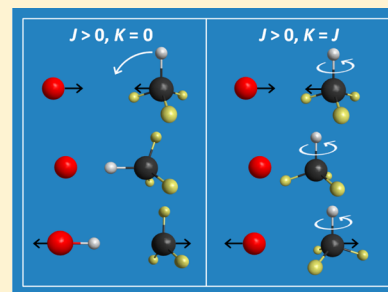


# Quasiclassical Trajectory Study of the Rotational Mode Specificity in the $O(^3P) + CHD_3(\nu_1 = 0, 1, JK) \rightarrow OH + CD_3$ Reactions

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**ABSTRACT:** Quasiclassical trajectory computations on an ab initio potential energy surface reveal that rotational excitation can significantly enhance the reactivity of the ground-state and CH stretching-excited  $O(^3P) + CHD_3(\nu_1 = 0, 1, JK) \rightarrow OH + CD_3$  reactions. The state-specific rotational effects investigated up to  $J = 8$  show that the  $K = 0$  (tumbling rotation) enhancement factors can be as large as 1.5–3.5 depending on  $J$  and the collision energy, whereas the  $K = J$  (spinning rotation about the CH axis) excitations do not have any significant effect on the reactivity. The shapes of the opacity functions and scattering angle distributions depend on the initial vibrational state, but show virtually no  $JK$  dependence. The origin of the  $K = 0$  rotational enhancements is that the tumbling rotation enlarges the range of the reactive initial attack angles, thereby increasing the reactivity.



## I. INTRODUCTION

Since the first theoretical and experimental studies on the  $H + H_2O/HDO$  reactions,<sup>1–4</sup> mode specificity has been shown to play a central role in polyatomic reaction dynamics.<sup>5–16</sup> It is well-known that vibrational excitation of a stretching mode of the reactant molecule usually enhances the reactivity. Current experimental techniques allow selectively exciting a specific bond of a polyatomic molecule, thereby promoting the reaction toward the desired products.<sup>5–8</sup> Whereas the vibrational mode specificity has been studied extensively, little has been known about the rotational mode specificity of polyatomic chemical reactions. Following a few previous work on  $H_2O^+ + H_2$  (refs 17 and 18) and  $F, Cl,$  and  $OH + CH_4$ ,<sup>19–21</sup> we recently found that reactant rotational excitations substantially enhance the reactivity of the  $Cl + CHD_3 \rightarrow HCl + CD_3$  reaction.<sup>22</sup> Unlike  $H_2O^+$  and  $CH_4$ ,  $CHD_3$  is a symmetric top that can be characterized by rotational quantum numbers  $J$  and  $K$ . One can ask whether the reactivity depends on the specific values of  $J$  and  $K$ . For  $Cl + CHD_3(\nu_1 = 1)$ , the reactivity increases with increasing  $J$  if  $K = 0$  and the enhancement factors are smaller and smaller as  $|K|$  approaches  $J$ .<sup>22</sup> For  $H + CHD_3(\nu = 0)$  a very recent 7-dimensional quantum dynamics study found that initial rotational excitation up to  $J = 2$  does not have any effect on the reactivity.<sup>23</sup> Here, for the first time, we investigate the rotational mode specificity of another fundamental polyatomic reaction, namely the  $O(^3P) + CHD_3 \rightarrow OH + CD_3$  reaction (classical(adiabatic) barrier height is  $\sim 14(10)$  kcal/mol and endothermicity is  $\sim 5(2)$  kcal/mol), using a quasiclassical trajectory (QCT) method, which allows studying the rotational effects up to relatively high  $J$  values.

## II. COMPUTATIONAL DETAILS

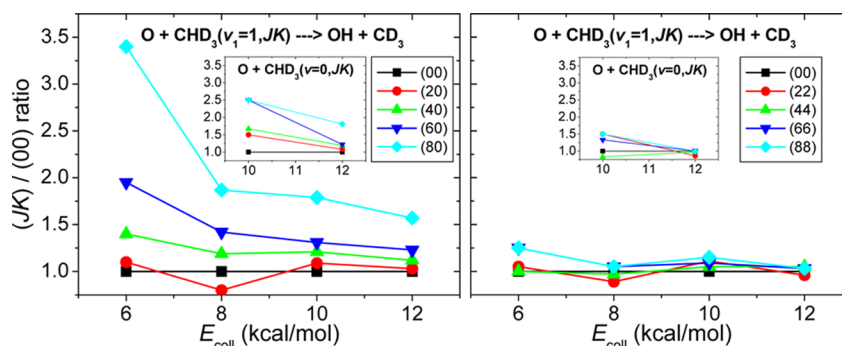
The QCT computations are performed on the Czakó–Bowman ab initio full-dimensional potential energy surface.<sup>24</sup>

We investigate the reaction of the ground-state  $O(^3P)$  atom with vibrational ground-state and CH stretching-excited  $CHD_3(\nu_1 = 0, 1, JK)$ . The latter ( $\nu_1 = 1$ ) state-specific reaction may also be studied experimentally in the near future, whereas the  $JK$ -effects on the former ( $\nu = 0$ ) can only be investigated theoretically at present. The quasiclassical  $\nu = 0$  and  $\nu_1 = 1$  vibrational states are prepared by standard normal-mode sampling and the  $JK$  rotational states are set by following the procedure described in refs 22 and 25. In brief, the three components ( $J_x, J_y, J_z$ ) of the classical angular momentum vector  $\mathbf{J}$  are sampled in the body-fixed principal axis system by setting  $J_z$  to  $K$  and sampling  $J_x$  and  $J_y$  randomly with the constraint of  $J_x^2 + J_y^2 + J_z^2 = J(J + 1)$ . Then,  $\mathbf{J}$  is transformed to the space fixed frame and standard modifications of the velocities are done to set the desired  $\mathbf{J}$ .<sup>25</sup> The initial distance between the O atom and the center of the mass of  $CHD_3$  is  $(x^2 + b^2)^{1/2}$ , where  $b$  is the impact parameter and  $x$  is set to 10 bohr. The orientation of  $CHD_3$  is randomly sampled and  $b$  is scanned from 0 to 5 bohr with a step size of 0.5 bohr. (Note that the cross sections are obtained by a  $b$ -weighted numerical integration of the reaction probabilities over  $b$  from 0 to  $b_{max}$ .) We run 25 000 trajectories at each  $b$ ; thus, the total number of trajectories is 275 000 for each collision energy ( $E_{coll}$ ) and  $JK$ . Trajectories are run at  $E_{coll}$  of 10.0 and 12.0 kcal/mol for  $\nu = 0$  and 6.0, 8.0, 10.0, and 12.0 kcal/mol for  $\nu_1 = 1$  and  $J$  values are increased up to 8 with  $K = 0$  or  $J$ . Thus, this study considers a total number of  $\sim 19$  million trajectories. The trajectories are analyzed with and without zero-point energy (ZPE) constraint. The ZPE constraint decreases the absolute cross sections, but does not have significant effects on the cross

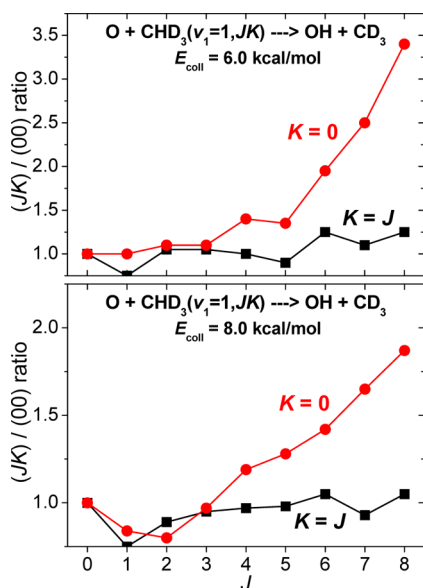
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**Figure 1.**  $JK$ -dependence of the cross section ratios ( $\sigma_{JK}/\sigma_{00}$ ) of the  $O(^3P) + CHD_3(v_1 = 0, 1, JK) \rightarrow OH + CD_3$  reactions as a function of collision energy.

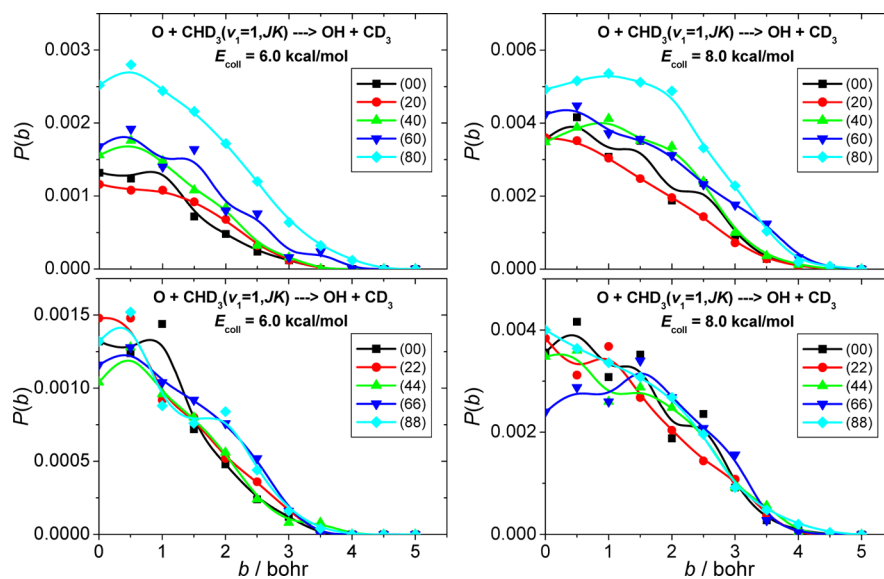


**Figure 2.**  $K$ -dependence of the cross section ratios ( $\sigma_{JK}/\sigma_{00}$ ) as a function of  $J$  at collision energies of 6.0 and 8.0 kcal/mol for the  $O(^3P) + CHD_3(v_1 = 1, JK) \rightarrow OH + CD_3$  reactions.

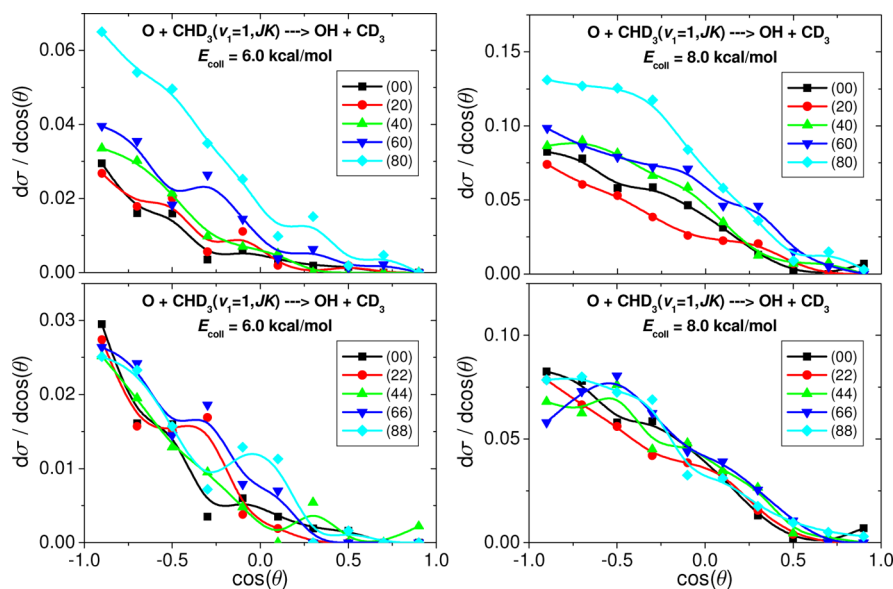
section ratios, angular distributions, etc. Therefore, in this study we show the statistically more robust nonconstrained results.

### III. RESULTS AND DISCUSSION

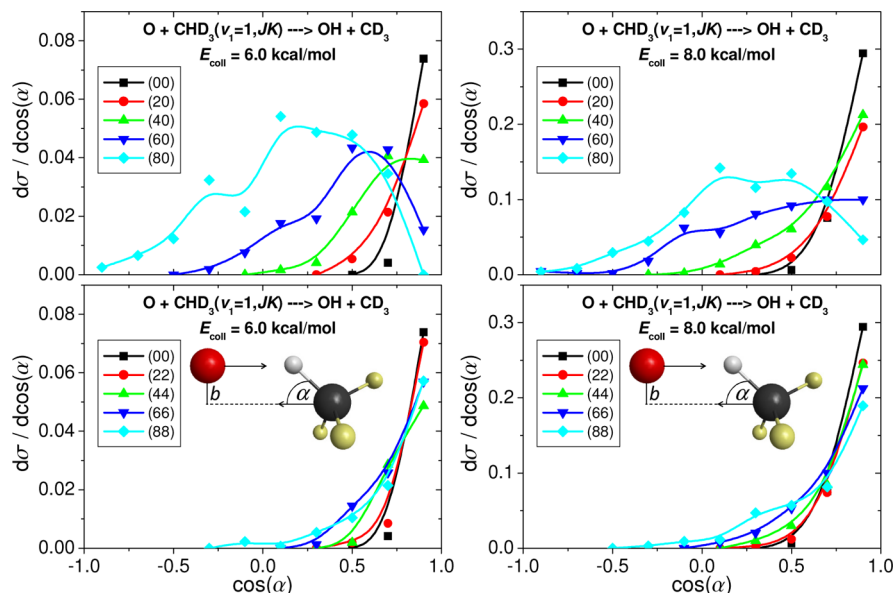
Rotational enhancement factors at different collision energies are given in Figure 1. As seen, the reactivity increases with increasing  $J$  if  $K = 0$ , whereas the enhancement factors are close to 1 if  $K = J$ . Despite the large number of trajectories, the cross section ratios have about 10% statistical uncertainty due to the very low reactivity of the  $O(^3P) + CHD_3$  reaction, especially at low  $E_{coll}$  and for  $v = 0$ . Nevertheless, the trends are clearly revealed: up to  $J = 3$  (see Figure 2) the rotational excitation has little effect on the reactivity of  $CHD_3(v_1 = 1)$ , for  $JK = 40, 60$ , and  $80$  the reactivity is enhanced by factors of about 1.2, 1.5, and 2.0, respectively, and for  $JK = 44, 66$ , and  $88$  the enhancement factors are close to 1. For  $K = 0$  the cross section ratios decrease with increasing  $E_{coll}$ , especially in the  $E_{coll}$  range of 6–8 kcal/mol. Between  $E_{coll}$ s of 8 and 12 kcal/mol just a slight decay is seen. The  $O(^3P) + CHD_3(v = 0)$  reaction has a threshold around 8 kcal/mol; thus, the  $JK$ -dependence is just studied at  $E_{coll}$  of 10.0 and 12.0 kcal/mol as shown in Figure 1. The rotational enhancement factors of  $O(^3P) + CHD_3(v_1 = 1)$  are qualitatively similar to those of  $O(^3P) + CHD_3(v_1 = 1)$ .



**Figure 3.**  $JK$ -dependence of the reaction probabilities as a function of impact parameter at collision energies of 6.0 and 8.0 kcal/mol for the  $O(^3P) + CHD_3(v_1 = 1, JK) \rightarrow OH + CD_3$  reactions.



**Figure 4.**  $JK$ -dependence of the scattering angle ( $\theta$ ) distributions at collision energies of 6.0 and 8.0 kcal/mol for the  $O(^3P) + CHD_3(v_1 = 1, JK) \rightarrow OH + CD_3$  reactions.

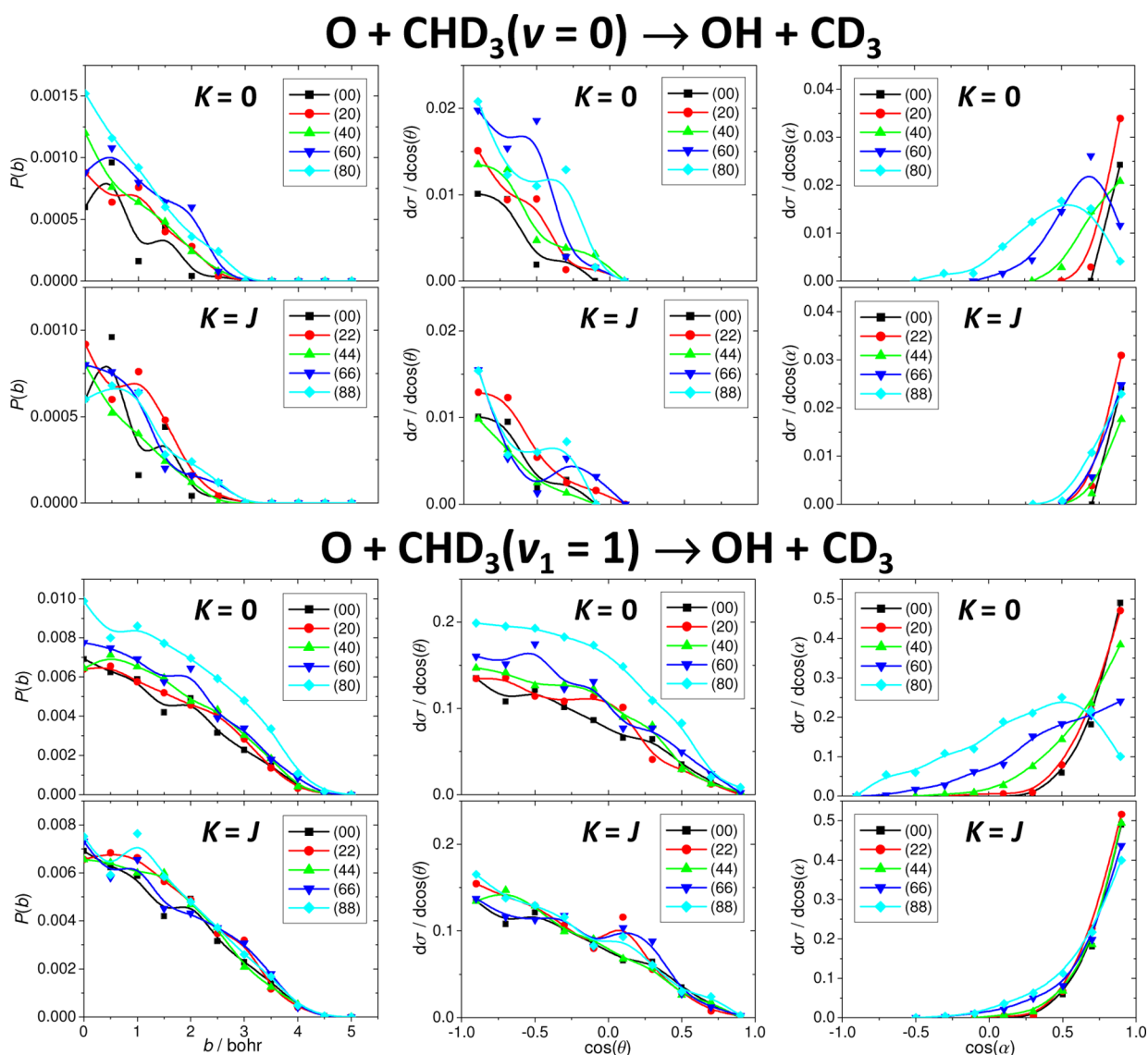


**Figure 5.**  $JK$ -dependence of the initial attack angle ( $\alpha$ ) distributions at collision energies of 6.0 and 8.0 kcal/mol for the  $O(^3P) + CHD_3(v_1 = 1, JK) \rightarrow OH + CD_3$  reactions.

Because of the significant statistical errors for the former reaction (reaction probabilities are usually less than 0.001), we cannot do a quantitative comparison between the rotational enhancement factors. Nevertheless, we can conclude that rotational enhancement is seen in the  $O(^3P) + CHD_3(v = 0)$  reaction as well. This finding suggests that the measured initial rotational effects in the CH stretching-excited reactions may also take place in the ground-state reaction.

The  $K$ -dependence of the rotational enhancement factors is shown in Figure 2 at  $E_{\text{coll}} = 6.0$  and 8.0 kcal/mol for the  $J = 1, 2, 3, \dots, 8$  and  $K = 0, J$  states of  $CHD_3(v_1 = 1)$ . As mentioned above, the  $K = 0$  ratios clearly increase with  $J$ , whereas the  $K = J$  ratios are almost constant 1 within the statistical uncertainty. Classically  $K = J$  corresponds to spinning rotation essentially about the CH axis, which is expected to have a little effect on the H-abstraction. However, in the case of  $K = 0$ , the tumbling

rotation may steer the reactants into a reactive orientation, thereby increasing the reactivity. Similar qualitative results were found recently for  $Cl + CHD_3(v_1 = 1, JK)$ , albeit the rotational enhancement factors are significantly larger for  $Cl + CHD_3$ .<sup>22</sup> For example,  $JK = 50$  and  $55$  enhance the  $Cl + CHD_3$  reaction by factors of 5.3 and 2.5, respectively,<sup>22</sup> whereas the corresponding enhancement factors of  $O(^3P) + CHD_3$  are only 1.4(1.3) and 0.9(1.0). However, it is important to note that the above data do not correspond to the same  $E_{\text{coll}}$ . For  $Cl + CHD_3$   $E_{\text{coll}} = 2.0$  kcal/mol, whereas for  $O(^3P) + CHD_3$   $E_{\text{coll}} = 6.0(8.0)$  kcal/mol, thus the smaller  $E_{\text{coll}}$  of the former reaction may explain the larger rotational effects. Note that the threshold of  $Cl + CHD_3(v_1 = 1)$  is below 0.5 kcal/mol, whereas  $O(^3P) + CHD_3(v_1 = 1)$  has a substantially higher threshold energy of about 4.5 kcal/mol.



**Figure 6.**  $JK$ -dependence of the opacity functions (left), scattering angle ( $\theta$ ) distributions (middle), and the initial attack angle ( $\alpha$ ) distributions (right) at a collision energy of 10.0 kcal/mol for the ground-state and CH stretching-excited  $O(^3P) + CHD_3(\nu_1 = 0, 1, JK) \rightarrow OH + CD_3$  reactions.

Opacity functions (reaction probabilities ( $P$ ) as a function of impact parameter) of the  $O(^3P) + CHD_3(\nu_1 = 1, JK)$  reaction are shown in Figure 3. As seen, the reactivity is small,  $P(b = 0)$  is less than 0.003 (0.005) at  $E_{\text{coll}} = 6.0$  (8.0) kcal/mol. In both the  $K = 0$  and  $K = J$  cases the shapes of the opacity functions are very similar and do not depend significantly on  $J$  and  $E_{\text{coll}}$ . This finding is consistent with the scattering angle distributions shown in Figure 4. As seen, the angular distributions of  $O(^3P) + CHD_3(\nu_1 = 1)$  are mainly backward and sideways scattered without any significant  $J$  or  $K$  dependence. Thus, the rotational effects found on the integral cross sections if  $K = 0$  do not affect the shapes of the opacity functions and angular distributions. Following our previous study on  $Cl + CHD_3$ ,<sup>22</sup> we have computed the initial attack angle ( $\alpha$ ) distributions for the  $O(^3P) + CHD_3(\nu_1 = 1, JK)$  reaction as shown in Figure 5.  $\alpha$  is defined as the angle between the initial velocity vector of  $CHD_3$  and the CH vector at the beginning of the trajectory. Note that unlike the attack angle at the transition state, the initial attack angle dependence of the reactivity can be probed experimentally. For the  $K = J$  states, the attack angle distributions are independent of  $J$  and show strong preference for angles

close to zero (front-side attack). However, for  $K = 0$  a clear  $J$ -dependence is seen, where the attack angle distributions shift from front-side attack to side-on attack orientations. For the  $JK = 80$  state the reactivity is even larger at  $\alpha = 90^\circ$  than at  $\alpha = 0^\circ$  and significant reactivity is found when the O atom initially approaches the back side of  $CHD_3$ . This side-on–back-side shift with increasing  $J$  is even more pronounced at lower  $E_{\text{coll}}$  as seen by comparing the  $\alpha$  distributions at 6.0 and 8.0 kcal/mol (Figure 5). Thus, these attack angle distributions reveal that the mechanistic origin of the rotational enhancement effect is that the tumbling rotation ( $K = 0$ ) opens up the reactive cone of acceptance, thereby promoting the H-abstraction. The spinning rotation ( $K = J$ ) does not have a significant effect on the cone of acceptance.

The  $JK$ -specific opacity functions, scattering angle, and attack angle distributions of the  $O(^3P) + CHD_3(\nu = 0)$  and  $O(^3P) + CHD_3(\nu_1 = 1)$  reactions are compared in Figure 6. Similar to the CH stretching-excited reaction, the opacity functions and scattering angle distributions of the  $O(^3P) + CHD_3(\nu = 0)$  reaction do not show significant  $JK$  dependence, whereas the attack angle distributions shift toward side-on attack with

increasing  $J$  if  $K = 0$ . Although the  $JK$ -dependence of the  $\nu = 0$  and  $\nu_1 = 1$  results are similar, the initial vibrational state has a significant effect on the dynamics. As Figure 6 shows, CH stretching excitation increases the maximum impact parameter from 3.0 to 4.5 bohr, thereby shifting the scattering angle distributions from backward to sideways–forward directions. This vibrational effect is in agreement with previous experimental<sup>8</sup> and theoretical<sup>24</sup> findings. Furthermore, here we also show that the attack angle distributions are also made broader by exciting the CH stretching mode.

#### IV. SUMMARY AND CONCLUSIONS

We have shown that adding a small rotational energy to a polyatomic reactant can have substantial effects on the reactivity. Furthermore, the rotational effects are state specific: in the case of a symmetric top the reactivities of the  $K = J$  rotational states are similar, whereas the excitations of the  $K = 0$  rotational states substantially promote the reaction. Unlike the vibrational enhancement effect, this rotational enhancement does not originate from enlarging the range of the reactive impact parameters, but the tumbling rotational opens up the range of the reactive initial attack angles, thereby increasing the reactivity. The present study may inspire future theoretical and experimental investigations of the rotational effects on polyatomic reactivity.

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##### Notes

The author declares no competing financial interest.

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