Rotational Mode Specificity in the F⁻ + CH₃I (v = 0, JK) SN₂ and Proton-Transfer Reactions

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1. INTRODUCTION

Mode-specific excitation of the reactant allows controlling the outcome of a chemical reaction, which has always been a major goal of chemistry. Following many vibrational mode-specific experimental and theoretical studies of polyatomic reaction dynamics,¹−¹⁰ the concept of “rotational mode specificity” was introduced in 2014 in the case of the Cl + CHD₃ → HCl + CD₃ reaction.¹¹ CHD₃ is a symmetric top, which can be characterized by the total rotational angular momentum quantum number J and its projection K to the body-fixed axis. Different J values, that is, 0, ±1, ..., ±J, correspond to different rotational “modes” (states), such as tumbling and spinning rotations considering the two limiting cases of K = 0 and K = ±J, respectively. On the one hand, it has long been well known that the excitation of different vibrational modes, such as stretching, bending, and torsion, may have significantly different effects on chemical reactivity. On the other hand, the rotational mode specific investigations do not have such a long history; nevertheless, several experimental and theoretical studies have recently started to uncover the effect of the initial rotational state on the reactivity of polyatomic reactions.¹²⁻²³ Rotational mode specificity was studied for the (H₂O⁺ + H⁺/D⁺)¹²,¹³ H/F/Cl + H₂O¹⁴,¹⁵ F/Cl/OH + CH₄¹⁶−¹⁹ and (H/C/O + CHD⁺¹¹,²⁰−²² F⁻ + CH₃F/CH₃Cl²³) reactions involving asymmetric, spherical, and symmetric top polyatomic reactants, respectively. In the present study, we focus on the reaction of another symmetric top molecule CH₃I with F⁻, thus the most relevant previous systems are H/Cl/O + CHD₃ and F⁻ + CH₃F/CH₃Cl. The former H-abstraction reactions are enhanced by rotational excitation,¹¹,²² except H + CHD₃, where rotational effects up to J = 2 were found to be negligible.²⁰ For Cl/O + CHD₃, significant rotational mode specificity was observed as tumbling and spinning rotations showed substantial and modest enhancement factors, respectively.¹¹,²² In the case of the F⁻ + CH₃F/CH₃Cl SN₂ reactions, rotational excitation hinders the reactivity with significant K dependence.²³ Unlike for Cl/O + CHD⁺,¹¹,²² for the F⁻ + CH₃Cl SN₂ reaction tumbling rotation has a less significant effect than spinning, whereas for F⁻ + CH₃F both rotational modes effectively hinder depending on collision energy as well.²³

The F⁻ + CH₃I reaction has recently been investigated by several theoretical and crossed-beam experimental studies.²⁴−³⁵ In 2017, we reported a high-level full-dimensional analytical ab initio potential energy surface (PES) for the F⁻ + CH₃I system, allowing efficient dynamics investigations of both the SN₂ and proton-transfer channels.²⁷ In 2018, our joint theoretical–experiment study showed that symmetric CH
stretching excitation is a spectator mode in the $S_N2$ reaction, whereas it enhances the proton-transfer channel. Later, we reported detailed vibrational mode specific simulations for the $F^+ + CH_3I$ $S_N2$ and proton-transfer reactions, which were followed by additional crossed-beam measurements by the Wester group. Rotational mode specific investigations have not been reported for the title reaction before; thus, the present study aims to be the first step toward this direction. Moreover, our previous study on the $JK$-specific dynamics computations for the $F^+ + CH_3F/CH_3Cl$ reactions considered the $S_N2$ channel only, whereas the present work reports rotational mode specific simulations for both the $S_N2$ and proton-transfer channels of the $F^+ + CH_3I$ reaction.

2. COMPUTATIONAL DETAILS

Reaction dynamics simulations are performed for the $F^+ + CH_3I (v = 0, JK)$ reaction using the quasi-classical trajectory method and a high-level full-dimensional ab initio PES taken from ref 27. Standard normal mode sampling is employed to prepare the initial quasi-classical ground vibrational state $(v = 0)$, and the $JK$ rotational states are set using the procedure described in detail in ref 23. In brief, the length of the classical angular momentum vector of the $CH_3I$ molecule is set to $[J(J + 1)]^{\frac{1}{2}}$ in atomic units and its direction is randomly sampled while keeping its projection to a principal axis (C$−I$ bond assuming $C_{3v}$ symmetry) fixed at the value of $K$. The interested reader can check eqs 1–6 of ref 23 to find the mathematical formulas used in the present implementation. Trajectories are run at collision energies ($E_{coll}$) of 1, 4, 7, 10, 15, 20, and 30 kcal/mol. The initial distance of the reactants is $(x^2 + b^2)^{\frac{1}{2}}$, where $x = 40$ bohr ($E_{coll} = 1$ kcal/mol), 30 bohr ($E_{coll} = 4$ kcal/mol), and 20 bohr ($E_{coll} \geq 7$ kcal/mol), the orientation of $CH_3I$ is randomly sampled, and the impact parameter $(b)$ is scanned from 0 to $b_{max}$ with a step size of 1 bohr. $b_{max}$ values of 30, 20, 18, 15, 14, 12, and 10 bohr are used at the above collision energies, respectively. For each $JK$ initial state, 1000 (5000) trajectories are computed at each $b$ at $E_{coll}$ of 1, 4, 7, and 10 kcal/mol, (15, 20, and 30 kcal/mol). In this study, we consider $J$ values of 0, 2, 4, 6, 8, 12, and 16 with $K = 0$ and $J$. Trajectories are propagated using a time step of 0.0726 fs until the maximum of the internuclear distances becomes one bohr larger than the initial one. Cross sections are obtained using a $b$-weighted numerical integration of the reaction probabilities over $b$ from 0 to $b_{max}$ without applying any zero-point energy constraint.

3. RESULTS AND DISCUSSION

The pathways of the $S_N2$ and proton-transfer channels of the $F^+ + CH_3I$ reaction leading to $I^− + CH_3F$ and $HF + CH_3I^-$, respectively, are shown in Figure 1. The Walden-inversion $S_N2$ channel is highly exothermic and goes through several submerged minima and transition states. The lowest-energy configuration of the entrance channel is a halogen-bonded front-side complex ($H_2Cl^-·F^-$), which steers the reactants away from the reactive configurations, thereby making the $S_N2$ reaction indirect. There are two different $S_N2$ retention pathways via DITS (double inversion) and FSTS (front-side attack), as can be seen in Figure 1, but these mechanisms have less relevance to the present study. The proton-transfer channel is endothermic with several stationary points between the reactant and product asymptotes. The tumbling $(K = 0)$ and spinning $(K = J)$ rotational modes and the initial rotational states of $CH_3I$ considered in the present study are also shown in Figure 1. The $A$ and $B$ rotational constants of the prolate-type $CH_3I$ molecule are 5.24 and 0.25 cm$^−1$, that is, 0.0150 and 0.0007 kcal/mol, respectively, which result in very low tumbling rotational energy levels such as $E(J, K = 0) = B(J + 1)$ and relatively higher spinning levels with energies of $E(J, K = J) = A^2 + BJ$. Thus, as seen in Figure 1, the $K = 0$ levels up to $J = 16$ spans an energy range from 0.00 to 0.20 kcal/mol, whereas the $K = J$ levels go up to 3.85 kcal/mol for $J = 0−16$. The $JK$-dependent excitation functions (cross sections as a function of $E_{coll}$) for the $S_N2$ and proton-transfer channels are shown in Figures 2 and 3, respectively. The $S_N2$ cross sections are large and sharply decrease with increasing $E_{coll}$, as expected in the case of a barrier-less exothermic reaction. Rotational excitation hinders the $S_N2$ channel especially at low collision energies, as seen in Figure 2. The inhibition is modest for tumbling rotation, that is, less than 5% for $J$ up to 8 and about 10–15% for $J = 12$–16, whereas it is more significant in the case of a spinning reactant, that is, around 5–10% for $J = 4$ and can be 25% for $J = 16$ depending on $E_{coll}$. These rotational inhibition effects are very similar to those previously found for the $F^+ + CH_3Cl$ $S_N2$ reaction. The picture is quite different for the proton-transfer (proton-abstraction) channel of the $F^+ + CH_3I$ reaction, as shown in Figure 3. The proton-transfer cross sections increase with collision energy and significant rotational enhancement is found upon spinning excitation, whereas tumbling rotation has a negligible effect (few % inhibition, which is comparable with statistical uncertainty) on proton abstraction. At $E_{coll} = 15$ kcal/mol, the $K = J$ rotational excitations increase the cross sections by factors of 1.1 and 2.2 for $J = 8$ and 16, respectively, and the enhancement factors decrease with increasing $E_{coll}$, as shown in Figure 3.

To get deeper insights into the rotational mode specific dynamics of the title reaction, opacity functions (reaction probabilities as a function of $b$) as well as scattering angle, initial attack angle, and product relative translational energy distributions are also computed at $E_{coll} = 15$ kcal/mol and presented in Figures 4 and 5 for the $S_N2$ and proton-transfer channels, respectively. The initial attack angle is defined as the angle between the center of the mass velocity vector of $CH_3I$ and the CI vector at the beginning of the trajectories. Attack
Figure 2. JK dependence of the cross sections and their ratios for the $F^- + CH_3I(v = 0, JK) \rightarrow I^- + CH_3F$ reaction as a function of collision energy.

Figure 3. JK dependence of the cross sections and their ratios for the $F^- + CH_3I(v = 0, JK) \rightarrow HF + CH_2I$ proton-transfer reaction as a function of collision energy.

Figure 4. JK dependence of the opacity functions ($P(b)$) as well as of the normalized scattering angle ($\theta$), initial attack angle ($\alpha$), and product relative translational energy ($E_{trans}$) distributions at a collision energy of 15 kcal/mol for the $F^- + CH_3I(v = 0, JK) \rightarrow I^- + CH_3F$ reaction.
angle $0^\circ$ corresponds to the approach of the iodine side, whereas $180^\circ$ describes the methyl-attack pathways.

For the $J = 0$ initial state, the $\text{S}_2\text{N}_2$ reaction probability is about 39% at $b = 0$, decreases almost linearly with increasing $b$ and vanishes at $b = 14$, as shown in Figure 4. On the one hand, tumbling rotational excitations ($K = 0$) have a modest effect on the opacity functions, which slightly decrease the reaction probabilities without affecting the shape of the opacity curves. On the other hand, spinning rotation ($K = J$) significantly decreases the reaction probabilities especially at small $b$ values. For example, at $b = 0$, the $f = 8$ and 16 reaction probabilities are only 31 and 29% for $K = J$, respectively, whereas the corresponding $K = 0$ values are 39 and 37%. The scattering angle distributions are backward-forward symmetric, isotropic in the $\cos(\theta)$ range from $-0.8$ and $+0.8$ (indicating significant complex-forming indirect trajectories), and peak both in the backward (direct rebound) and forward (direct stripping) directions. The initial attack angle distributions clearly favor the backside (methyl-side) attack and the reactivity decreases as the attack angle goes from $180$ to $0^\circ$ as expected for an $\text{S}_2\text{N}_2$ reaction. However, it is important to note that the reactivity corresponding to the $0-90^\circ$ (front-side) attack angle range is not negligible (about 25% of the total reactivity), indicating again nontraditional indirect dynamics. Significant $JK$ dependence is not found for the scattering and attack angle distributions, except for some decrease of the backward scattering upon spinning excitations, in accordance with the decreasing $\text{S}_2\text{N}_2$ reaction probabilities at small impact parameters. Product relative translational energy distributions are broad and rather cold, peaking at the lowest energies supporting the indirect nature of the $\text{S}_2\text{N}_2$ reaction. Tumbling rotation does not affect these distributions significantly; however, spinning excitations clearly shift the distributions toward higher product relative translational energies making the reaction more direct. A similar conclusion about the indirect–direct nature was previously found for the $\text{F}^- + \text{CH}_3\text{Cl}$ $\text{S}_2\text{N}_2$ reaction based on the analysis of the integration time.$^{23}$

The proton-transfer reaction opacity functions are nearly constant in the $b = 0-6$ bohr range and then decrease reaching $b_{\text{max}}$ values around 13 bohr, as shown in Figure 5. Tumbling rotational excitation has a negligible effect on the reaction probabilities, whereas spinning excitation significantly increases the reactivity especially at large $b$ values, although the $b_{\text{max}}$ value is not affected. Scattering angle distributions are backward-forward symmetric without significant $JK$-depend-
ence, similar to the S$_{n2}$ channel. Attack angle distributions are rather isotropic with some preference for the methyl-side attack, and again, the rotational dependence is within the level of statistical uncertainty. Product relative translational energy distributions range between 0 and 15 kcal/mol (Figure 5), which is significantly colder than those of the S$_{n2}$ channel spanning the 0–50 kcal/mol energy range (Figure 4). This is expected, because the S$_{n2}$ reaction is highly exothermic, whereas proton-transfer is endothermic. The $J = 0$ proton-transfer translational energy distribution peaks at about 3 kcal/mol without any significant $J$ dependence in the case of $K = 0$. However, for $K = J$ the peak shifts toward 5 kcal/mol and the distributions become hotter as $J$ increases, indicating that the proton transfer becomes more direct upon excitation of the spinning rotation.

On the basis of the above-described results, we propose the following explanation for the rotational mode specificity in the title reaction. Considering the magnitudes of the rotational constants of the CH$_3$I molecule ($A = 5.24$ cm$^{-1}$ and $B = 0.25$ cm$^{-1}$), one can see that the spinning rotation about the $a$ principal axis (C–I bond) is $A/B = I_a/I_b = 21$ times faster than tumbling rotation corresponding to the same $J$ because the rotational constants are inversely proportional to the components of the principal moment of inertia ($I_a$ and $I_b$), and the angular velocity is $\Gamma^{-1}J$. The large angular velocity in the case of the spinning rotation about the C–I axis induces a substantial centrifugal force which facilitates C–H bond cleavage, thereby enhancing the proton-abstractation channel, on the expense of substitution. Furthermore, the centrifugal force hinders long-lived complex formation by breaking H-bonds; thus, making the S$_{n2}$ process more direct and less orientation specific tumbling ($K = 0$) and spinning ($K = J$) rotational states up to $J = 16$. The reaction dynamics computations utilize our recently developed high-level analytical ab initio PES$^{27}$, which describes both the S$_{n2}$ and proton-transfer channels of the title reaction. Rotational excitations hinder the S$_{n2}$ reaction more and more significantly with increasing $J$, especially for spinning rotation and low or modest collision energies. The proton-transfer channel is virtually not affected upon tumbling excitations however substantially enhanced by spinning rotation. Scattering and initial attack angle distributions do not show significant JK-dependence, whereas product relative translation energy distributions become hotter and hotter as $J$ increases with $K = J$, showing that spinning excitations make the reactions more direct. The present findings for the S$_{n2}$ channel are similar to those of our previous study on the F$^-+$ CH$_3$I S$_{n2}$ reaction, where we suggested that tumbling and spinning rotations may hinder orientation and complex formation, respectively, thereby suppressing the substitution reactivity.$^{23}$ Here, for the first time, we study the proton-transfer channel as well, which helps to complete the picture. We propose that the centrifugal force induced by fast spinning rotation about the C–I bond axis facilitate C–H bond breaking, thereby enhancing the proton-abstractation channel, on the expense of the S$_{n2}$ reactivity. Thus, spinning excitations hinder the S$_{n2}$ channel because of breaking H-bonds (low $E_{coll}$) and C–H bond (modest $E_{coll}$) where the abstraction channel opens. The situation of the mainly indirect F$^-+$ CH$_3$I reaction is quite different from the case of the previously studied Cl/O + CHD$_3$ direct H-abstractation reactions, where tumbling rotation enhanced the reactivity because of enlarging the reactive attack angle range, whereas spinning excitations had less significant enhancement effects.$^{11,22}$ We hope that following the JK-specific measurements for the Cl + CHD$_3$ reaction,$^{31}$ rotational mode specific experiments will be carried out for the title reaction in the near future.

4. SUMMARY AND CONCLUSIONS

We have performed rotational mode specific quasi-classical simulations for the F$^-+$ CH$_3$I reaction considering several different tumbling ($K = 0$) and spinning ($K = J$) rotational states up to $J = 16$. The reaction dynamics computations utilize our recently developed high-level analytical ab initio PES$^{27}$, which describes both the S$_{n2}$ and proton-transfer channels of the title reaction. Rotational excitations hinder the S$_{n2}$ reaction more and more significantly with increasing $J$, especially for spinning rotation and low or modest collision energies. The proton-transfer channel is virtually not affected upon tumbling excitations however substantially enhanced by spinning rotation. Scattering and initial attack angle distributions do not show significant JK-dependence, whereas product relative translation energy distributions become hotter and hotter as $J$ increases with $K = J$, showing that spinning excitations make the reactions more direct. The present findings for the S$_{n2}$ channel are similar to those of our previous study on the F$^-+$ CH$_3$I S$_{n2}$ reaction, where we suggested that tumbling and spinning rotations may hinder orientation and complex formation, respectively, thereby suppressing the substitution reactivity.$^{23}$ Here, for the first time, we study the proton-transfer channel as well, which helps to complete the picture. We propose that the centrifugal force induced by fast spinning rotation about the C–I bond axis facilitate C–H bond breaking, thereby enhancing the proton-abstractation channel, on the expense of the S$_{n2}$ reactivity. Thus, spinning excitations hinder the S$_{n2}$ channel because of breaking H-bonds (low $E_{coll}$) and C–H bond (modest $E_{coll}$) where the abstraction channel opens. The situation of the mainly indirect F$^-+$ CH$_3$I reaction is quite different from the case of the previously studied Cl/O + CHD$_3$ direct H-abstractation reactions, where tumbling rotation enhanced the reactivity because of enlarging the reactive attack angle range, whereas spinning excitations had less significant enhancement effects.$^{11,22}$ We hope that following the JK-specific measurements for the Cl + CHD$_3$ reaction,$^{31}$ rotational mode specific experiments will be carried out for the title reaction in the near future.

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Notes

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