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# High-level *ab initio* potential energy surface and dynamics of the $F^- + CH_3I$ $S_N2$ and proton-transfer reactions

Balázs Olasz, István Szabó,<sup>a</sup> and Gábor Czako\*

Department of Physical Chemistry and Materials Science, Institute of Chemistry, University of Szeged,  
Rerrich Béla tér 1, Szeged H-6720, Hungary

<sup>a</sup> Present address: Department of Chemistry, King's College London, London SE1 1DB, United Kingdom

\* E-mail: gczako@chem.u-szeged.hu.

## Abstract

Bimolecular nucleophilic substitution ( $S_N2$ ) and proton transfer are fundamental processes in chemistry and  $F^- + CH_3I$  is an important prototype of these reactions. Here we develop the first full-dimensional *ab initio* analytical potential energy surface (PES) for the  $F^- + CH_3I$  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  $S_N2$  channel producing  $I^- + CH_3F$  via Walden-inversion, front-side attack, and double-inversion pathways as well as the proton-transfer channel leading to  $HF + CH_2I^-$ . 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.

**Electronic supplementary information (ESI) available:** Benchmark classical and adiabatic relative energies (Table S1), vibrational frequencies of all the stationary points (Tables S2 and S3), direct/indirect trajectory separation function parameters (Table S4), entrance-channel potential (Figure S1), structures of the minima and saddle points corresponding to the abstraction channel (Figure S2), reaction probabilities (Figure S3), trajectory integration time distributions (Figure S4), trajectory integration time vs.  $I^-$  velocity distributions (Figure S5), and mechanism-specific reaction probabilities (Figure S6).



## Introduction

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Bimolecular nucleophilic substitution ( $S_N2$ ) 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  $S_N2$  reactions was already presented in the book of Ingold in 1953.<sup>1</sup> According to the simple picture of the  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$  [ $X, Y = F, Cl, Br, I$ ] reactions, the back-side attack Walden-inversion pathway involves a  $C_{3v}$  ion-dipole pre-reaction complex ( $X^- \cdots H_3CY$ ), a central transition state (TS) ( $X \cdots H_3C \cdots Y^-$ ), and a  $C_{3v}$  post-reaction complex ( $XCH_3 \cdots Y^-$ ), whereas the front-side attack pathway goes through a high-energy ( $H_3CXY$ )<sup>-</sup> 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  $S_N2$  reactions are much more complex.<sup>2,3,4,5,6,7,8</sup> Beside the above described direct pathways, indirect mechanisms play a key role in the dynamics. For the  $Cl^- + CH_3I$  reaction a so-called roundabout mechanism<sup>9</sup> was found in 2008 and for the  $F^- + CH_3Cl$  reaction simulations revealed a double-inversion<sup>6</sup> pathway in 2015, which was also identified in aqueous solution<sup>10</sup> in 2016. Furthermore, in the case of the  $F^-$  nucleophile a hydrogen-bonded pre-reaction complex ( $F^- \cdots HCH_2Y$ ) was found to play an important role in the dynamics.<sup>5,11</sup> In the case of the  $F^- + CH_3Y$   $S_N2$  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  $F^- + CH_3Cl$  reaction was found to be significantly more direct than  $F^- + CH_3I$ .<sup>7</sup> This means that the direct rebound mechanism dominates in  $F^- + CH_3Cl$ , whereas slow indirect complex-forming pathways are more likely in the  $F^- + CH_3I$  reaction.

The present study focuses on the  $F^- + CH_3I$  reaction, which has been recently investigated both experimentally and theoretically.<sup>11,12,13,14</sup> Previous reaction dynamics simulations<sup>11,12,13</sup> 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  $F^- + CH_3I$  system, which PES 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.<sup>11,12,14</sup> We can also determine whether double-inversion trajectories can occur in the  $F^- + CH_3I$  reaction, which have never been seen before in this system even if smaller double-inversion barrier height was recently predicted<sup>15</sup> for  $F^- + CH_3I$  than that of  $F^- + CH_3Cl$ . Furthermore, beside the  $S_N2$

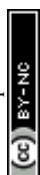


pathways, a proton transfer between the reactants can also occur. The present study aims to simulate both the  $S_N2$  and proton-transfer channels using the newly developed global PES.

## Methods

The PES is represented by fitting high-level *ab initio* energies using the permutationally invariant polynomial approach.<sup>16,17,18,19,20</sup> Roughly 50 000 energy points are computed at the explicitly-correlated CCSD(T)-F12b/aug-cc-pVTZ level of theory<sup>21,22</sup> using a relativistic effective core potential and the corresponding aug-cc-pVTZ-PP basis set<sup>23</sup> 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-pwCVDZ-PP level of theory. The PES is fitted using a 5th order polynomial expansion of Morse-type variables,  $\exp(-r_{ij}/a)$ , where  $r_{ij}$  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.<sup>24</sup> However, in the case of  $S_N2$  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 Figure S1 of the ESI. 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  $E_0 / (E + E_0)$ , where  $E_0$  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<sup>5,6</sup> on  $F^- + CH_3Cl$  used  $E_0 = 0.05$  a.u.; here a larger  $E_0$  is chosen, because  $F^- + CH_3I$  is more exothermic than  $F^- + CH_3Cl$ .

The new PES accurately describes the  $S_N2$  channel via the above-mentioned different reaction pathways as well as the proton-transfer channel leading to  $HF + CH_2I^-$ . The energy diagram of the complex PES is shown in Figure 1, where the relative energies obtained from the PES are compared to high-level benchmark *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 Figure 2 and Figure S2 for the  $S_N2$  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-pwCVTZ-PP core correlation corrections at CCSD(T)-F12b/aug-cc-pVTZ-PP geometries (Table S1). The best adiabatic relative energies

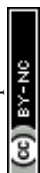


are determined by adding a harmonic zero-point energy (ZPE) correction, obtained at the CCSD(T)-F12b/aug-cc-pVTZ-PP level of theory, to the classical energies. The CCSD(T)-F12b/aug-cc-pVnZ-PP ( $n = D$  and  $T$ ) and PES harmonic vibrational frequencies of all the stationary points are given in Tables S2 and S3. All the electronic structure computations are performed with the Molpro package.<sup>25</sup>

QCT computations are carried out for the  $F^- + CH_3I(v=0)$  reaction on the new analytical PES using standard normal-mode sampling<sup>26</sup> to prepare the initial vibrational ground state ( $v=0$ ) of  $CH_3I$ . Trajectories are run at collision energies ( $E_{coll}$ ) of 1.0, 4.0, 7.4, 10.0, 15.9, 35.3, and 50.0 kcal/mol using a time step of 0.0726 fs. The impact parameters,  $b$ , are scanned from 0 to  $b_{max}$  with a step size of 0.5 bohr and 5000 trajectories are computed at each  $b$ . The  $b_{max}$  values are found to be 30, 20, 17, 15, 13, 10, and 9 bohr for the above collision energies, respectively. Note that  $b_{max}$  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  $b_{max}$ . This approach is different from that which generates non-uniform  $b$  values between 0 and  $b_{max}$  using a Monte Carlo sampling, where the accurate value of  $b_{max}$  is important.<sup>27,28,29</sup> 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  $S_N2$  and abstraction channels at all the above collision energies are shown in the ESI (Figure 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 Figure 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

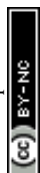
As shown in Table S1, the CCSD(T)-F12b energies with aug-cc-pVDZ-PP and aug-cc-pVTZ-PP bases agree within about 0.2 kcal/mol, the core correlation effects have positive signs and are in the range of 0.0–0.8 kcal/mol, and the ZPE corrections are ranging from –3.5 to +2.0 kcal/mol for all the stationary points shown in Figure 1. Thus, the ZPE corrections can



be significant, since they decrease the exothermicity of the  $S_N2$  channel by 1.8 kcal/mol and decrease the endothermicity of the abstraction channel by 3.5 kcal/mol. 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. As shown in Figure 1, the PES reproduces the high-level benchmark energies with 1 kcal/mol accuracy for the  $S_N2$  pathways and somewhat larger differences of about 2 kcal/mol are seen for the abstraction channel. It is important to note that Zhang, Xie, and Hase<sup>13</sup> 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 on average (the maximum deviation is 1.2 kcal/mol 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  $F^- + CH_3I$  reaction. The  $S_N2$  reaction is highly exothermic (−46.9 kcal/mol) with a submerged Walden-inversion TS (−17.0, relative to the reactant asymptote), a double-inversion barrier (9.1 kcal/mol), and a much higher front-side attack barrier (20.1 kcal/mol). The proton-abstraction channel is endothermic (19.4 kcal/mol) with several minima and saddle points above the reactants by about 5–10 kcal/mol, but well below the  $HF + CH_2I^-$  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  $F^- + CH_3Cl$  reaction, where the double-inversion pathway was discovered.<sup>6</sup> Thus, one can expect double-inversion trajectories below the threshold energy of the abstraction and front-side attack  $S_N2$  pathways. In the entrance channel of the  $F^- + CH_3I$  reaction we have found several stationary points. Besides the  $C_{3v}$  ion-dipole complex (−17.2 kcal/mol), there is a hydrogen-bonded  $C_s$  complex (−19.3 kcal/mol) which corresponds to a significantly deeper minimum than the  $C_{3v}$  complex. The two minima is separated by a TS (−16.6 kcal/mol) above the  $C_s$  and  $C_{3v}$  minima by 2.7 and 0.6 kcal/mol, respectively. Furthermore, a front-side  $F^- \cdots ICH_3$   $C_{3v}$  complex (−22.1 kcal/mol), where  $F^-$  is connected to the I atom, also exists in the entrance channel. This complex may play a significant role in the dynamics, because the  $F^- \cdots ICH_3$  minimum is deeper by 4.9 and 2.8 kcal/mol than the above-mentioned back-side  $C_{3v}$  and hydrogen-bonded minima, respectively.

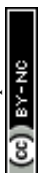
As seen in Figures 2 and S2 and Tables S2 and S3, the PES reproduces the benchmark bond lengths and angles as well as the vibrational frequencies with reasonable accuracy. Here





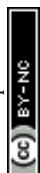
we just emphasize a few points. Even if the Walden-inversion barrier of  $S_N2$  reactions is usually called “central”, in the present case, the C-I distance is only stretched by 0.2 Å relative to the corresponding equilibrium distance in the reactant molecule, whereas the C-F distance is 0.8 Å longer than that in the product molecule. Thus, for the  $F^- + CH_3I$  reaction we can say that the Walden inversion has an early barrier (reactant-like TS), in accord with the Hammond postulate<sup>30</sup> 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  $cm^{-1}$ , 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,<sup>13</sup> 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.

Figure 3 shows the cross sections as a function of collision energy for the different reaction pathways of the title reaction. The  $S_N2$  cross sections are extremely large at low  $E_{coll}$  and sharply decrease as  $E_{coll}$  increases, as expected for a highly exothermic barrierless reaction. Applying ZPE constraint, the abstraction channel opens around  $E_{coll} = 15$  kcal/mol in accord with its endothermicity of 15.9 kcal/mol. 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 (obtained from the harmonic approximation), whereas the hard constraint discards trajectories if either HF or  $CH_2F$  has less vibrational energy than the corresponding ZPE. Note that a sophisticated alternative of treating the ZPE issue is the use of the one-dimensional Gaussian binning (1GB) method,<sup>31,32,33</sup> but this technique cannot provide realistic absolute cross sections due to the normalization issue, therefore we rely on



the simpler soft and hard ZPE constraints. The soft and hard ZPE constraints give similar, physically correct thresholds, but the hard cross sections are substantially smaller as shown in Figure 3. Recently, Zhang, Xie, and Hase<sup>13</sup> reported cross sections of  $30.7 \pm 7.9$  and  $7.5 \pm 2.9$  bohr<sup>2</sup> for the S<sub>N</sub>2 and abstraction channels, respectively, obtained from a DFT/B91-1 direct dynamics computation at  $E_{\text{coll}} = 35.3$  kcal/mol. When they applied ZPE constraint for the CH<sub>2</sub>I<sup>•</sup> product, the abstraction cross section became  $5.4 \pm 1.4$  bohr<sup>2</sup>. Our PES gives substantially smaller cross section (8.8 bohr<sup>2</sup>) for the S<sub>N</sub>2 channel, which, however, agrees better with an MP2 direct dynamics result of  $6.4 \pm 1.1$  bohr<sup>2</sup>.<sup>34</sup> For the abstraction, the present cross section of 11.7 bohr<sup>2</sup> without ZPE constraint is in reasonable agreement with the DFT/B91-1 result of  $7.5 \pm 2.9$  bohr<sup>2</sup>. Furthermore, our soft constrained cross section (5.7 bohr<sup>2</sup>) agrees well with the above-cited CH<sub>2</sub>I<sup>•</sup> constrained value of  $5.4 \pm 1.4$  bohr<sup>2</sup>. 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<sub>N</sub>2 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<sub>N</sub>2 and proton-abstraction channels was recently measured by Wester and co-workers.<sup>14</sup> In the  $E_{\text{coll}}$  range of 30–50 kcal/mol 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<sub>N</sub>2 cross sections are also shown in Figure 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 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<sup>•</sup> + CH<sub>3</sub>Cl, F<sup>•</sup> + CH<sub>3</sub>F, and F<sup>•</sup> + CHD<sub>2</sub>Cl reactions.<sup>6,35,36</sup> Figure 3 also shows the cross sections for the induced inversions of the CH<sub>3</sub>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. 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  $\text{F}^- + \text{CH}_3\text{I}$  reaction (7.0 kcal/mol) is significantly smaller than that of the  $\text{F}^- + \text{CH}_3\text{Cl}$  reaction (14.0 kcal/mol),<sup>6</sup> we predicted<sup>15</sup> that the double inversion could be more likely in the  $\text{F}^- + \text{CH}_3\text{I}$  system. The present QCT results support this, since the double-inversion cross sections can be as high as 0.3 bohr<sup>2</sup> for  $\text{F}^- + \text{CH}_3\text{I}$ , whereas the corresponding value is only 0.05 bohr<sup>2</sup> for  $\text{F}^- + \text{CH}_3\text{Cl}$ .<sup>6</sup> Furthermore, the maximum of the double-inversion cross sections, that is at  $E_{\text{coll}} = 30$  kcal/mol for  $\text{F}^- + \text{CH}_3\text{Cl}$ , is at a smaller  $E_{\text{coll}}$  of 20 kcal/mol for  $\text{F}^- + \text{CH}_3\text{I}$ .

Comparison of the computed and measured<sup>12</sup> differential cross sections as well as product internal energy distributions of the  $\text{S}_{\text{N}}2$  channel is shown in Figure 4. The computed scattering angle distributions are broad with forward preference at low  $E_{\text{coll}}$  and slight backward dominance at larger  $E_{\text{coll}}$ . The broad nearly isotropic feature shows the dominance of the indirect reaction pathways in the  $\text{F}^- + \text{CH}_3\text{I}$   $\text{S}_{\text{N}}2$  reaction. At low  $E_{\text{coll}}$  up to about 20 kcal/mol the  $\text{CH}_3\text{F}$  product internal energy distributions are hot peaking at the highest energies showing that most of the available energy transfers into product vibration and rotation which also supports the dominance of the indirect mechanisms. At a higher  $E_{\text{coll}}$  of 35.3 kcal/mol, the internal energy distributions are broader indicating mixed direct-indirect mechanisms. For the internal energy distributions theory and experiment are in good qualitative or semi-quantitative agreement as shown in Figure 4. The finding that the maximum internal energy obtained from the simulation is higher by 1-2 kcal/mol than the experimental value is due to the fact that the analytical PES overestimates the exothermicity of the  $\text{S}_{\text{N}}2$  channel by about 1 kcal/mol. The agreement between the computed and measured angular distributions is excellent at  $E_{\text{coll}} = 15.9$  kcal/mol. At  $E_{\text{coll}} = 7.4$  kcal/mol, theory shows more forward scattering than experiment, whereas at  $E_{\text{coll}} = 35.4$  kcal/mol theory is more isotropic than the backward-scattered experiment. At this latter  $E_{\text{coll}}$ , the present computed angular distribution shows some agreement with the previous DFT/B91-1 direct dynamics result, which is also isotropic-like.<sup>12</sup> We should also note that the MP2 direct dynamics simulation starts to pick up the backward preference of the experiment.<sup>34</sup> However, it is clear that more work needs to be done to obtain definitive theoretical predictions for the angular distributions at high collision energies. Furthermore, it is interesting to note that the present angular distributions are much more isotropic and the internal energy distributions are



significantly hotter than the corresponding distributions of the  $F^- + CH_3Cl$  reaction. This supports our previous finding that the  $F^- + CH_3Cl$  reaction is more direct than the analogous  $F^- + CH_3I$  reaction showing a significant leaving group effect on the dynamics of  $S_N2$  reactions.<sup>7</sup>

In order to further investigate the competition between direct and indirect mechanisms, we have determined the direct rebound, direct stripping, and indirect cross sections based on trajectory-integration-time-leaving-group-velocity correlation diagrams and scattering angle distributions as shown in more detail in Figure S5. The mechanism-specific reaction probabilities at different collision energies are given in Figure S6. As seen, the direct reactions proceed with rebound mechanism at small impact parameters and stripping trajectories occur at large  $b$  values. The overlaps between the rebound and stripping opacity functions are almost negligible. The indirect reaction probabilities usually decrease with increasing  $b$ . At the highest collision energies the indirect reactions vanish at the largest  $b$  values and almost solely stripping trajectories are found. The fractions of the rebound, stripping, and indirect cross sections as a function of the collision energy are shown in Figure 5. At low  $E_{coll}$  up to about 20 kcal/mol the indirect mechanism dominates and at higher  $E_{coll}$  the direct pathways, especially via the rebound mechanism, become more significant. The computed direct rebound fractions of 17 and 49 % at  $E_{coll} = 7.4$  and 35.3 kcal/mol, respectively, are in excellent agreement with the corresponding experimental values of 20 and 52 %.<sup>12</sup> At  $E_{coll} = 35.3$  kcal/mol the previous DFT/B91-1 direct dynamics simulation<sup>34</sup> gave cross section percentages of 29, 12, and 59 for the direct rebound, direct stripping, and indirect mechanisms, respectively, in disagreement with experiment and the present results of 49, 31, and 20 %, respectively. Nevertheless, the agreement with the MP2 direct dynamics results<sup>34</sup> of 46, 43, and 11 % is much better, which indicates that the DFT/B91-1 method may not give a reasonably accurate description of the PES at high energies. Although both experiment and the present theoretical results show that the direct rebound is the dominant mechanism of the  $F^- + CH_3I$  reaction at high  $E_{coll}$ , the roughly 50 % direct rebound fraction is significantly less than that (~80 %) of the  $F^- + CH_3Cl$  reaction, supporting our previous findings.<sup>7</sup>

## Summary and conclusions

We have developed the first analytic global *ab initio* PES for the title reaction, which accurately describes both the  $S_N2$  and proton-transfer channels. QCT simulations on the new PES reveal double-inversion trajectories for the  $F^- + CH_3I$  reaction. Furthermore, the absolute

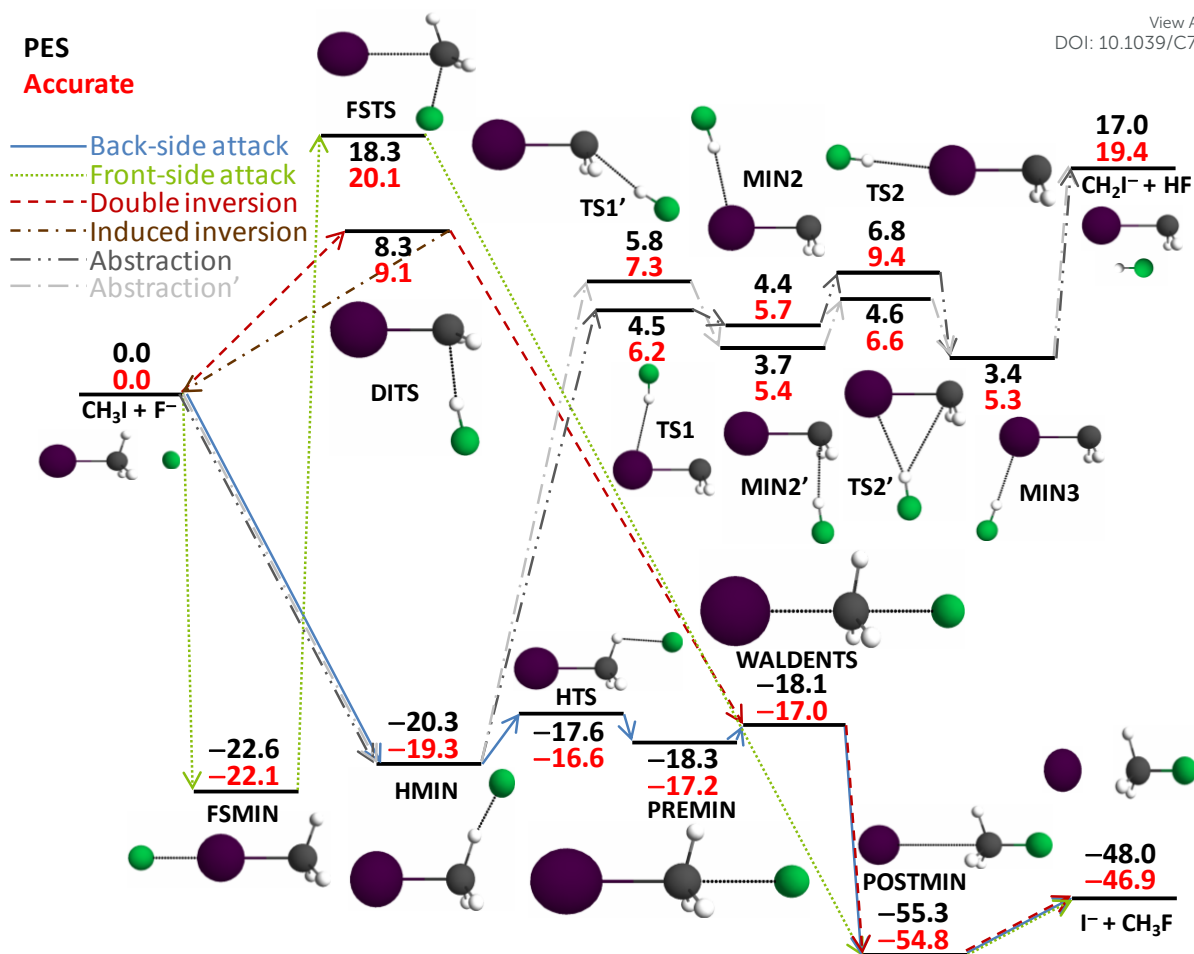


cross sections of  $F^- + CH_3I$  double inversion are found to be larger than those of the  $F^- + CH_3Cl$  reaction. At low collision energies clearly the back-side attack dominates, at high energies the proton-transfer and  $S_N2$  channels have similar reactivity. About 1 % of the  $S_N2$  trajectories occur via the double-inversion and front-side attack pathways. At low collision energies the double-inversion is the dominant retention mechanism, at higher energies the front-side attack pathway opens. The differential cross sections and product internal energy distributions of the  $F^- + CH_3I$   $S_N2$  reaction usually show good agreement with experiment, although some differences can be observed, especially at high collision energies. Some of the results agree well with previous direct dynamics simulations, but there are also differences. The above findings clearly show that the title reaction is a challenging system and the standard single-reference electronic structure methods and effective core potentials used for the iodine atom may not give a good description at high potential energies. Nevertheless, the above-described dynamical results are just certainly the beginning of a fruitful research utilizing the analytical PES reported here for the  $F^- + CH_3I$  reaction. We hope that the new PES will open the door for several future dynamical investigations using quantum<sup>37</sup> as well as quasi-classical methods and considering vibrational and/or rotational mode specificity, isotope effects as well as different high-energy reaction channels.

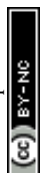
### Acknowledgements

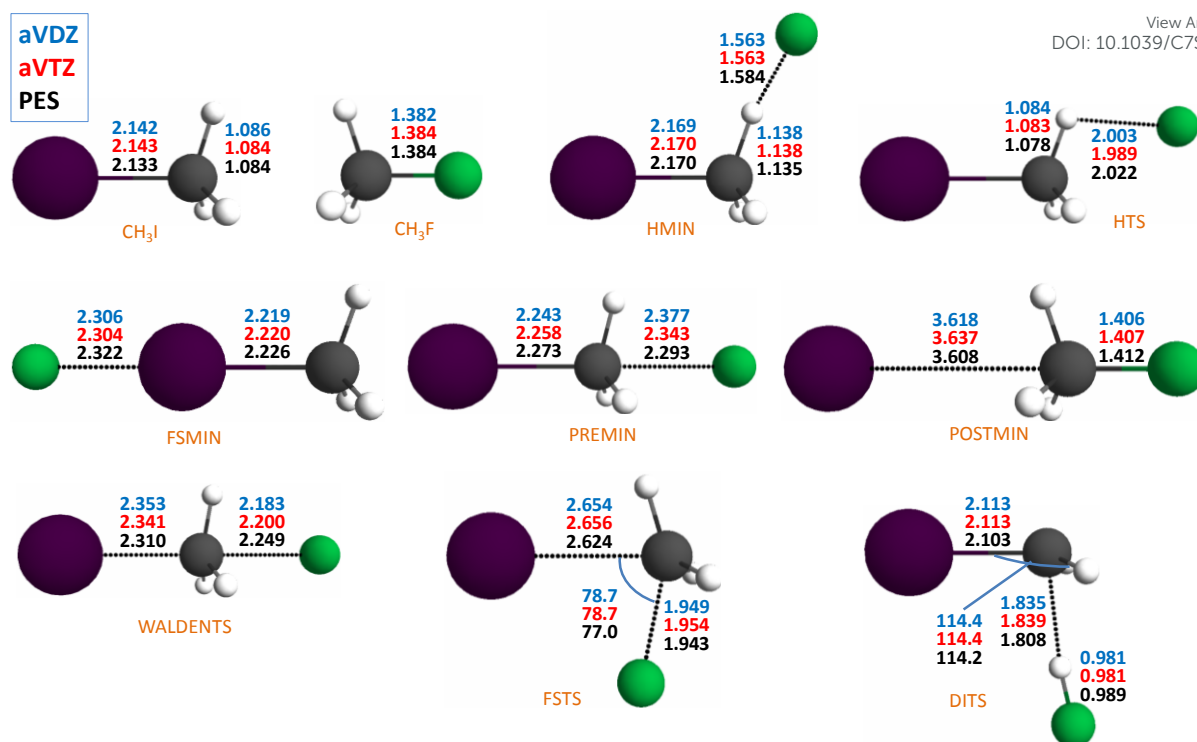
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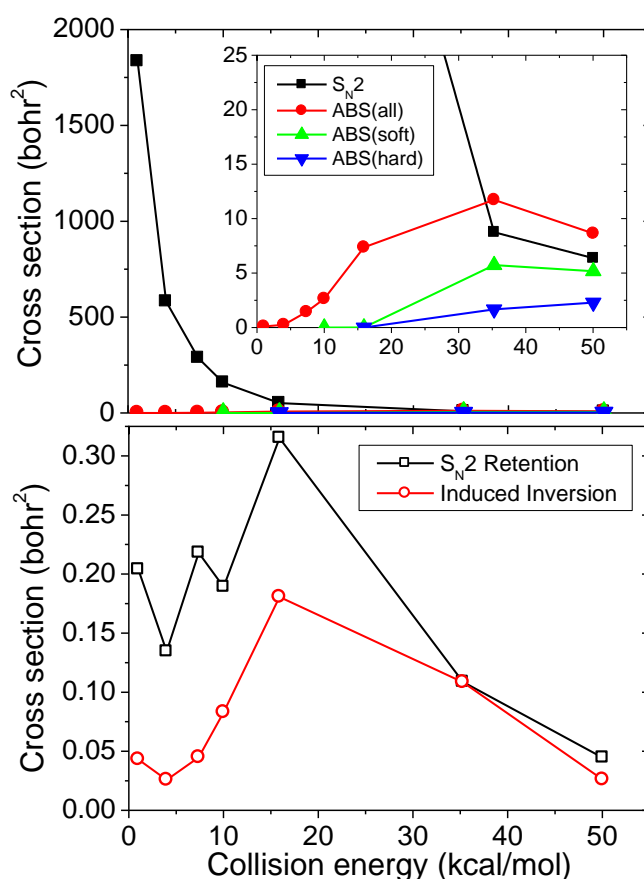


**Figure 1.** Potential energy surface of the F<sup>-</sup> + CH<sub>3</sub>I S<sub>N</sub>2 and proton-abstraction reactions showing the classical relative energies (kcal/mol) of the stationary points obtained from the analytical PES and by an accurate explicitly-correlated composite *ab initio* method.





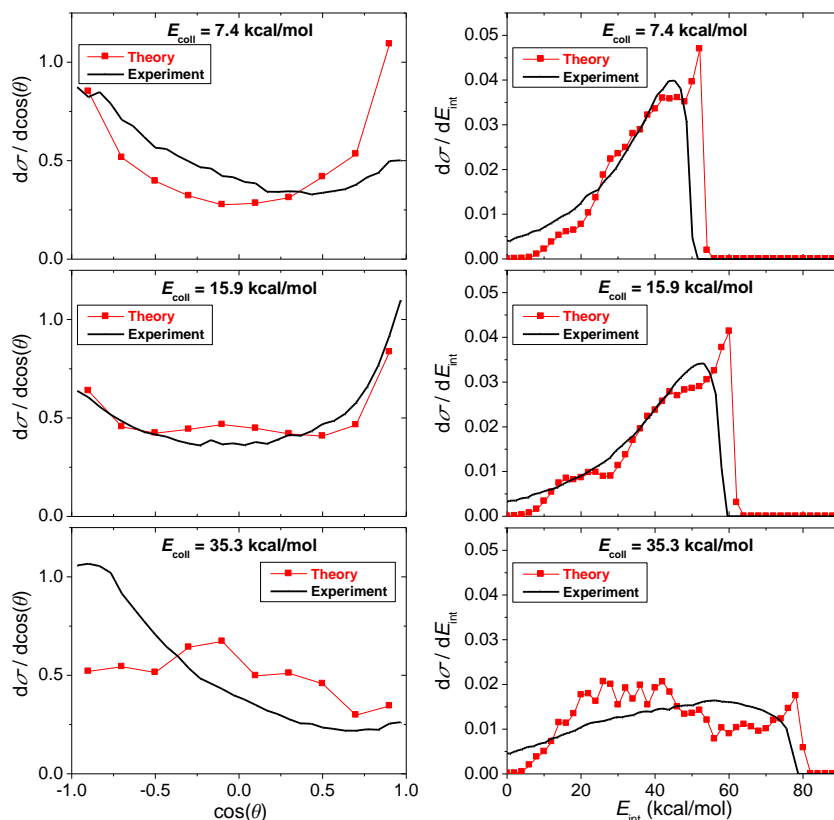
**Figure 2.** Stationary-point structures corresponding to the  $S_N2$  channel of the  $F^- + CH_3I$  reaction showing the representative structural parameters (distance in Å and angles in degrees) obtained at CCSD(T)-F12b/aug-cc-pVDZ-PP (aVDZ) and CCSD(T)-F12b/aug-cc-pVTZ-PP (aVTZ) as well as by using the analytical potential energy surface (PES).



**Figure 3.** Cross sections as a function of collision energy for the  $S_N2$ , abstraction,  $S_N2$  retention (front-side attack + double inversion), and induced-inversion pathways of the  $F^- + CH_3I$  reaction. For the abstraction (ABS) channel results are shown without (all), with soft (discarding 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.

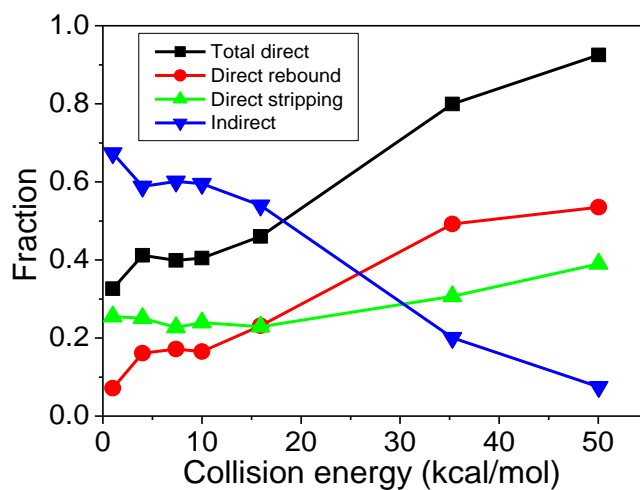






**Figure 4.** Theoretical (this work) and experimental (ref 12) normalized scattering angle and product internal energy distributions for the  $F^- + CH_3I$   $S_N2$  reaction at different collision energies.





**Figure 5.** Total direct (rebound + stripping), direct rebound, direct stripping, and indirect  $F^- + CH_3I$   $S_N2$  cross section ratios as a function of collision energy.



## References

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- <sup>1</sup> C. K. Ingold, *Structure and Mechanisms in Organic Chemistry* (Cornell Univ. Press, Ithaca, NY, 1953).
- <sup>2</sup> J. I. Brauman, *Science*, 2008, **319**, 168–168.
- <sup>3</sup> P. Manikandan, J. Zhang and W. L. Hase, *J. Phys. Chem. A*, 2012, **116**, 3061–3080.
- <sup>4</sup> J. Xie, R. Otto, J. Mikosch, J. Zhang, R. Wester and W. L. Hase, *Acc. Chem. Res.*, 2014, **47**, 2960–2969.
- <sup>5</sup> I. Szabó, A. G. Császár and G. Czako, *Chem. Sci.*, 2013, **4**, 4362–4370.
- <sup>6</sup> I. Szabó and G. Czako, *Nat. Commun.*, 2015, **6**, 5972.
- <sup>7</sup> M. Stei, E. Carrascosa, M. A. Kainz, A. H. Kelkar, J. Meyer, I. Szabó, G. Czako and R. Wester, *Nature Chem.*, 2016, **8**, 151–156.
- <sup>8</sup> J. Xie and W. L. Hase, *Science*, 2016, **352**, 32–33.
- <sup>9</sup> J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J.-X. Zhang, W. L. Hase, M. Weidemüller and R. Wester, *Science*, 2008, **319**, 183–186.
- <sup>10</sup> P. Liu, D. Y. Wang and Y. Xu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31895–31903.
- <sup>11</sup> J. Zhang, J. Mikosch, S. Trippel, R. Otto, M. Weidemüller, R. Wester and W. L. Hase, *J. Phys. Chem. Lett.*, 2010, **1**, 2747–2752.
- <sup>12</sup> J. Mikosch, J. Zhang, S. Trippel, C. Eichhorn, R. Otto, R. Sun, W. A. de Jong, M. Weidemüller, W. L. Hase and R. Wester, *J. Am. Chem. Soc.*, 2013, **135**, 4250–4259.
- <sup>13</sup> J. Zhang, J. Xie and W. L. Hase, *J. Phys. Chem. A*, 2015, **119**, 12517–12525.
- <sup>14</sup> E. Carrascosa, T. Michaelsen, M. Stei, B. Bastian, J. Meyer, J. Mikosch and R. Wester, *J. Phys. Chem. A*, 2016, **120**, 4711–4719.
- <sup>15</sup> I. Szabó and G. Czako, *J. Phys. Chem. A*, 2015, **119**, 3134–3140.
- <sup>16</sup> B. J. Braams and J. M. Bowman, *Int. Rev. Phys. Chem.*, 2009, **28**, 577–606.
- <sup>17</sup> J. M. Bowman, G. Czako and B. Fu, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8094–8111.
- <sup>18</sup> R. Conte, P. L. Houston, and J. M. Bowman, *J. Chem. Phys.*, 2014, **140**, 151101.
- <sup>19</sup> R. Conte, C. Qu and J. M. Bowman, *J. Chem. Theory Comput.*, 2015, **11**, 1631–1638.
- <sup>20</sup> Y. Wang and J. M. Bowman, *Phys. Chem. Chem. Phys.*, 2016, **18**, 24057–24062.
- <sup>21</sup> T. B. Adler, G. Knizia and H.-J. Werner, *J. Chem. Phys.*, 2007, **127**, 221106.
- <sup>22</sup> T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- <sup>23</sup> K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2003, **119**, 11113–11123.
- <sup>24</sup> G. Czako and J. M. Bowman, *J. Phys. Chem. A*, 2014, **118**, 2839–2864.
- <sup>25</sup> MOLPRO, version 2015.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz and others, see <http://www.molpro.net>.
- <sup>26</sup> W. L. Hase, *Encyclopedia of Computational Chemistry* (Wiley, New York, 1998), p. 399–407.
- <sup>27</sup> R. Conte, P. L. Houston and J. M. Bowman, *J. Phys. Chem. A*, 2014, **118**, 7742–7757.



- <sup>28</sup> P. L. Houston, R. Conte and J. M. Bowman, *J. Phys. Chem. A*, 2014, **118**, 7758–7775.
- <sup>29</sup> R. Conte, P. L. Houston and J. M. Bowman, *J. Phys. Chem. A*, 2015, **119**, 12304–12317.
- <sup>30</sup> G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334–338.
- <sup>31</sup> G. Czako and J. M. Bowman, *J. Chem. Phys.*, 2009, **131**, 244302.
- <sup>32</sup> L. Bonnet and J. Espinosa-García, *J. Chem. Phys.*, 2010, **133**, 164108.
- <sup>33</sup> G. Czako, *J. Phys. Chem. A*, 2012, **116**, 7467–7473.
- <sup>34</sup> R. Sun, C. J. Davda, J. Zhang and W. L. Hase, *Phys. Chem. Chem. Phys.*, 2015, **17**, 2589–2597.
- <sup>35</sup> I. Szabó, H. Telekes and G. Czako, *J. Chem. Phys.*, 2015, **142**, 244301.
- <sup>36</sup> I. Szabó and G. Czako, *J. Chem. Phys.*, 2016, **145**, 134303.
- <sup>37</sup> Y. Wang, H. Song, I. Szabó, G. Czako, H. Guo and M. Yang, *J. Phys. Chem. Lett.*, 2016, **7**, 3322–3327.

