# High-Level-Optimized Stationary Points for the $F^{-}(H_2O) + CH_3I$ System: Proposing a New Water-Induced Double-Inversion Pathway

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Supporting Information

ABSTRACT: We report 29 stationary points for the  $F^{-}(H_2O) + CH_3I$  reaction obtained by using the high-level explicitly correlated CCSD(T)-F12b method with the aug-ccpVDZ basis set for the determination of the benchmark structures and frequencies and the aug-cc-pVQZ basis for energy computations. The stationary points characterize the monohydrated F-- and OH--induced Walden-inversion pathways and, for the first time, the front-side attack and F<sup>-</sup>-induced double-inversion mechanisms leading to CH<sub>3</sub>F with retention as well as the novel H2O-induced doubleinversion retention pathway producing CH<sub>3</sub>OH. Hydration effectively increases the relative energies of the stationary



points, but the monohydrated inversion pathways are still barrierless, whereas the front-side attack and double-inversion barrier heights are around 30 and 20 kcal/mol, respectively.

# I. INTRODUCTION

Halide + methyl-halide bimolecular nucleophilic substitution  $(S_N 2)$  reactions are of fundamental importance in chemistry. Besides the investigation of gas-phase S<sub>N</sub>2 reactions, the hydration effects, which always increase the energy barriers because of the greater solvation energy of the reactants than the intermediate states, are also very important and frequently studied both experimentally and theoretically.<sup>1-34</sup> Although it seems to be insufficient to consider only one water molecule describing these effects, a recent study<sup>26</sup> assumes that in the case of the hydrated  $F^-$  + CH<sub>3</sub>I system even if several water molecules are bonded to the F<sup>-</sup> reactant, the reaction will proceed only with one water molecule presumably due to stereochemical reasons. Similar conclusion was drawn by Davico for the S<sub>N</sub>2 reactions of microsolvated fluoride ions with methylhalides.<sup>27</sup> The author wrote based on MP2-optimized geometries that the nucleophile needs to be desolvated partially before nucleophilic attack can occur, causing larger activation energy and much slower reaction rates.

There are a couple of direct dynamics simulations which suppose several stationary points on the basis of trajectory animations for the  $F^{-}(H_2O) + CH_3I$  reaction,<sup>26,28,29</sup> but only those structures were optimized which are parts of the traditional Walden-inversion pathway. This characterization of the Walden-inversion stationary points was carried out by Zhang and co-workers<sup>30</sup> who performed geometry optimizations with the MP2 method and density functional theory (DFT) and reported CCSD(T) energies based on the MP2 geometries.

One of the goals of the present study is to confirm the suppositions of the stationary-point-characters of the structures taken from trajectory pathways. For the first time in the case of a microhydrated S<sub>N</sub>2 reaction, the high-level explicitly correlated CCSD(T)-F12b method is to be employed to obtain benchmark structures and energies for the stationary points, thereby proposing definitive predictions for possible reaction pathways of the title reaction. Furthermore, it is important to mention that the water molecule may become a reactant in the  $F^{-}(H_2O)$  + CH<sub>3</sub>I S<sub>N</sub>2 reaction, and so methanol can be produced. Such a reaction pathway proceeding with Walden inversion involving a OH<sup>-</sup> obtained by a proton transfer between H<sub>2</sub>O and F<sup>-</sup> has already been described by Yang and co-workers.<sup>28</sup> We assume now that there is another possible mechanism which can result in methanol formation via a new water-induced doubleinversion pathway producing methanol with retention of configuration, which will be investigated in the present work. In section II we describe the computational details, and the results are presented and discussed in section III. The paper ends with summary and conclusions in section IV.

# **II. COMPUTATIONAL DETAILS**

We use the second-order Møller-Plesset perturbation theory (MP2) (ref 35) and the explicitly correlated coupled-cluster

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**Figure 1.** All the benchmark stationary-point structures (bond lengths in Å and angles in degrees) and their point-group symmetries in parentheses obtained in this work for the  $F^{-}(H_2O) + CH_3I$  system at the CCSD(T)-F12b/aug-cc-pVDZ level of theory.

singles, doubles, and perturbative triples CCSD(T)-F12b (ref 36) methods with the correlation-consistent polarized valence *n*-zeta basis sets augmented with diffuse functions denoted as augcc-pVnZ (ref 37), where n = 2(D), 3(T), and in some cases 4(Q). For the iodine atom the small-core relativistic pseudopotential (ECP28MDF), which replaces the 28 inner core electrons of iodine, and the corresponding aug-cc-pVnZ-PP basis sets are employed.<sup>38</sup> All the stationary points, reactants,

Table 1. Energies (kcal/mol) of the Stationary Points Relative to  $F^-(H_2O) + CH_3I$  Obtained at Different Levels of Theory (See Figure 1 for the Structures)

	MP2		CCSD(T)-F12b			
	AVDZ <sup>a</sup>	AVTZ <sup>b</sup>	AVDZ <sup>c</sup>	AVTZ <sup>d</sup>	AVQZ <sup>e</sup>	AVQZ + $\Delta ZPE^{f}$
$CH_3I + F^- + H_2O$	26.8	27.6	27.8	27.7	27.5	26.8
$CH_3F + I^- + H_2O$	-16.2	-15.2	-19.6	-19.5	-20.2	-19.2
$CH_3OH + I^- + HF$	-16.0	-14.8	-18.6	-18.6	-19.4	-19.9
$CH_2I^- + HF + H_2O$	50.7	50.2	46.8	46.5	46.3	42.0
$CH_3OH + I^-(HF)$	-32.4	-32.2	-35.4	-35.4	-35.8	-35.1
$CH_3OH(HF) + I^-$	-25.8	-24.7	-28.5	-28.3	-28.3	-25.8
HMIN1	0.8	1.9	1.0	1.3	1.4	1.7
HMIN2	-14.7	-14.0	-15.0	-14.7	-14.4	-13.3
HMIN2'	-14.7	-14.0	-15.0	-14.5	-14.4	-13.5
HMIN3	-14.0	-13.3	-14.4	-14.1	-13.9	-12.5
HMIN4	-13.9	-13.3	-14.4	-14.2	-14.0	-13.0
HMIN5	-13.8	-13.3	-14.3	-14.0	-13.8	-13.0
PREMIN1	-14.0	-13.3	-14.4	-14.1	-13.9	-12.8
PREMIN2	-14.0	-13.3	-14.1	-13.9	-13.7	-13.1
HTS	-13.9	-13.3	-14.2	-13.9	-13.7	-12.9
WALDENTS1	-8.0	-5.6	-8.7	-8.8	-8.8	-7.6
WALDENTS2	-3.3	-2.1	-3.9	-3.9	-3.8	-3.7
POSTMIN1	-34.3	-33.3	-37.5	-37.0	-37.2	-34.0
POSTMIN2	-34.8	-33.1	-37.3	-36.9	-37.2	-34.2
POSTMIN3	-35.5	-34.4	-38.5	-38.2	-38.5	-35.7
POSTMIN4	-46.3	-45.9	-49.0	-48.6	-48.8	-45.1
ABSMIN1	27.8	26.7	23.4	23.4	23.6	22.8
ABSMIN2	24.6	23.8	20.8	21.1	21.3	21.1
ABSMIN3	17.8	17.2	14.8	15.2	15.4	15.1
ABSMIN4	19.0	18.2	16.1	16.5	16.7	16.2
ABSTS1	23.3	22.9	23.2	23.3	23.5	22.0
ABSTS2	23.3	22.8	23.2	23.2	23.4	22.0
FSMIN	-13.6	-13.7	-14.6	-14.6	-14.5	-13.4
FSPRETS	-4.7	-4.9	-4.8	-4.7	-4.6	-4.8
FSTS1	32.2	34.1	30.0	29.7	29.7	30.7
FSTS2	33.4	35.7	31.6	31.4	31.4	32.1
DITS1	23.2	21.2	20.5	20.8	21.0	20.0
DITS2	21.2	20.5	20.5	20.8	21.1	17.5
DIMIN1	19.0	17.9	15.8	16.0	16.3	15.1
DIMIN2	20.2	19.7	19.8	20.2	20.5	18.9

<sup>a</sup>MP2/aug-cc-pVDZ energies at MP2/aug-cc-pVDZ geometries <sup>b</sup>MP2/aug-cc-pVTZ energies at MP2/aug-cc-pVTZ geometries. <sup>c</sup>CCSD(T)-F12b/aug-cc-pVDZ geometries <sup>d</sup>CCSD(T)-F12b/aug-cc-pVTZ energies at CCSD(T)-F12b/aug-cc-pVDZ geometries. <sup>e</sup>CCSD(T)-F12b/aug-cc-pVQZ energies at CCSD(T)-F12b/aug-cc-pVDZ geometries. <sup>f</sup>CCSD(T)-F12b/aug-cc-pVQZ energies. <sup>f</sup>CCSD(T)

and products are optimized at the MP2/aug-cc-pVDZ, MP2/ aug-cc-pVTZ, and CCSD(T)-F12b/aug-cc-pVDZ levels of theory and at the same levels harmonic vibrational frequency computations are performed. In some cases intrinsic reaction coordinate (IRC) computations are carried out using the MP2 method with the aug-cc-pVDZ basis set. The initial structures for optimizations are constructed based on (a) previous work,  $\frac{2^{8}-30}{2}$  (b) addition a water molecule to a nonhydrated stationary-point structure using chemical intuition, and (c) IRC computations from saddle points obtained by (a) and (b). Utilizing the benchmark CCSD(T)-F12b/aug-cc-pVDZ structures, single-point energies are computed using the CCSD(T)-F12b/aug-cc-pVTZ and CCSD(T)-F12b/aug-cc-pVQZ levels of theory. Thus, our benchmark classical relative energies are obtained as CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/ aug-cc-pVDZ and the best adiabatic energies are determined as CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-ccpVDZ + zero-point energy (ZPE) correction obtained with

CCSD(T)-F12b/aug-cc-pVDZ, where the dual-level A//B denotes single-point energies computed with level A at level-B geometries. All the ab initio computations are performed using the Molpro program package.<sup>39</sup>

# **III. RESULTS AND DISCUSSION**

We have found many stationary points for the  $F^-(H_2O) + CH_3I$ system, whose geometries with the most important structural parameters are shown in Figure 1 and their relative energies obtained at different ab initio levels of theory are presented in Table 1. All the structural parameters and the harmonic vibrational frequencies of the stationary points are given in the Supporting Information. The energies are given relative to the  $F^-(H_2O)$  complex plus  $CH_3I$ , because experimentally such hydrated complexes are usually used as reactants, when the dynamics of microhydrated  $S_N2$  reactions are studied.<sup>31–33</sup> The formation of the  $F^-(H_2O)$  complex from  $F^-$  and  $H_2O$  is an exothermic process, and our best predictions for the  $D_e$  and  $D_0$ 



Figure 2. Stationary-point structures (bond lengths in Å and angles in degrees) and relative energies (kcal/mol) along the Walden-inversion pathway of the  $F^-(H_2O) + CH_3I$  reaction. Structures are determined at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Classical (upper blue) and adiabatic (lower red) relative energies are obtained at the CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ (T)-F12b/aug-cc-pVDZ) and CCSD(T)-F12b/aug-cc-pVDZ) levels of theory, respectively.

109.6 57.7

dissociation energies of  $F^{-}(H_2O)$  are 27.5 and 26.8 kcal/mol, respectively. The point-group symmetries of the stationarypoint structures are either  $C_1$  or  $C_s$ , as indicated in Figure 1. As Table 1 shows, the MP2 relative energies with the aug-cc-pVDZ (DZ) and aug-cc-pVTZ (TZ) basis sets usually agree within 1 kcal/mol, except for FSTS1, FSTS2, and DITS1, where the DZ and TZ energies differ by 1.9, 2.3, and 2.0 kcal/mol, respectively. In the case of the explicitly correlated CCSD(T)-F12b method the basis-set convergence is much better; here, the DZ and TZ results agree within 0.5 kcal/mol, and the above-mentioned substantial FSTS1, FSTS2, and DITS1 deviations reduce to only 0.3, 0.2, and, 0.3 kcal/mol, respectively. The agreement between the CCSD(T)-F12b TZ and QZ energies is usually even better, showing that most of the QZ benchmark data are converged within 0.3 kcal/mol. Comparison of the MP2 and CCSD(T)-F12b relative energies reveals in some cases large deviations of around 4 kcal/mol, such as for the product channels, POSTMINs, FSTS1, and FSTS2. ZPE corrections are significant, especially for some of the product-like structures. For example, the ZPE effects are around 3 kcal/mol for the hydrated postreaction ion-dipole complexes (POSTMIN1, POSTMIN2, POSTMIN3, and POSTMIN4), and the correction decreases the endothermicity of the CH<sub>2</sub>I<sup>-</sup> + HF + H<sub>2</sub>O channel by 4.3 kcal/mol. For most of the other stationary points including prereaction complexes and various transition states, the ZPE effects are around 1 kcal/mol.

On the basis of chemical intuition and prior work<sup>28–30</sup> we construct reaction energy diagrams using the stationary points found in this study. In some cases, stationary points are definitely missing from the reaction pathways because it is not possible to find all of the stationary points for such a complex system. Nevertheless, using the stationary points shown in Figure 1 we can confirm and benchmark previously known reaction mechanisms and can predict novel pathways of the title reaction.

Figure 2 shows the Walden-inversion pathway of the  $F^{-}(H_2O) + CH_3I S_N 2$  reaction, which was previously described by Zhang et al.<sup>29,30</sup> using MP2 and DFT methods. Similar to the nonhydrated  $F^{-} + CH_3I$  system, hydrogen-bonded (HMIN2) and ion-dipole (PREMIN1) complexes are seen in the entrance

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channel of the monohydrated reaction. These two minima are connected via a small barrier (HTS), again similar to the nonhydrated reaction (for nonhydrated results, see Figure 2b of ref 30 or Figure 1 of ref 40). These prereaction stationary points are below the reactants by 13-14 kcal/mol, whereas the corresponding energies are deeper by 3-5 kcal/mol for the nonhydrated case. The reaction proceeds forward via a Waldeninversion transition state (WALDENTS1), whose classical (adiabatic) energy is below the  $F^{-}(H_2O) + CH_3I$  reactants by 8.8(7.6) kcal/mol. This submerged barrier is higher than the corresponding nonhydrated analogue by about 8 kcal/mol,<sup>4</sup> showing that hydration of the reactant ion is stronger than that of the transition states. In the exit channel three complexes are found with similar energies below the reactants by 37-39 and 34–36 kcal/mol without and with ZPE correction, respectively. These hydrated minima are about 18 kcal/mol higher than the nonhydrated FCH<sub>3</sub>…I<sup>-</sup> complex,<sup>40</sup> in accord with the fact that the hydration energy of  $F^-$  is significantly larger than that of  $I^-$ . The reaction provides  $I^- + CH_3F + H_2O$  products with classical (adiabatic) exothermicity of -20.2 (-19.2) kcal/mol. Considering the structures of the stationary points, we find that HMIN2 has no symmetry because the  $C_s$  structure has somewhat higher energy. The H-bonded CH bond length is slightly stretched by 0.014 Å in comparison with the CH bond length in the CH<sub>3</sub>I molecule, but this bond is somewhat shorter than in the case of the hydrogen-bonded complex without water. The CH…F distance is longer here than in the nonhydrated case. The H<sub>2</sub>O molecule is connected to F<sup>-</sup> with a single H-bond, causing a slightly stretched OH distance (1.030 Å) relative to the non-Hbonded OH bond length (0.958 Å) of the H<sub>2</sub>O unit. Zhang and co-workers<sup>30</sup> found a somewhat similar HMIN2(im1) structure at the MP2/PP/d level (HMIN2 is im1 in ref 30) with similar OH…F and CH…F distances of 1.444(1.485) and 1.823(1.731) Å but with a very different H–F–C angle of  $75.1^{\circ}(109.9^{\circ})$ . Note that we have found several other H-bonded prereaction complexes (HMIN3, HMIN4, HMIN5 as seen in Figure 1), whose  $F^- \cdots HCH_2I$  units have similar structures to the corresponding part of HMIN2; the differences are in the orientations of the F…H-bonded H<sub>2</sub>O. If we consider the



Figure 3. Stationary-point structures (bond lengths in Å and angles in degrees) and relative energies (kcal/mol) along a OH<sup>-</sup>-induced Waldeninversion pathway of the  $F^-(H_2O) + CH_3I$  reaction. Structures are determined at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Classical (upper blue) and adiabatic (lower red) relative energies are obtained at the CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ +  $\Delta$ ZPE(CCSD(T)-F12b/aug-cc-pVDZ) levels of theory, respectively.



Figure 4. Stationary-point structures (bond lengths in Å and angles in degrees) and relative energies (kcal/mol) along possible front-side attack retention pathways of the  $F^{-}(H_2O) + CH_3I$  reaction. Structures are determined at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Classical (upper blue) and adiabatic (lower red) relative energies are obtained at the CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ have cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ have composed at the CCSD(T)-F12b/aug-c

benchmark F–C–I angles in the row of HTS (157.2°), PREMIN1 (176.0°), and WALDENTS1 (178.7°), we can see that these angles come increasingly closer to 180° and the F– C–I atoms are almost collinear at the WALDENTS1. (Of course, in the nonhydrated case both the ion–dipole complex and the Walden-inversion TS have  $C_{3\nu}$  symmetry and thus collinear fluorine, carbon, and iodine atoms.) The above benchmark angles are in good agreement with the DFT results of Zhang and co-workers,<sup>30</sup> who reported F–C–I angles of 158.2°, 175.4°, and 178.9°, respectively. The C–F distances of HTS, PREMIN1, and WALDENTS1 decrease as 2.760(2.744), 2.657(2.604), and 2.003(2.125) Å, respectively, while the C–I bond lengths increase as 2.171(2.211), 2.181(2.235), and 2.512(2.495) Å, in order, in qualitative agreement with the previous DFT results shown in parentheses. Comparing the above distances to the corresponding nonhydrated values<sup>40</sup> we find that the C-F distances are longer and the C-I distances are shorter for the monohydrated HTS and PREMIN1 structures, whereas the reverse is seen for WALDENTS1. The H<sub>2</sub>O molecule binds to the F atom with a single H-bond, where the OH…F distances are 1.409, 1.405, and 1.557 Å and the H-F-C angles are 77.6°, 81.1°, and 105.8° for HTS, PREMIN1, and WALDENTS1, respectively, whereas the corresponding DFT values are 1.437, 1.442, and 1.550 Å and 81.4°, 87.4°, and 113.8°. The postsubstitution complexes have cyclic structures, where H<sub>2</sub>O binds to CH<sub>3</sub>F and I<sup>-</sup> as well. In POSTMIN1 and POSTMIN2 the OH…I bond lengths are 2.729(2.774) and 2.719(2.701) Å, respectively, while OH…F distances are

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Figure 5. Stationary-point structures (bond lengths in Å and angles in degrees) and relative energies (kcal/mol) along a  $F^-$ -induced double-inversion pathway of the  $F^-(H_2O) + CH_3I$  reaction. Structures are determined at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Classical (upper blue) and adiabatic (lower red) relative energies are obtained at the CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ) levels of theory, respectively. The yellow H atom helps to follow the first inversion of the double-inversion mechanism.

2.152(2.234) and 2.312(2.969) Å, in order, where the DFT results of Zhang and co-workers<sup>30</sup> are given in parentheses for comparison. At POSTMIN3 the OH…I bond is the shortest with a length of 2.601(2.632) Å; however, unlike the case of the other two complexes, here the F–C–I atoms are close to a collinear arrangement, and therefore an OH…F bond cannot form, but a CH…O bond with a length of 2.635 Å is formed. The C…I distances are 3.946(4.035), 3.760(4.058), and 3.727(3.906) Å for POSTMIN1, POSTMIN2, and POST-MIN3, respectively, whereas the C…I separation is 3.618 Å in the nonhydrated case.<sup>40</sup>

Figure 3 describes an inversion process with OH<sup>-</sup> which is qualitatively the same as Yang at al. found using DFT computations.<sup>28</sup> Here, after the formation of a hydrogenbonded complex (HMIN2) F<sup>-</sup> abstracts a proton from H<sub>2</sub>O while the O atom binds to the C atom forming a Waldeninversion transition state (WALDENTS2) with almost collinear O-C-I arrangement. Then, the hydroxide inverts the methyliodide forming a postsubstitution complex (POSTMIN4), where I<sup>-</sup> connects to the HO group of the methanol unit while HF connects to the O atom with a H-bond. Then POSTMIN4 can dissociate into the  $CH_3OH + HF + I^-$  products (-19.9) or CH<sub>3</sub>OH…HF + I<sup>-</sup> (-25.8) or CH<sub>3</sub>OH + FH…I<sup>-</sup> (-35.1) complexes can be formed. The reaction is exothermic in every case, as the 0 K reaction enthalpies, in kcal/mol, show in parentheses. We can compare the POSTMIN4 geometry to that of the CH<sub>3</sub>OH…HF complex. In POSTMIN4 the O-C bond is somewhat stronger because of the iodine-hydrogen interaction. This interaction has other consequences as well, such as the O-H bond length is longer and the H–O–C angle is smaller in the methanol unit of POSTMIN4 relative to the corresponding values in CH<sub>3</sub>OH…HF. If we consider the H–O distance, where the hydrogen is that which bonds to the fluorine, this distance is shorter in the POSTMIN4 because of the hydrogen-iodine interaction. This has the consequence that the H-F bond is weaker in the POSTMIN4, so the bond length is longer than in

the CH<sub>3</sub>OH…HF complex. POSTMIN4 is also comparable with the postreaction complex of the OH<sup>-</sup> + CH<sub>3</sub>I S<sub>N</sub>2 reaction (PostHMIN in ref 41), where I<sup>-</sup> also binds to the OH group as seen in POSTMIN4. The I…HO distance, the I–H–O angle, and the O–C distance are 2.448 Å, 162.1°, and 1.415 Å in the nine-atom system and 2.584 Å, 163.4°, and 1.410 Å in the sevenatom system, respectively.

Unlike the inversion pathways, retention mechanisms of the monohydrated F<sup>-</sup> + CH<sub>3</sub>I S<sub>N</sub>2 reaction were unknown prior to the present study. Here, we find stationary points along the front-side attack pathway of the title reaction resulting in  $I^-$  +  $CH_3F + H_2O$  products with retention of the initial methyl-halide configuration as shown in Figure 4. In the entrance channel a front-side complex (FSMIN) can form, where F<sup>-</sup> connects to the I atom of the CH<sub>3</sub>I unit with almost collinear F-I-C arrangement, while  $H_2O$  binds to  $F^-$  with a single H-bond. FSMIN is below the reactants by 14.5(13.4) kcal/mol without(with) ZPE correction, similar to HMIN2, 14.4(13.3)kcal/mol, whereas in the nonhydrated case FSMIN and HMIN have larger depths of 22.1(22.2) and 19.3(19.3) kcal/mol,<sup>40</sup> respectively. The fact that the water molecule weakens the interaction between F<sup>-</sup> and CH<sub>3</sub>I is in accord with the increase of the F<sup>-</sup>…I distance from 2.306 to 2.426 Å upon monohydration. We also find another prereaction stationary point (FSPRETS), where  $F^{-}$ ... $H_2O$  connects to the I atom with O and the F–I–C angle is far from being collinear. FSPRETS is just below the reactants by 4.6(4.8) kcal/mol, in accord with the longer F<sup>-</sup>…I distance (3.398 Å) relative to that of FSMIN (2.426 Å). The front-side attack pathway goes through a high barrier of either 29.7(30.7) or 31.4(32.1) kcal/mol corresponding to transitions states FSTS1 or FSTS2, respectively. In both cases the FICH<sub>3</sub><sup>-</sup> unit is similar, where the C–I bond is significantly stretched from 2.1 to 2.7 Å and F connects to C with a bond length of 1.9 Å and a F–C–I angle of about 80°. This structure of the monohydrated FICH<sub>3</sub><sup>-</sup> unit is semiquantitatively the same as the geometry of the nonhydrated FSTS.<sup>40</sup> The water



Figure 6. Stationary-point structures (bond lengths in Å and angles in degrees) and relative energies (kcal/mol) along a water-induced double-inversion pathway of the  $F^-(H_2O) + CH_3I$  reaction. Structures are determined at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. Classical (upper blue) and adiabatic (lower red) relative energies are obtained at the CCSD(T)-F12b/aug-cc-pVQZ//CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ (T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVDZ) levels of theory, respectively. Note that the dissociation of  $F^-(H_2O)$  occurs in the vicinity of CH<sub>3</sub>I; thus, this step may demand less energy than Figure 6 shows. The yellow H atom helps to follow the first inversion of the water-induced double-inversion mechanism.

molecule binds to the F atom with a single H-bond for both FSTS1 and FSTS2; however, unlike the case of FSTS2, for FSTS1 another weak "H-bond" is present between H<sub>2</sub>O and I forming a ring-like structure and decreasing the classical-(adiabatic) energy by 1.7(1.4) kcal/mol relative to FSTS2. Due to the fact that the hydration of the reactant F<sup>-</sup> is stronger than that of the FICH<sub>3</sub><sup>-</sup> unit, the front-side attack barrier of the monohydrated F<sup>-</sup> + CH<sub>3</sub>I S<sub>N</sub>2 reaction is about 10 kcal/mol higher than the corresponding barrier height of the nonhydrated system.

Besides the front-side attack retention mechanism, in 2015 our trajectory simulations for the gas-phase F<sup>-</sup> + CH<sub>3</sub>Cl S<sub>N</sub>2 reaction revealed a new pathway for S<sub>N</sub>2 reactions, called double inversion, which results in retention of configuration.<sup>42</sup> Later we found this mechanism for the nonhydrated  $F^-$  + CH<sub>3</sub>I system as well.<sup>40</sup> Furthermore, the QM/MM computations of Wang and co-workers identified double inversion in aqueous solution for both the  $F^-$  + CH<sub>3</sub>Cl (ref 34) and  $F^-$  + CH<sub>3</sub>I (ref 43) reactions. In the present study we investigate the double inversion in the monohydrated F<sup>-</sup> + CH<sub>3</sub>I system. As seen in Figure 5 first a Hbonded complex forms (HMIN3) and F<sup>-</sup> abstracts a proton from CH<sub>3</sub>I. Then the HF fragment may move around the CH<sub>2</sub>I<sup>-</sup> unit forming a DITS1-like transition state, where a new CH bond forms while the configuration is being inverted around the carbon center. This is the first inversion of the double-inversion process, which may be followed by a substitution event via the usual Walden-inversion pathway resulting in  $I^- + CH_3F + H_2O$ products with retention of configuration. The above-described double-inversion mechanism is similar to the pathway revealed by trajectory simulations,<sup>40,42</sup> but it is not an IRC pathway as shown in Figure 5. As also shown in Figure 5, IRC connects DITS1 to ABSMIN3 and HMIN1; thus, the IRC pathway may describe how the first inversion occurs while the CH bond reforms. However, prior to ABSMIN3, F<sup>-</sup> should abstract a proton from the opposite side of the methyl group and the HF

unit should move around to form a new CH bond from the other side, thereby inverting the configuration around the carbon center. This rearrangement of the HF fragment is not described by the present IRC; thus, double inversion may not be an IRC pathway, as Hase and co-workers<sup>44</sup> found in the case of the nonhydrated F<sup>-</sup> + CH<sub>3</sub>I system. Nevertheless, DITS1 may play a central role in the double-inversion process as previous analytic-PES-based<sup>40,42</sup> as well as direct dynamics<sup>44</sup> simulations showed for nonhydrated  $S_N 2$  reactions. The structure of the FH…CH<sub>2</sub>I<sup>-</sup> unit of the monohydrated DITS1 is almost the same as the nonhydrated analogue<sup>40</sup> with C…HF distances of 1.801 and 1.835 Å, respectively. Hydration effectively increases the barrier height; thus, the classical(adiabatic) double-inversion barriers are 21.0(20.0) and 9.1(7.0) kcal/mol with and without<sup>40</sup> H<sub>2</sub>O, respectively. Nevertheless, the monohydrated DITS1 is still below the front-side attack TSs (~30 kcal/mol), showing that double inversion is the lowest energy retention pathway of the  $F^{-}(H_2O) + CH_3I S_N^2$  reaction.

In microhydrated S<sub>N</sub>2 reactions H<sub>2</sub>O can serve as a reactant as in the OH<sup>-</sup> inversion mechanism shown in Figure 3. In this study we investigate a possible double-inversion mechanism, where H<sub>2</sub>O and then OH<sup>-</sup> participate in the first and second inversions as shown in Figure 6. First a H-bonded prereaction complex (HMIN1) is formed which is preceded by the dissociation of the  $F^{-}(H_2O)$  complex, resulting in a structure where F<sup>-</sup> connects to the CH<sub>3</sub>I unit with a single H-bond and  $H_2O$  is on the other side of  $CH_3I$ . Then while  $F^-$  abstracts a proton and the resulting HF fragment moves toward the I atom, from the opposite side H<sub>2</sub>O donates a proton forming a CH bond and inverting the configuration around the carbon center via a transition state called DITS2 (Figure 6). At DITS2 the CH bond length is 1.297 Å, longer by 0.211 Å than the CH bond in the CH<sub>3</sub>I molecule, and the breaking OH bond length is 1.322 Å, stretched by 0.363 Å relative to the bond length in the  $H_2O$ molecule. IRC computations show that the H<sub>2</sub>O-induced

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inversion occurs as DIMIN1  $\rightarrow$  DITS2  $\rightarrow$  DIMIN2 as shown in Figure 6. However, stationary points are certainly involved before this IRC step, because even at DIMIN1 the configuration is already inverted. After this H2O-induced inversion a FH··· ICH<sub>3</sub>...OH<sup>-</sup>-type structure forms, which eventually leads to WaldenTS2 via several stationary points involving DIMIN2, ABSTS1, ABSTS2, etc. Then, as in the OH<sup>-</sup> S<sub>N</sub>2 inversion process, a Walden inversion occurs where OH<sup>-</sup> replaces I<sup>-</sup>, forming CH<sub>3</sub>OH with double inversion, i.e., retention of configuration. Here it may be possible that the FH…ICH<sub>3</sub>… OH<sup>-</sup> structure dissociates into HF + ICH<sub>3</sub>...OH<sup>-</sup> before WaldenTS2 is formed and the substitution occurs via an I- $CH_3-OH^{-}$  Walden-inversion transition state. However, the dissociation of ABSTS2 requires about 8.5 kcal/mol energy; thus, it is more likely that the reaction proceeds in the vicinity of the HF unit. Considering the classical(adiabatic) DITS2 barrier height of 21.1(17.5) kcal/mol and the other high-energy stationary points likely involved in this process, we find that this water-induced double inversion may have similar activation energy compared to that for the F<sup>-</sup> double inversion shown in Figure 5. By comparing the mechanisms of the  $F^-$  and  $H_2O$ induced double inversions, the latter may be favored, because during the F<sup>-</sup>-induced inversion the HF fragment has to move around the CH2I- unit to form a new CH bond from the opposite side, thereby causing inversion, whereas in the waterinduced case the proton abstraction by F- and, from the opposite side, the H<sub>2</sub>O-induced proton donation may occur simultaneously, possibly involving DITS1 besides DITS2, without any moving-around motions. Of course the detailed understanding of these newly proposed mechanisms requires further ab initio and dynamical investigations, which may reveal additional stationary points and the role of these structures in the dynamics.

Finally we note that besides the  $S_N^2$  channels proton abstraction (proton transfer between F<sup>-</sup> and CH<sub>3</sub>I in the presence of a water molecule) can occur in the title reaction leading to CH<sub>2</sub>I<sup>-</sup> + HF + H<sub>2</sub>O, which is an endothermic process ( $\Delta H_0 = 42.0 \text{ kcal/mol}$ ). Even in the nonhydrated F<sup>-</sup> + CH<sub>3</sub>I reaction many stationary points characterize the proton-transfer pathway;<sup>40,44</sup> therefore, the detailed mapping of the monohydrated abstraction pathways is out of the scope of the present study. Nevertheless, some of the stationary points shown in Figure 1, e.g., ABSMIN1, ABSMIN2, ABSMIN3, ABSMIN4, ABSTS1, and ABSTS2, are certainly involved in the protontransfer process. A possible monohydrated proton-transfer pathway is shown in a very recent DFT study.<sup>45</sup>

### **IV. SUMMARY AND CONCLUSIONS**

We have performed high-level ab initio computations for characterizing the stationary points of the complex potential energy surface of the  $F^-(H_2O) + CH_3I$  reaction. Our study follows some previous work,<sup>28–30</sup> but provides novel results from both quantitative and qualitative points of view. Quantitatively, following previous DFT and MP2 computations,<sup>28–30</sup> we report the first explicitly correlated CCSD(T)-F12b structures, harmonic vibrational frequencies, and relative energies for the  $F^-(H_2O) + CH_3I$  system, thereby providing benchmark data for future theoretical and experimental investigations. Qualitatively, several new stationary points and reaction pathways are found in the present study. Besides the previously known Walden-inversion and OH<sup>-</sup> inversion mechanisms, we describe three new retention pathways via front-side attack and double inversion resulting in I<sup>-</sup> + CH<sub>3</sub>F +

 $H_2O$  products and water-induced double inversion leading to I<sup>-</sup> +  $CH_3OH$  + HF with retention of configuration around the carbon atom.

The present study is of course just a first step toward a better understanding of (mono/micro)-hydrated  $S_N 2$  reactions, and future work is desired in the following directions: (1) searching for additional stationary points, which may allow constructing complete IRC pathways for all the mechanisms, (2) performing dynamics simulations to confirm the proposed retention mechanisms, (3) performing experiments to directly study the collision dynamics of  $F^-(H_2O)$  with  $CH_3I$ , (4) studying the new retention pathways with more than one water molecules, and (5) comparing the monohydrated dynamics and mechanisms with reactions in aqueous solution.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b10630.

Stationary-point geometries, frequencies as well as absolute, relative, and zero-point energies computed by MP2 and CCSD(T)-F12b with different basis sets (PDF)

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#### Notes

The authors declare no competing financial interest.

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