High-level \textit{ab initio} potential energy surface and dynamics of the F\textsuperscript{−} + CH\textsubscript{3}I S\textsubscript{N}2 and proton-transfer reactions\textsuperscript{†}

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Bimolecular nucleophilic substitution (S\textsubscript{N}2) and proton transfer are fundamental processes in chemistry and F\textsuperscript{−} + CH\textsubscript{3}I is an important prototype of these reactions. Here we develop the first full-dimensional \textit{ab initio} analytical potential energy surface (PES) for the F\textsuperscript{−} + CH\textsubscript{3}I system using a permutationally invariant fit of high-level composite energies obtained with the combination of the explicitly-correlated CCSD(T)-F12b method, the aug-cc-pVTZ basis, core electron correlation effects, and a relativistic effective core potential for iodine. The PES accurately describes the S\textsubscript{N}2 channel producing I\textsuperscript{−} + CH\textsubscript{2}F via Walden-inversion, front-side attack, and double-inversion pathways as well as the proton-transfer channel leading to HF + CH\textsubscript{2}I\textsuperscript{−}. The relative energies of the stationary points on the PES agree well with the new explicitly-correlated all-electron CCSD(T)-F12b/QZ-quality benchmark values. Quasiclassical trajectory computations on the PES show that the proton transfer becomes significant at high collision energies and double-inversion as well as front-side attack trajectories can occur. The computed broad angular distributions and hot internal energy distributions indicate the dominance of indirect mechanisms at lower collision energies, which is confirmed by analyzing the integration time and leaving group velocity distributions. Comparison with available crossed-beam experiments shows usually good agreement.

Introduction

Bimolecular nucleophilic substitution (S\textsubscript{N}2) is one of the best-known reaction classes in organic chemistry. The atomic-level description of the back-side attack inversion and front-side attack retention mechanisms of S\textsubscript{N}2 reactions was already presented in the book of Ingold in 1953.\textsuperscript{1} According to the simple picture of the X\textsuperscript{−} + CH\textsubscript{3}Y \rightarrow XCH\textsubscript{3} + Y \ [X, Y = F, Cl, Br, I] reactions, the back-side attack Walden-inversion pathway involves a C\textsubscript{3v} ion–dipole pre-reactive complex (X \cdots H\textsubscript{3}CY), a central transition state (TS) (X \cdots H\textsubscript{3}C \cdots Y\textsuperscript{−}), and a C\textsubscript{3v} post-transition state (XCH\textsubscript{3} \cdots Y\textsuperscript{−}), whereas the front-side attack pathway goes through a high-energy (H\textsubscript{3}CX\textsubscript{Y})\textsuperscript{−} TS, where X directly replaces Y without inversion. However, recent theoretical and experimental studies show that this simple picture is not complete and the dynamics of S\textsubscript{N}2 reactions are much more complex.\textsuperscript{2–8} Besides the above described direct pathways, indirect mechanisms play a key role in the dynamics. For the Cl\textsuperscript{−} + CH\textsubscript{3}I reaction a so-called roundabout mechanism\textsuperscript{9} was found in 2008 and for the F\textsuperscript{−} + CH\textsubscript{3}I reaction simulations revealed a double-inversion\textsuperscript{10} pathway in 2015, which was also identified in aqueous solution\textsuperscript{11} in 2016. Furthermore, in the case of the F\textsuperscript{−} nucleophile a hydrogen-bonded pre-reactive complex (F\textsuperscript{−} \cdots H\textsubscript{3}C\textsubscript{Y})\textsuperscript{12} was found to play an important role in the dynamics.\textsuperscript{13,14} In the case of the F\textsuperscript{−} + CH\textsubscript{3}Y S\textsubscript{N}2 reactions, where Y = Cl and I, a recent joint crossed-beam and trajectory study showed that the leaving group can also influence the dynamics, since the F\textsuperscript{−} + CH\textsubscript{3}I reaction was found to be significantly more direct than F\textsuperscript{−} + CH\textsubscript{3}Cl.\textsuperscript{15} This means that the direct rebound mechanism dominates in F\textsuperscript{−} + CH\textsubscript{3}Cl, whereas slow indirect complex-forming pathways are more likely in the F\textsuperscript{−} + CH\textsubscript{3}I reaction.

The present study focuses on the F\textsuperscript{−} + CH\textsubscript{3}I reaction, which has been recently investigated both experimentally and theoretically.\textsuperscript{16–18} Previous reaction dynamics simulations\textsuperscript{19–21} of the title reaction have been restricted to the use of the direct dynamics approach due to the lack of an analytical potential energy surface (PES). Here, we report such a PES for the F\textsuperscript{−} + CH\textsubscript{3}I system, which allows efficient quasiclassical trajectory (QCT) computations and opens the door for future quantum dynamics studies. Utilizing the large number of trajectories...
obtained on the PES, we can compute statistically robust integral and differential cross sections as well as product internal energy distributions allowing quantitative comparisons with previous crossed-beam experiments.\textsuperscript{11,12,14} We can also determine whether double-inversion trajectories can occur in the F\textsuperscript{−} + CH\textsubscript{3}I reaction, which have never been seen before in this system even if smaller double-inversion barrier height was recently predicted\textsuperscript{23} for F\textsuperscript{−} + CH\textsubscript{3}I than that of F\textsuperscript{−} + CH\textsubscript{3}Cl. Furthermore, besides the Sn2 pathways, a proton transfer between the reactants can also occur. The present study aims to simulate both the Sn2 and proton-transfer channels using the newly developed global PES.

Methods

The PES is represented by fitting high-level \textit{ab initio} energies using the permutationally invariant polynomial approach.\textsuperscript{16–20} Roughly 50 000 energy points are computed at the explicitly-correlated CCSD(T)-F12b/aug-cc-pVTZ level of theory\textsuperscript{21,22} using a relativistic effective core potential and the corresponding aug-cc-pVTZ-PP basis set\textsuperscript{23} for iodine. Core correlation effects, which can be important for the heavy iodine, are also considered as an additive correction obtained as difference between all-electron and frozen-core energies at the CCSD(T)/aug-cc-pVDZ-PP level of theory. The PES is fitted using a 5th order polynomial expansion of Morse-type variables, exp(−rij/a), where rij denotes inter-atomic distances and a = 3 bohr. Note that in many previous studies considering, for example, reactions of atoms with methane, an a value of 2 bohr was used.\textsuperscript{24} However, in the case of Sn2 reactions, where long-range ion–dipole interactions present, a larger a value, i.e., more diffuse fitting basis, is needed. After several test fits with different a values, we have chosen a = 3 bohr, which provides a good description at large distances as shown in Fig. S1 of the ESL.\textsuperscript{†} The number of the linear fitting parameters is 3313, which are determined by a weighted least-squares fit, where each energy, E that is relative to the global minimum, has a weight of E0(E + E0), where E0 is 0.1 in atomic units. Weights are used to suppress the high-energy data, which are out of the range of chemical importance. Our previous studies\textsuperscript{25} on F\textsuperscript{−} + CH\textsubscript{3}I used E0 = 0.05 a.u.; here a larger E0 is chosen, because F\textsuperscript{−} + CH\textsubscript{3}I is more exothermic than F\textsuperscript{−} + CH\textsubscript{3}Cl.

The new PES accurately describes the Sn2 channel via the above-mentioned different reaction pathways as well as the proton-transfer channel leading to HF + CH\textsubscript{2}I. The energy diagram of the complex PES is shown in Fig. 1, where the relative energies obtained from the PES are compared to high-level benchmark \textit{ab initio} data. The most important structural parameters of the stationary points obtained at CCSD(T)-F12b with aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets as well as from the PES are shown in Fig. 2 and S2\textsuperscript{†} for the Sn2 and abstraction channels, respectively. The benchmark classical relative energies of the stationary points are computed using a composite method based on CCSD(T)-F12b/aug-cc-pVQZ-PP energies and CCSD(T)/aug-cc-pCVTZ-PP core correlation corrections at CCSD(T)-F12b/aug-cc-pVPTZ-PP geometries (Table S1†). The best adiabatic relative energies are determined by adding a harmonic zero-point energy (ZPE) correction, obtained at the CCSD(T)-F12b/aug-cc-pVTZ-PP level of theory, to the classical energies. The CCSD(T)-F12b/aug-cc-pVnZ-PP (n = D and T) and PES harmonic vibrational frequencies of all the stationary points are given in Tables S2 and S3.\textsuperscript{†} All the

![Fig. 1](image-url)  
Potential energy surface of the F\textsuperscript{−} + CH\textsubscript{3}I Sn2 and proton-abstraction reactions showing the classical relative energies (kcal mol\textsuperscript{−1}) of the stationary points obtained from the analytical PES and by an accurate explicitly-correlated composite \textit{ab initio} method.
electronic structure computations are performed with the Molpro package.25

QCT computations are carried out for the $\text{F}^- + \text{CH}_3\text{I}$ ($v = 0$) reaction on the new analytical PES using standard normal-mode sampling26 to prepare the initial vibrational ground state ($v = 0$) of CH$_3$I. Trajectories are run at collision energies ($E_{\text{coll}}$) of 1.0, 4.0, 7.4, 10.0, 15.9, 35.3, and 50.0 kcal mol$^{-1}$ using a time step of 0.0726 fs. The impact parameters, $b$, are scanned from 0 to $b_{\text{max}}$ with a step size of 0.5 bohr and 5000 trajectories are computed at each $b$. The $b_{\text{max}}$ values are found to be 30, 20, 17, 15, 13, 10, and 9 bohr for the above collision energies, respectively. Note that $b_{\text{max}}$ values are determined by running trajectories at increasing fixed $b$ values using a step of 0.5 bohr until the reaction probability becomes 0. The final cross sections are obtained by a $b$-weighted numerical integration of the reaction probabilities over impact parameters from 0 to $b_{\text{max}}$. This approach is different from that which generates non-uniform $b$ values between 0 and $b_{\text{max}}$ using a Monte Carlo sampling, where the accurate value of $b_{\text{max}}$ is important.27–29 Of course, the two approaches converge to the same results with increasing number of trajectories and decreasing $b$ steps for the former method. The impact parameter dependence of the reaction probabilities for both the $\text{Sn}_2$ abstraction and $\text{Sn}_2$ channels at all the above collision energies are shown in the ESI (Fig. S3†). The present study considers more than 1 million trajectories. The maximum number of time steps for each trajectory is 5 million (363 ps), but the direct trajectories are only about 0.5–2 ps long and most of the trajectories finish within ~30 ps (for more details see Fig. S4†). The average CPU time of a trajectory is between 8 and 200 s strongly depending on the collision energy, impact parameter, and computer hardware. Note that the analytical potential ensures that the computation of forces during the trajectory propagation has almost no cost compared to direct dynamics simulations at the same level of theory.

Results and discussion

As shown in Table S1, the CCSD(T)-F12b energies with aug-cc-pVDZ-PP and aug-cc-pVTZ-PP bases agree within about 0.2 kcal mol$^{-1}$, the core correlation effects have positive signs and are in the range of 0.0–0.8 kcal mol$^{-1}$, and the ZPE corrections are ranging from −3.5 to +2.0 kcal mol$^{-1}$ for all the stationary points shown in Fig. 1. Thus, the ZPE corrections can be significant, since they decrease the exothermicity of the $\text{Sn}_2$ channel by 1.8 kcal mol$^{-1}$ and decrease the endothermicity of the abstraction channel by 3.5 kcal mol$^{-1}$. For the Walden-inversion TS the ZPE effect is negligible, whereas the ZPE correction decreases the abstraction as well as double-inversion barriers by about 2 kcal mol$^{-1}$. As shown in Fig. 1, the PES reproduces the high-level benchmark energies with 1 kcal mol$^{-1}$ accuracy for the $\text{Sn}_2$ pathways and somewhat larger differences of about 2 kcal mol$^{-1}$ are seen for the abstraction channel. It is important to note that Zhang, Xie, and Hase recently reported the same stationary points for the abstraction channel using B97-1/ECP/d/aug-cc-pVDZ level of theory, which usually overestimate the present benchmark values by 0.7 kcal mol$^{-1}$ on average (the maximum deviation is 1.2 kcal mol$^{-1}$ for TS1 using our notation). Thus, our high-level energies confirm the reliability of the B97-1/ECP/d method for direct dynamics studies of the title reaction, at least at not too high energies.

Utilizing the benchmark classical relative energies we can characterize the different reaction pathways of the $\text{F}^- + \text{CH}_3\text{I}$ reaction. The $\text{Sn}_2$ reaction is highly exothermic (~46.9 kcal mol$^{-1}$) with a submerged Walden-inversion TS (~17.0, relative to the reactant asymptote), a double-inversion barrier (9.1 kcal mol$^{-1}$), and a much higher front-side attack barrier (20.1 kcal mol$^{-1}$). The proton-abstraction channel is endothermic (19.4 kcal mol$^{-1}$) with several minima and saddle points above the reactants by about 5–10 kcal mol$^{-1}$, but well below the HF + CH$_3$I products. It is important to emphasize that the energy
level of the proton-abstraction products is significantly above the double-inversion TS and slightly below the front-side attack TS, similar to the \( \text{F}^- + \text{CH}_3\text{I} \) reaction, where the double-inversion pathway was discovered.\(^4\) Thus, one can expect double-inversion trajectories below the threshold energy of the abstraction and front-side attack \( \text{S}_{\text{n}2} \) pathways. In the entrance channel of the \( \text{F}^- + \text{CH}_3\text{I} \) reaction we have found several stationary points. Besides the \( \text{C}_{3\text{v}} \) ion-dipole complex (\(-17.2 \text{ kcal mol}^{-1}\)), there is a hydrogen-bonded \( \text{C}_6 \) complex (\(-19.3 \text{ kcal mol}^{-1}\)) which corresponds to a significantly deeper minimum than the \( \text{C}_{3\text{v}} \) complex. The two minima is separated by a TS (\(-16.6 \text{ kcal mol}^{-1}\)) above the \( \text{C}_6 \) and \( \text{C}_{3\text{v}} \) minima by 2.7 and 0.6 \text{ kcal mol}^{-1}, respectively. Furthermore, a front-side \( \text{F}^- \cdots \text{ICH}_3 \) \( \text{C}_{3\text{v}} \) complex (\(-22.1 \text{ kcal mol}^{-1}\)), where \( \text{F}^- \) is connected to the I atom, also exits in the entrance channel. This complex may play a significant role in the dynamics, because the \( \text{F}^- \cdots \text{ICH}_3 \) minimum is deeper by 4.9 and 2.8 \text{ kcal mol}^{-1} than the above-mentioned back-side \( \text{C}_{3\text{v}} \) and hydrogen-bonded minima, respectively.

As seen in Fig. 2 and S2 and Tables S2 and S3, the PES reproduces the benchmark bond lengths and angles as well as the vibrational frequencies with reasonable accuracy. Here we just emphasize a few points. Even if the Walden-inversion barrier of \( \text{S}_{\text{n}2} \) reactions is usually called “central”, in the present case, the C–I distance is only stretched by 0.2 Å relative to the corresponding equilibrium distance in the reactant molecule, whereas the C–F distance is 0.8 Å longer than that in the product molecule. Thus, for the \( \text{F}^- + \text{CH}_3\text{I} \) reaction we can say that the Walden inversion has an early barrier (reactant-like TS), in accord with the Hammond postulate\(^{30} \) for an exothermic reaction. At the double-inversion TS the H–F distance is stretched by 0.06 Å relative to the bond length of the HF molecule, whereas at the proton-abstraction minima and saddle points the corresponding effects are only around 0.02 Å. Furthermore, the intermolecular H–C distance at the double-inversion TS is 1.8 Å, that is much shorter than the corresponding distances of 2.1–2.2 Å at the similar abstraction stationary points. Among the TSs the double-inversion, the front-side attack, and the Walden-inversion saddle points have the largest imaginary frequencies that are 767i, 591i, and 231i, in \( \text{cm}^{-1} \), respectively, at the CCSD(T)-F12b/aug-cc-pVTZ-PP level, in good agreement with the corresponding PES values of 775i, 582i, and 206i. Note that the large imaginary frequency of the double-inversion saddle point makes this TS different from the abstraction TSs, which have imaginary frequencies around 100i. Thus, on one hand, there are several properties of the double-inversion TS which separate it from the abstraction TSs. On the other hand, as pointed out by Zhang, Xie, and Hase\(^{31} \) intrinsic reaction coordinate (IRC) computations show that the double-inversion TS is connected to the proton-transfer TSs. However, trajectories may not follow the IRC reaction path; therefore, the investigation of the role of the TSs in the double-inversion dynamics of the title reaction is an important future research direction.

Fig. 3 shows the cross sections as a function of collision energy for the different reaction pathways of the title reaction. The \( \text{S}_{\text{n}2} \) cross sections are extremely large at low \( E_{\text{coll}} \) and sharply decrease as \( E_{\text{coll}} \) increases, as expected for a highly exothermic barrierless reaction. Applying ZPE constraint, the abstraction channel opens around \( E_{\text{coll}} = 15 \text{ kcal mol}^{-1} \) in accord with its endothermicity of 15.9 \text{ kcal mol}^{-1}. Without ZPE constraint, the abstraction cross sections are significantly larger and do not have a threshold. We consider both soft and hard ZPE constraints. The soft constraint discards trajectories if the sum of the product vibrational energies is less than the sum of ZPEs, and with hard (discarding trajectories if either product violates ZPE) ZPE constraints.
constrained cross section (5.7 bohr$^2$) agrees well with the above-cited CH$_2$I constraned value of 5.4 ± 1.4 bohr$^2$. Note that the error bars of the direct dynamics results reflect the statistical uncertainty of the simulation, which is negligible in our case. The uncertainty due to the inaccuracy of the on-the-fly or analytical PES is hardly predictable, but obviously large especially for the $S_{N2}$ channel where the B97-1/ECP/d/aug-cc-pVDZ level and the present PES seem to deviate significantly, at least at high energies. The branching ratio between the $S_{N2}$ and proton-abstraction channels was recently measured by Wester and co-workers.$^{14}$ In the $E_{\text{coll}}$ range of 30–50 kcal mol$^{-1}$ the abstraction channel was found to contribute about 20% to the total reactivity. Without ZPE constraint the present simulation overestimates the abstraction cross sections and gives about 60% contribution. Nevertheless, using the hard ZPE constraint the abstraction cross sections drop to around 20% of the total cross section, in good agreement with experiment. This indicates that the use of the ZPE constraint can be important to get realistic results from a QCT simulation.

Configuration-retaining $S_{N2}$ cross sections are also shown in Fig. 3. These retention cross sections are about two orders of magnitude smaller than the inversion ones. Examination of many retention trajectories indicates that at low $E_{\text{coll}}$ all of the retention trajectories occur via the double-inversion mechanism, whereas at collision energies above 20 kcal mol$^{-1}$ the front-side attack pathway also opens. Double inversion is usually a slow indirect process, whereas the front-side attack is fast and direct. However, we found that one cannot distinguish between the two mechanisms based on simply the integration time, as we did in the case of the $F^- + CH_3Cl$, $F^- + CH_3F$, and $F^- + CHD_2Cl$ reactions.$^6$ Fig. 3 also shows the cross sections for the induced inversions of the CH$_3$I reactant, which are not followed by a substitution resulting in an inverted reactant. The $E_{\text{coll}}$ dependence of the induced and double inversions is similar, both have a maximum at $E_{\text{coll}} = 20$ kcal mol$^{-1}$. At low $E_{\text{coll}}$ the probability of induced inversion is smaller than that of the double inversion, showing that the first inversion is usually followed by a second inversion. Due to the fact that the adiabatic double-inversion barrier height of the $F^- + CH_3I$ reaction (7.0 kcal mol$^{-1}$) is significantly smaller than that of the $F^- + CH_3Cl$ reaction (14.0 kcal mol$^{-1}$), we predicted$^{15}$ that the double inversion could be more likely in the $F^- + CH_3I$ system. The present QCT results support this, since the double-inversion cross sections can be as high as 0.3 bohr$^2$ for $F^- + CH_3I$, whereas the corresponding value is only 0.05 bohr$^2$ for $F^- + CH_3Cl$. Furthermore, the maximum of the double-inversion cross sections, that is at $E_{\text{coll}} = 30$ kcal mol$^{-1}$ for $F^- + CH_3Cl$, is at a smaller $E_{\text{coll}}$ of 20 kcal mol$^{-1}$ for $F^- + CH_3I$.

Comparison of the computed and measured$^{12}$ differential cross sections as well as product internal energy distributions of the $S_{N2}$ channel is shown in Fig. 4. The computed scattering angle distributions are broad with forward preference at low

Fig. 4  Theoretical (this work) and experimental (ref. 12) normalized scattering angle and product internal energy distributions for the $F^- + CH_3I$ $S_{N2}$ reaction at different collision energies.


open the door for several future dynamical investigations using quantum\textsuperscript{77} as well as quasi-classical methods and considering vibrational and/or rotational mode specificity, isotope effects as well as different high-energy reaction channels.

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