

Supporting Information for “Theoretical Study on the Gas-Phase  
 $S_N2$  Reaction of Microhydrated Fluoride with Methyl Fluoride”

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Six pages, details of dynamics calculation, two tables of calculated rate constants and KIEs, two figures of calculated geometry.

## I . The details of dynamics calculations

The low-level reaction path was calculated at the MP2/aug-cc-pVDZ level. The dual-level correction was based on the TS and the ion-dipole complexes on the reactant side ( $\text{CH}_3\text{F}\cdots\text{F}^- (\text{H}_2\text{O})$ ) and on the product side ( $\text{CH}_3\text{F}(\text{H}_2\text{O}) \cdots\text{F}^-$ ). The high-level energies were based on the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ results. The moment of inertias and vibrational frequencies of stationary points were obtained using the low-level values without further corrections. On the product side, the ion dipole complex geometry was taken from the last point of reaction-path calculation. The SIL-1 interpolated correction scheme was applied in the dual-level calculation using the CCSD(T)/aug-cc-pVTZ energies along the low-level reaction path geometry to estimate the barrier width. The reaction coordinates at half-height width of the high-level classical barrier were estimated  $-1.20$  bohr (reactant side) and  $1.83$  bohr (product side), respectively.

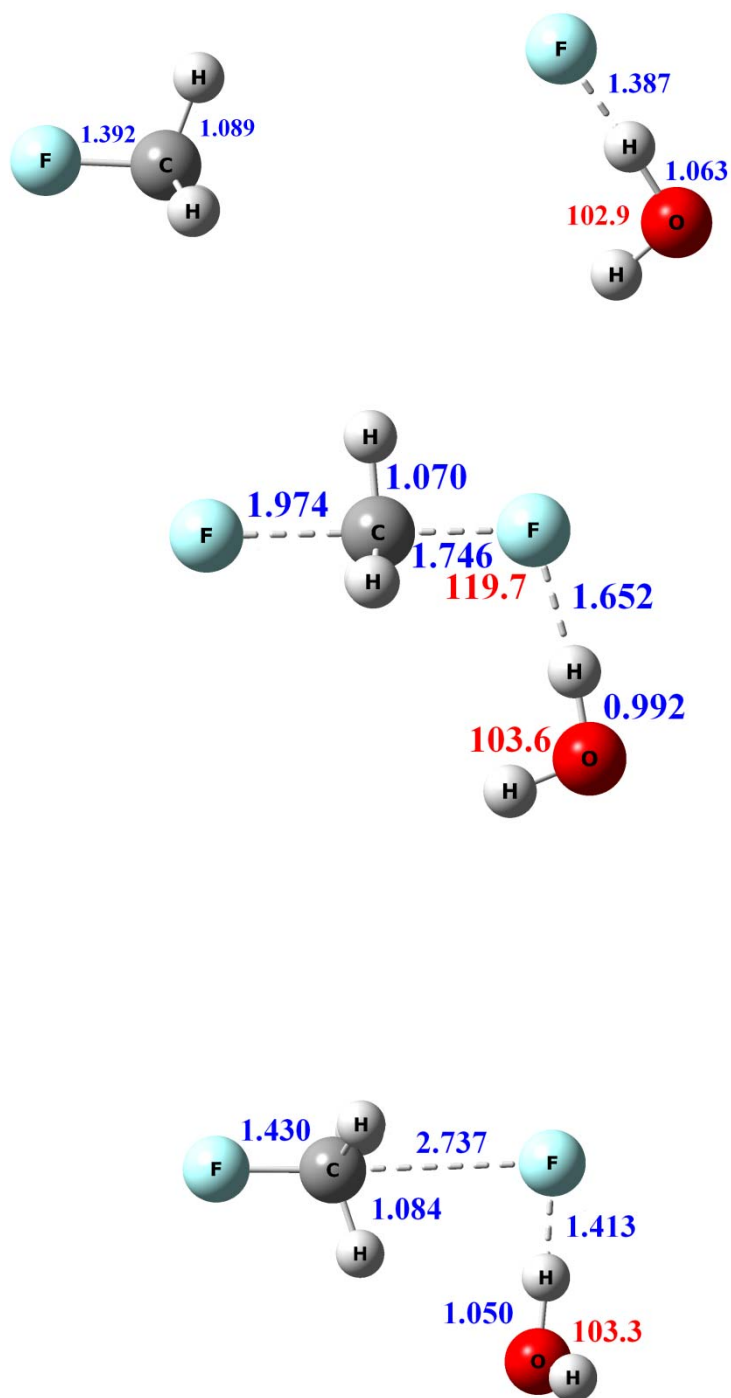
Table S1 The calculated Constants (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of  $\text{CH}_3\text{F}+\text{F}^-(\text{H}_2\text{O})$  and  $\text{CH}_3\text{F}+\text{F}^-$  reactions

T (K)	$\text{CH}_3\text{F}+\text{F}^-(\text{H}_2\text{O})$		$\text{CH}_3\text{F}+\text{F}^-$	
	TST	CVT/SCT	TST	CVT/SCT
50	6.73(-64) <sup>a</sup>	1.45(-48)	9.82(-8)	9.82(-8)
60	1.69(-55)	1.62(-44)	1.53(-8)	1.53(-8)
70	1.70(-49)	1.55(-41)	4.02(-9)	4.02(-9)
80	5.46(-45)	3.30(-39)	1.46(-9)	1.46(-9)
90	1.77(-41)	2.67(-37)	6.64(-10)	6.64(-10)
100	1.15(-38)	1.15(-35)	3.52(-10)	3.52(-10)
125	1.41(-33)	3.22(-32)	1.13(-10)	1.13(-10)
150	3.70(-30)	2.10(-29)	5.35(-11)	5.34(-11)
175	1.09(-27)	3.39(-27)	3.19(-11)	3.19(-11)
200	8.11(-26)	1.84(-25)	2.21(-11)	2.21(-11)
250	3.80(-23)	6.19(-23)	1.38(-11)	1.38(-11)
300	2.57(-21)	3.57(-21)	1.07(-11)	1.07(-11)
400	6.22(-19)	7.43(-19)	8.62(-12)	8.62(-12)
500	2.03(-17)	2.26(-17)	8.38(-12)	8.38(-12)

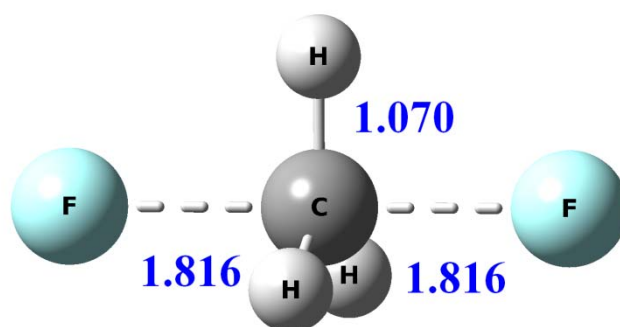
<sup>a</sup>6.73(-64) means  $6.73 \times 10^{-64}$

Table S2 Calculated KIEs of  $\text{CH}_3\text{F}+\text{F}^-$  reaction by the TST method

T (K)	KIE( $\text{CD}_3$ )	KIE( $^{13}\text{C}$ )	KIE( $^{14}\text{C}$ )
50	0.24	1.35	1.74
60	0.31	1.29	1.61
70	0.38	1.25	1.52
80	0.45	1.22	1.46
90	0.50	1.20	1.41
100	0.55	1.18	1.37
125	0.65	1.15	1.30
150	0.72	1.13	1.26
175	0.77	1.11	1.22
200	0.81	1.10	1.20
250	0.86	1.08	1.16
300	0.89	1.07	1.14
400	0.92	1.06	1.11
500	0.93	1.05	1.09



**Figure S1.** Calculated structures, from top: reactant, transition state, and ion-dipole complex by B3LYP/aug-cc-pVTZ methods. Bond lengths are in Å (blue) and bond angles in degrees (red).



**Figure S2.** Calculated structure ( $C_{3v}$ ) of the gas-phase  $S_N2$  transition state of the  $CH_3F + F^-$  reaction by MP2/aug-cc-pVTZ methods.