectively, for the six reactions investigated in this study. The electron correlation effects beyond CCSD(T) are ∼100 cm^{-1} for the F and O + CH_4 reactions.

(7) The CBS(Q,5) extrapolation is accurate within 30 cm^{-1}, whereas the CBS(T,Q) extrapolation has a much larger uncertainty of ∼100 cm^{-1}. The AE-CCSD(T)-F12b/cc-pCVQZ-F12 computations agree with the corresponding CBS(Q,5) limit within 35 cm^{-1} (0.1 kcal mol^{-1}), thereby outperforming AE-CCSD(T)/aug-cc-pCVQZ and AE-CCSD(T)/aug-cc-pCV5Z, which have uncertainties of about 100 and 50 cm^{-1}, respectively.

Finally, a few notes are in order. First, the methods tested in this study are size-extensive, and thus we can expect similar accuracy of a given method/basis for larger systems as well. Second, our experience, supported by the T_1 diagnostics, is that the abstraction and substitution reactions investigated in the present study can be well-described by using a single-reference ab initio method. Of course, for other systems, static electron correlation can be important in certain regions of the PESs, where multireference computations are desirable. The investigation of various multireference methods is out of the scope of the present study. Nevertheless, one may consider dividing the global PES into "single- and multi-reference regions", and one may perform single-reference computations at the "single-reference regions" because CCSD(T) usually outperforms the MRCI method if the static electron correlation is not significant.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total electronic energies and errors of the relative energies at different standard and explicitly correlated F12 ab initio levels relative to the accurate reference data obtained at the AE-UCCSD(T)-F12b/cc-pCVQZ-F12 level of theory for the F + CH_4, $O(^3P)$ + CH_4, Cl + CH_4, F^- + CH_3F, OH^- + CH_3F, and F^- + CH_3Cl reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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