Rotational Mode Specificity in the $\text{F}^- + \text{CH}_3\text{Y}$ [$\text{Y} = \text{F} \text{ and Cl}$] $\text{S}_\text{N}2$ Reactions

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**ABSTRACT:** More than 12 million quasiclassical trajectories are computed for the $\text{F}^- + \text{CH}_3\text{Y}(v = 0, JK)$ [$\text{Y} = \text{F} \text{ and Cl}$] $\text{S}_\text{N}2$ reactions using full-dimensional ab initio analytical potential energy surfaces. The initial ($J, K = 0$) and ($J, K = J$) [$J = 0, 2, 4, 6, 8$] rotational state specific cross sections are obtained at different collision energies ($E_\text{coll}$) in the 1–20 kcal mol$^{-1}$ range, and the scattering angle and initial attack angle distributions as well as the mechanism-specific opacity functions are reported at $E_\text{coll} = 10$ kcal mol$^{-1}$. The tumbling rotation ($K = 0$) inhibits the $\text{F}^- + \text{CH}_3\text{F}$ reaction by a factor of 3 for $J = 8$ at $E_\text{coll} = 10$ kcal mol$^{-1}$. This tumbling rotational effect becomes smaller at low and high $E_\text{coll}$ and the tumbling motion affects the cross sections of $\text{F}^- + \text{CH}_3\text{Cl}$ by only a few percent. The spinning rotation ($K = J$) hinders both reactions by factors in the 1.3–1.7 range for $J = 8$ at low $E_\text{coll}$ whereas slight promotion is found as the $E_\text{coll}$ increases. The tumbling rotation may counteract the attractive ion-dipole forces, and the spinning motion hinders the complex formation, thereby decreasing the reactivity.

I. INTRODUCTION

Chemical reactivity depends on how the total energy of the systems is distributed among the translational, vibrational, and rotational degrees of freedom. For atom + diatom reactions both reactant’s vibration and rotation can be characterized by single quantum numbers, $v$ and $J$, respectively. Vibrational excitations usually promote the atom + diatom reactions, whereas the $J$ dependence of the reactivity can be more complicated showing promotion or inhibition depending on the magnitude of $J$ and the type of the system. For polyatomic reactants the picture is even more complicated. An N-atomic nonlinear molecule has $3N - 6$ vibrational modes, and the excitation of different modes can have different effects on the reactivity. Furthermore, symmetric or asymmetric polyatomic rotors are characterized by the total rotational angular momentum quantum number $J$ and its projections, $K$ (symmetric top) or $K_C$ (asymmetric top), to the body-fixed axes. The vibrational mode specificity in polyatomic systems has been widely studied; however, little is known about rotational mode specificity, that is, $K$-dependent, effects on chemical reactivity. Nevertheless, there are a couple of recent experimental and theoretical studies on rotational mode specificity. In 2012 rotational enhancement effects were observed experimentally for the $\text{H}_2\text{O}^+(J, K_\rho, K_\phi) + \text{D}_2$ reaction, and later in 2014, ab initio computations showed that rotational excitation facilitates the reorientation of $\text{H}_2\text{O}^+$, thereby enhancing the reactivity. The $JK$-dependent reactivity of $\text{CH}_3\text{F}$ with $\text{H}, \text{Cl}$, and $\text{O}^\text{(P)}$ was studied in 2014. For $\text{H} + \text{CH}_3\text{D}(v = 0) \rightarrow \text{H}_2 + \text{CD}_3$ a seven-dimensional time-dependent wave packet study found that rotational excitation up to $J = 2$ has negligible effect on the reactivity. For the $\text{Cl} + \text{CHD}_3(v_1 = 1) \rightarrow \text{HCl} + \text{CD}_3$ reaction a joint crossed-beam, quantum dynamics, and quasiclassical trajectory (QCT) study showed that tumbling rotation ($K = 0$) significantly increases the reactivity, whereas the spinning rotation ($K = J$) about the CH axis gives smaller enhancement factors. Similar behavior was recently found by QCT calculations for the $\text{O}^\text{(P)} + \text{CH}_3\text{D}(v_1 = 0, 1) \rightarrow \text{OH} + \text{CD}_3$ reactions. In 2015 Liu and co-workers showed that the total reactivity (integral cross sections) of the $\text{Cl} + \text{CH}_3\text{D}(v_1 = 1)$ reaction depends on the initial $JK$ states, but rotational excitations have virtually no effect on the angular distributions (differential cross sections).

A previous QCT study reported the same findings for the $\text{O}^\text{(P)} + \text{CHD}_3$ reaction. In 2015 the rotational effects in the $\text{OH} + \text{CH}_3 \rightarrow \text{O} + \text{CH}_4$ reaction were studied by Wang and co-workers using six- and seven-dimensional quantum models. It was shown, albeit not $JK$ specifically, that the rotational excitation of $\text{CH}_3$ (and $\text{OH}$) significantly hinders the reactivity. The polyatomic reactant in the $\text{X}^- + \text{CH}_3\text{Y}$ [$\text{X} = \text{F, Cl, Br, I}$] bimolecular nucleophilic substitution ($\text{S}_\text{N}2$) reactions is a symmetric top, like the above-discussed $\text{CH}_3\text{F}$ molecule. Although the dynamics of $\text{S}_\text{N}2$ reactions have been widely studied, to the best of our knowledge, the $JK$ rotational state specific reactivity of $\text{S}_\text{N}2$ reactions has not been investigated yet. We recently developed global full-dimensional...
analytical potential energy surfaces (PESs) for the F$^-$ + CH$_3$F (ref 24) and F$^-$ + CH$_3$Cl (ref 25) reactions by fitting high-level coupled-cluster-based ab initio energy points. In the present study we investigate the $JK$-dependence of the reactivity of the F$^-$ + CH$_3$Y($v = 0$, $JK$) $[$Y = F and Cl$]$ SN$_2$ reactions by performing QCT calculations on the analytical PESs. Although both CHD$_3$ and CH$_3$Y are symmetric tops, CHD$_3$ is an oblate-type rotor with rotational constants $A = 3.29$ and $C = 2.64$ cm$^{-1}$, whereas CH$_3$Y is a prolate top with $A = 5.25/5.27$ and $B = 0.86/0.44$ cm$^{-1}$ for Y = F/Cl. The X + CHD$_3$ $[$X = H, Cl, O(3P)$]$ reactions are endothermic with substantial barriers, whereas the SN$_2$ reactions F$^-$ + CH$_3$F and F$^-$ + CH$_3$Cl are isoenergetic with a slightly negative barrier and highly exothermic with negative barrier, respectively, as seen in Figure 1. Furthermore, in the SN$_2$ reactions one can expect significant stereodynamical effects due to the relatively strong long-range attractive ion-dipole forces, whereas in the X + CHD$_3$ reactions only weak van der Waals interactions can occur. Thus, the very different rotational constants and PES shapes indicate that the state-specific rotational excitations may have different effects on the dynamics of the X + CHD$_3$ and F$^-$ + CH$_3$Y reactions. In Section II we describe the quasiclassical initial JK-specific rotational mode sampling and give the details of the QCT calculations. In Section III we present the JK-dependent QCT results for the F$^-$ + CH$_3$Y($v = 0$, $JK$) S$_0$2 reactions and compare the rotational effects for two different leaving groups, Y = F and Cl. The paper ends with summary and conclusions in Section IV.

II. METHODS

QCT computations are performed for the F$^-$ + CH$_3$F and F$^-$ + CH$_3$Cl reactions using the recently developed full-dimensional analytical ab initio PESs. According to the standard QCT methodology, the vibrational energy of the polyatomic reactants is set to the zero-point energy (ZPE) by random distribution of the harmonic ground state ($v = 0$) mode-specific vibrational energy in the phase space of each normal mode. The initial rotational quantum numbers ($JK$) for the CH$_3$F and CH$_3$Cl reactants are set following the procedure described in detail below.

A. Rotational Mode Sampling. If the rigid-rotor approximation is assumed, the CH$_3$F and CH$_3$Cl molecules are prolate-type symmetric tops characterized by the $J$ and $K$ rotational quantum numbers. The length of the classical angular momentum vector ($j$) is related to the $J$ quantum number according to (in atomic units)

$$j = \sqrt{J(J+1)}$$

where $j$ satisfies the following relation:

$$j = \sqrt{j_x^2 + j_y^2 + j_z^2}$$

In principal axis system (PAS) the $j_x^{PAS}$ component of the angular momentum vector corresponds to the $K$ projection quantum number:

$$j_x^{PAS} = K$$

(Note that this convention applies only to prolate-type symmetric tops.) To perform computations with fixed $J$ and $K$, the two remaining components of $j$ should be sampled employing the following expressions:

$$j_y^{PAS} = (j^2 - K^2)^{1/2} \sin 2\pi R$$

and

$$j_z^{PAS} = (j^2 - K^2)^{1/2} \cos 2\pi R$$

where $R \in [0, 1]$ is a real random number. Note that eqs 3, 4, and 5 satisfy eq 2. The $j^{PAS}$ vector is then transformed to the space-fixed Cartesian coordinate system, defined during the QCT computation, using the similarity transformation matrix obtained by the diagonalization of the moment of inertia tensor (I). The desired angular momentum $j$ is tuned by the modification of the velocity vectors for each atom.
\[ \mathbf{v} = \mathbf{v}_0 + \Omega \times \mathbf{q}_i \]  

where \( \Omega = \Gamma^{-1}(j - j_0) \), and \( \mathbf{q}_i \) stands for the Cartesian coordinates of the \( i \)th atom, and \( j_0 \) denotes the preexisting angular momentum.

**B. Computational Details.** The initial orientation of CH\(_3\)Y is randomly selected and the distance of its center of mass from F\(^{-} \) is \((x^2 + b^2)^{1/2}\), where \( b \) is the impact parameter scanned with a step size of \( \Delta b \) from 0 to \( b_{\text{max}} \), where \( b_{\text{max}} \) is the maximum value of \( b \), where reactive substitution event can occur. The settings for \( x, \Delta b, \) and \( b_{\text{max}} \) values at each collision energy \( (E_{\text{coll}}) \) are shown in Table 1. Trajectories are run at \( E_{\text{coll}} = 1, 2, 4, 7, 10, 15, 20 \) kcal mol\(^{-1}\). The trajectories in this study are propagated using a \( 0.0726 \) fs time step, and each trajectory is stopped when the \( \Delta \) value is increased from 0 to 8.

**III. RESULTS AND DISCUSSION**

The \( J \) initial rotational state specific integral cross sections and the rotational enhancement factors for the \( \text{F}^{-} + \text{CH}_3\text{Y}(r = 0, JK) \) \([Y = \text{F} \text{and C}]\) \( \text{S}_0 \text{S}_2 \) reactions in the \( 1-20 \) kcal mol\(^{-1}\) \( E_{\text{coll}} \) range are shown in Figure 2. The excitation function (cross sections vs \( E_{\text{coll}} \)) of the \( \text{F}^{-} + \text{CH}_3\text{Cl} \) reaction decreases rapidly with increasing \( E_{\text{coll}} \) as expected for an exothermic barrierless reaction. The cross sections of the \( \text{F}^{-} + \text{CH}_3\text{F} \) reaction are approximately an order of magnitude smaller and decrease at low \( E_{\text{coll}} \) have a minimum at \( E_{\text{coll}} \approx 4-7 \) kcal mol\(^{-1}\), and become nearly constant above \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\). In the present study the cross sections are investigated in the \( 1-20 \) kcal mol\(^{-1}\) \( E_{\text{coll}} \) range, but as shown in ref 24 the \( J = 0 \) excitation function of \( \text{F}^{-} + \text{CH}_3\text{F} \) remains almost constant up to \( E_{\text{coll}} = 80 \) kcal mol\(^{-1}\). The shape of the \( J > 0 \) excitation functions at \( E_{\text{coll}} \) larger than 20 kcal mol\(^{-1}\) may be different. Furthermore, we should note that at low \( E_{\text{coll}} \) the ZPE violation effect on the absolute cross sections is significant for \( \text{F}^{-} + \text{CH}_3\text{F} \), as discussed in ref 24.

The \( (JK)/(J = 0) \) cross-section ratios show that rotational excitations usually inhibit the reactivity in the \( 1-20 \) kcal mol\(^{-1}\) \( E_{\text{coll}} \) range for both the \( \text{F}^{-} + \text{CH}_3\text{F} \) and \( \text{F}^{-} + \text{CH}_3\text{Cl} \) reactions. As Figure 2 shows, the inhibition factors depend sensitively on the \( J \) and \( K \) rotational quantum numbers, \( E_{\text{coll}} \) and the leaving group. For \( \text{F}^{-} + \text{CH}_3\text{F} \), the \( K = 0 \) rotational effects are small (~10%) at low and high \( E_{\text{coll}} \) values, whereas the inhibition is substantial around \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\). At \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\) the \( K = 0 \) rotational enhancement factors are 0.93, 0.74, 0.56, and 0.35 for \( J = 2, 4, 6, \) and 8, respectively. For the \( K = J \) states the rotational enhancement factors are in the 0.6–1.0 range for \( E_{\text{coll}} \) up to \( \sim 10 \) kcal mol\(^{-1}\) and tend to 1.0–1.1 as \( E_{\text{coll}} \) increases. The picture is quite different for the \( \text{F}^{-} + \text{CH}_3\text{Cl} \) reaction. For the \( \text{CH}_3\text{Cl}(J, K = 0) \) enhancement factors are the most significant at low \( E_{\text{coll}} \) especially at \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\), and increase in the \( E_{\text{coll}} \) range of \( 10-20 \) kcal mol\(^{-1}\). At \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\), the enhancement factors are 0.97, 0.89, 0.79, and 0.75 for \( J = 2, 4, 6, \) and 8, respectively, whereas the corresponding values at \( E_{\text{coll}} = 20 \) kcal mol\(^{-1}\) are 1.03, 1.00, 0.94, and 0.90. As seen, at \( E_{\text{coll}} = 20 \) kcal mol\(^{-1}\) the \( (JK) = (22) \) state starts to promote the reaction, and we expect promotion for higher \( J \) values as well, as we further increase \( E_{\text{coll}} \). To check this, we have computed the \( (JK) = (44) \) enhancement factor at \( E_{\text{coll}} = 30 \) kcal mol\(^{-1}\), which turned out 1.06.

Before we move forward, let us consider the “rotational modes” of the CH\(_3\)Y molecule. The \( (J > 0, K = 0) \) case means that the classical angular momentum vector is perpendicular to the CY axis (\( C_4 \) axis); thus, this motion corresponds to tumbling rotation. For \( (J > 0, K = J) \), the angular momentum vector is parallel with the CY axis, resulting in spinning rotation about the CY bond. Since CH\(_3\)Y is a prolate top, where \( A > B = C \), the angular velocity of the spinning rotation is significantly larger than that of the tumbling rotation.

To get deeper insight into the mechanistic origin of the rotational effects we computed the product angular and initial attack angle distributions as well as the opacity functions (reaction probabilities vs \( b \)) at \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\), as shown in Figures 3 and 4, respectively. \( (E_{\text{coll}} = 10 \) kcal mol\(^{-1}\) is chosen, because the rotational effects are the most significant at this \( E_{\text{coll}} \). The attack angle (\( \alpha \)) is defined at the beginning of each trajectory as the angle between the velocity vector of CH\(_3\)Y and the CY vector. Thus, \( \alpha = 0^\circ \) corresponds to frontal attack, and \( \alpha = 180^\circ \) means backside attack initial orientation. On the basis of the integration time, we could distinguish between direct and indirect trajectories as shown for the opacity functions in Figure 4.

For F\(^-\) + CH\(_3\)F, the \( J = 0 \) angular distributions show the dominance of backward scattering, which indicates the preference of the direct rebound mechanism at \( E_{\text{coll}} = 10 \) kcal mol\(^{-1}\), as shown in Figure 4. As we increase \( J \) while \( K = 0 \), the

<table>
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<th>( E_{\text{coll}} )</th>
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Table 1. Settings for the Initial Distance of the Reactants and Impact Parameter Scans (in bohr) and the Total Number of Trajectories at Each Collision Energy (in kcal mol\(^{-1}\)) and Each JK Rotational State

"The initial distance of the reactants is \((x^2 + b^2)^{1/2}\), where \( b = 0, \Delta b, 2\Delta b, \cdots, b_{\text{max}} \) and \( N_{\text{int}} = (b_{\text{max}}/\Delta b + 1) \times 5000 \)."
angular distributions become more isotropic (Figure 3), which indicates that the indirect mechanisms dominate at high \( J \). This is confirmed by the direct vs indirect \( (J = 8, K = 0) \) reaction probabilities shown in Figure 4. If \( K = J \), the shift from direct to indirect mechanism is less significant; thus, the angular distributions show less pronounced \( J \) dependence. The \( J = 0 \) attack angle distributions show the preference of backside attack, whereas the \( (J > 0, K = 0) \) distributions show that the rotational excitation hinders the backside attack reactivity, while virtually not affecting the frontal attack reactivity. This suggests that the tumbling rotation counteracts the orientation effects, thereby decreasing the reactivity of the \( \text{F}^- + \text{CH}_3\text{F} \) reaction by a factor of 3 at \( E_{\text{coll}} = 10 \text{ kcal mol}^{-1} \). At lower and higher \( E_{\text{coll}} \) the \( K = 0 \) rotational effects are smaller (Figure 2). This may be because at low \( E_{\text{coll}} \) the reaction is mainly indirect even at \( J = 0 \) and at high \( E_{\text{coll}} \) the reaction is so direct and fast that the slow tumbling rotation cannot divert the trajectories from their reaction path. In the \( K = J \) case, the spinning rotation does not significantly affect the attack angle distributions. However, at low \( E_{\text{coll}} \) in the 1–4 kcal mol\(^{-1}\) range, the rotational effects are found to be larger for \( K = J \) than for \( K = 0 \). This may be explained by the fact that the relatively fast spinning rotation can inhibit the indirect substitutions by hindering the complex formations, which is not significantly affected by the slow tumbling motion.

In the case of the \( \text{F}^- + \text{CH}_3\text{Cl} \) reaction the rotational effects are less significant than those for \( \text{F}^- + \text{CH}_3\text{F} \). For \( K = 0 \), the rotational inhibition is almost negligible, and the scattering angle and attack angle distributions are virtually not affected by rotational excitations. The \( J = 0 \) and \( (J = 8, K = 0) \) direct and indirect mechanism-specific opacity functions are also very similar. This shows that the tumbling rotation does not have any significant effect on the dynamics of the \( \text{F}^- + \text{CH}_3\text{Cl} \) reaction, whereas substantial inhibition was found for the \( \text{F}^- + \text{CH}_3\text{F} \) reaction at \( E_{\text{coll}} = 10 \text{ kcal mol}^{-1} \). This may be explained by the fact that the attractive forces are stronger in \( \text{F}^- + \text{CH}_3\text{Cl} \) than in \( \text{F}^- + \text{CH}_3\text{F} \); thus, the tumbling rotation cannot counteract the steering effects for the former system. The potential profile shown in Figure 1 supports this statement, since the entrance-channel well is \( \sim2–3 \) kcal mol\(^{-1}\) deeper for \( \text{F}^- + \text{CH}_3\text{Cl} \). The \( K = J \) rotational excitations inhibit the \( \text{F}^- + \text{CH}_3\text{Cl} \) reaction and the effects are similar to those in \( \text{F}^- + \text{CH}_3\text{F} \), as shown in Figure 2. The opacity functions reveal that the \( \text{F}^- + \text{CH}_3\text{Cl} \) reaction becomes more direct upon the excitation of the spinning rotation. Thus, the spinning rotational motion hinders the indirect reaction paths and makes most of the indirect trajectories nonreactive or speeds up their reactivity at small impact parameters.

One may wonder whether the different tumbling rotational effects found for the two reactions at \( E_{\text{coll}} = 10 \text{ kcal mol}^{-1} \) originate from the different PESs or from the different rotational constants of the reactants. Rotational constant \( A \) is almost the same for \( \text{CH}_3\text{F} \) and \( \text{CH}_3\text{Cl} \), whereas \( B \) is 0.86 and 0.44 cm\(^{-1}\) for \( \text{CH}_3\text{F} \) and \( \text{CH}_3\text{Cl} \), respectively. This means that the spinning motion of \( \text{CH}_3\text{F} \) and \( \text{CH}_3\text{Cl} \) has similar angular velocity, whereas the tumbling rotation of \( \text{CH}_3\text{F} \) is about twice as fast as that of \( \text{CH}_3\text{Cl} \). Does this explain the rotational effects? To address this question we performed QCT computations for
the $F^- + CH_3F'$ reaction using the PES of $F^- + CH_3F$ and setting the mass of $F'$ to 35.5 amu. The opacity functions of the $F^- + CH_3F'$ reaction at $E_{\text{coll}} = 10$ kcal mol$^{-1}$ are shown in Figure 4. As seen, the overall reaction probability decreases as we increased the mass of the leaving group; however, the mechanism-specific opacity functions are rather like $F^- + CH_3F$ than $F^- + CH_3Cl$. For $F^- + CH_3F'$ the $(J = 8)/(J = 0)$ cross-section ratios are $0.34(K = 0)$ and $0.71(K = J)$, which are very similar to the corresponding values of $0.35(K = 0)$ and $0.64(K = J)$ for $F^- + CH_3F$. Thus, we can conclude that the different tumbling rotational effects found for the two reactions are caused by the different PESs and not by the different rotational speed of the two reactants.

Finally, it is interesting to contrast the rotational mode specificity in the $F^- + CH_3Y$ [$Y = F$ and $Cl$] $S_\text{N2}$ and the $X + CHD_3$ [$X = Cl$ and $O(3P)$] abstraction reactions. Unlike for the above-discussed $S_\text{N2}$ reactions, for $X + CHD_3$ rotational excitations enhance the reactivity and tumbling rotation has usually larger effects than spinning rotation. This may be explained by considering the following facts: (a) unlike $CH_3Y$, CHD$_3$ is an oblate-type rotor, which means that the tumbling rotation of CHD$_3$ is faster than the spinning about the CH axis and (b) strong attractive forces present in the entrance channel
of the $S_2$ reactions and the prereaction well is $\sim 13$–$17$ kcal mol$^{-1}$ deep involving H-bonded and ion-dipole complexes separated by barriers (Figure 1), whereas the van der Waals interactions for $X + CHD_3$ are weak resulting in a well depth of only $\sim 0.3$–$0.6$ kcal mol$^{-1}$. Thus, we may expect that that rotational motion counteracts the orientation effects in the SN2 reactions, thereby inhibiting the reactions. In $X + CHD_3$ these steering effects are less pronounced; here the rotational motion, especially if $K = 0$, enlarges the range of the reactive attack angles, thereby promoting the reaction. An alternative explanation of the different rotational effects may be related to the fact that the rotational energy can easily flow to the other degrees of freedom once the trajectory enters the deep well of the $S_2$ reactions, whereas the $X + CHD_3$ reactions are much more direct without significant energy redistribution in the entrance channel.

**IV. SUMMARY AND CONCLUSIONS**

Following the pioneering initial rotational state specific studies on the reactions of the symmetric top $CHD_3$ molecule with Cl and O(1P) atoms, we have investigated the rotational mode specificity in the $F^- + CH_3F$ and $F^- + CH_3Cl$ $S_2$ reactions. The QCT calculations utilized our recent full-dimensional ab initio analytical PESs allowing the computation of $\sim 12.5$ million trajectories, which is unprecedented for $S_2$ reactions. The initial JK-specific cross sections show that the tumbling rotation ($K = 0$) inhibits significantly the $F^- + CH_3F$ reaction at $E_{coll} \approx 10$ kcal mol$^{-1}$, whereas the tumbling rotational effects are almost negligible for the $F^- + CH_3Cl$ reaction. The spinning rotation ($K = J$) hinders both $S_2$ reactions at low $E_{coll}$ and the inhibition diminishes and even slight promotion is seen as $E_{coll}$ increases. For $F^- + CH_3F$ the $K = 0$ rotational excitations made the scattering angle distributions more isotropic at $E_{coll} = 10$ kcal mol$^{-1}$, which correlates with the dominance of the indirect mechanisms characterized by the integration time. Test computations for the artificial $F^- + CH_3F$ reaction, where the mass of $F$ is set to the mass of Cl, showed that the different PES shapes are responsible for the different rotational effects, because the change of the rotational constants of the polyatomic reactant does not significantly affect the rotational inhibition factors. We explain the rotational inhibition by considering the fact that the
tumbling rotation counteracts the orientation effects caused by ion-dipole interactions. This orientation effect is stronger in the F+ + CH3Cl reaction, which may diminish the rotational effects. The spinning rotation can hinder the complex formation, thereby reducing the reactivity.

Recent studies showed that rotational excitations, especially the tumbling rotation, promote the Cl/O + CH3D reactions.13–15 The present study shows opposite rotational effects for the F+ + CH3F/CH3Cl S22 reactions. Our detailed QCT analysis provides some insight into the mechanistic origin of the JK-specific rotational effects; however, a clear picture has not emerged that explains all the subtle features of the collision energy dependence of the JK-specific rotational enhancement/inhibition factors. The present study may inspire future experimental and theoretical work to investigate the rotational mode specificity in S22 reactions. One may study the deuteron substitution effect, which slows the spinning rotation, and/or the JK-dependent reactivity of CH3Y with different nucleophiles.

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**Notes**
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