

Communication: Mode specific quantum dynamics of the $F + CHD_3 \rightarrow HF + CD_3$ reaction

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Communication: Mode specific quantum dynamics of the $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ reaction

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The mode specific reactivity of the $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ reaction is investigated using an eight-dimensional quantum dynamical model on a recently developed *ab initio* based full-dimensional potential energy surface. Our results indicate prominent resonance structures at low collision energies and absence of an energy threshold in reaction probabilities. It was also found that excitation of the C–D stretching or CD_3 umbrella mode has a relatively small impact on reactivity. On the other hand, the excitation of the C–H vibration (ν_1) in CHD_3 is shown to significantly increase the reactivity, which, like several recent quasi-classical trajectory studies, is at odds with the available experimental data. Possible sources of the disagreement are discussed. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4948547>]

The hydrogen abstraction reactions of CH_4 and its isotopomers by H, F, Cl, and $\text{O}(^3\text{P})$ have become prototypes for understanding mode specificity and bond selectivity in polyatomic bimolecular reactions.^{1,2} Among these reactions, the $F + \text{CH}_4$ reaction is special because it has a very low (~ 0.8 kcal/mol) and reactant-like barrier. Before the reactants reach the transition state, they have to pass through a region that is strongly affected by a pre-reaction van der Waals well and non-adiabatic curve crossing due to the spin-orbit states of $F(^2\text{P})$.^{3,4} As a result, the collision, particularly at low collision energies, is expected to be strongly affected by stereodynamic forces. Despite many experimental and theoretical studies performed for this system,^{3–40} a clear picture of the reaction dynamics is yet to emerge.

In a thought-provoking experiment, Zhang *et al.* reported a crossed molecular beam study of the $F + \text{CHD}_3$ reaction at low collision energies (< 4.0 kcal/mol) and found, surprisingly, that the excitation of the C–H vibration (ν_1) significantly (10 fold) reduces the overall reactivity. In addition, the reaction with the vibrationally excited CHD_3 favors the $\text{DF} + \text{CHD}_2$ channel at the expense of the $\text{HF} + \text{CD}_3$ channel.²⁰ The reduction of reactivity was also reported by Yang *et al.* for the $\text{HF} + \text{CD}_3$ channel at a higher collision energy (9.0 kcal/mol), but the reduction is much less ($\sim 26\%$).³⁶ At the same energy, the reactivity to the $\text{DF} + \text{CHD}_2$ channel was also found to be reduced.³⁷ The suppression of reactivity into the $\text{HF} + \text{CD}_3$ channel in favor

of the $\text{DF} + \text{CHD}_2$ channel was supported by quasi-classical trajectory (QCT) studies by Czako and Bowman^{22,23} on an *ab initio* based potential energy surface (PES) developed by Czako, Shepler, Braams, and Bowman (CSBB).²¹ These theoretical studies attributed the reduction in reactivity in the $\text{HF} + \text{CD}_3$ channel to stereodynamic forces in the pre-reaction well, which steer the reactants to the $F\text{--}D\text{--}CHD_2$ transition state.²² Nevertheless, the QCT study found that the CH vibrational excitation enhances the overall reactivity. More recently, an improved PES^{4,35,38} has been developed by Palma, Westermann, Eisfeld, and Manthe by considering the spin-orbit coupling in the reactant channel (PWEM-SO), which provides a more accurate description of the reactant channel than the CSBB PES. In the transition-state and product region, the PWEM-SO PES is smoothly switched to the CSBB PES. QCT calculations on the PWEM-SO PES found that C–H vibrational excitation also enhances the reactivity into the $\text{HF} + \text{CD}_3$ channel, while it has a limited impact on the $\text{DF} + \text{CHD}_2$ channel.³⁸ No reduction of reactivity was reported³⁹ on another PES.¹⁵ These theoretical results disagree with the experimental observations on the effect of C–H vibrational excitation on the reactivity.^{20,36,37} One of the possible reasons for the theory-experiment disagreement is the classical model used for describing the dynamics, which has an imperfect treatment of quantum effects such as zero-point energy and tunneling.

To shed light on this possibility, detailed quantum dynamics (QD) calculations on the $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ reaction are required. However, the accurate quantum-mechanical description of the title reaction is challenging. The van der Waals well in the reactant channel gives rise

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to long-lived resonance states which strongly affect the reaction dynamics. Consequently, very long propagation times are required in the dynamical simulations. While detailed quantum mechanical calculations studying FCH₄ transition state spectra and low-lying pre-reaction complexes have been reported,^{4,31,32,35,40} QD studies of reactive scattering have so far been restricted to low dimensionality studies of the F + CH₄ → HF + CH₃ reaction.^{17,24,34} These calculations included a maximum of five coordinates and thus had to ignore important degrees of freedom.

In the present work, eight-dimensional (8D) QD studies for the F + CHD₃ → HF + CD₃ reaction with zero total angular momentum J are presented. Our approach is based on the reduced-dimensional model introduced by Palma and Clary⁴¹ and uses an established wave packet method to study atom-methane reactions.^{42,43} Only coordinates which break the C_{3v} symmetry of the CD₃ group are excluded from the dynamical treatment. Since the neglected coordinates can be expected to act largely as spectators in the reaction process, the calculations should provide a reliable description of the reaction dynamics (for $J = 0$). This methodology has already been used in numerous studies.^{42–49} Thus, only a short outline of the coordinate system is given here.

Polar coordinates corresponding to \mathbf{R} , the vector from the center of mass of HCD₃ to F atom, and \mathbf{r} , the vector from the center of mass of CD₃ to the H atom, are used. For the description of the internal motion of the CD₃ group, two scaled-polar coordinates (q, γ) defined as $q = \sqrt{x^2 + y^2}$ and $\gamma = \arctan(y/x)$ with $y = \sqrt{m_C/(m_C + 3m_D)}s$ are used to simplify the vibrational kinetic operator expression.⁴³ Here, x denotes the distance between atom D and the C_{3v} symmetry axis \mathbf{S} and s is the distance between atom C and the center of three D atoms.

The PWEM-SO PES used in the current calculations is based on the lower adiabat of a coupled set of PESs in the reactant channel,⁴ which is smoothly connected to the CSBB PES²¹ in the transition-state and product regions.³⁸ The PWEM-SO PES has been successfully used to obtain the photodetachment spectrum of FCH₄^{–35} and is thus known to be accurate in the pre-reaction region.

The integral cross section (ICS) is obtained by summing the total reaction probabilities. In this work, only the reaction probabilities for $J_{tot} = 0$, $P_i^{J_{tot}=0}(E)$ are calculated explicitly and a J - K -shifting approximation⁵⁰ is employed to calculate partial wave contributions for $J_{tot} > 0$. The system is approximated as a symmetric rotor at the transition state with the rotational constants $A_{TS} = 2.65$ cm^{–1} and $B_{TS} = 0.23$ cm^{–1}. Since only methane reactants in the rotational ground state are considered ($J = K = 0$), the helicity quantum number K_{tot} associated with the projection of J on vector \mathbf{R} vanishes and only summation with respect to the total angular momentum quantum number J_{tot} is required (J -shifting). Thus, the ICS is calculated by

$$\sigma_i(E) = \frac{\pi}{2\mu E} \sum_{J_{tot}} (2J_{tot} + 1) P_i^{J_{tot}=0}(E - B_{TS}J_{tot}(J_{tot} + 1)).$$

A total of 240 sine basis functions ranging from 3.0 to 15.0 bohrs were used for the R basis set expansion with 80 nodes in the interaction region; and 5 and 25 basis

TABLE I. Comparison of calculated and measured vibrational energy levels of CHD₃.

	Calculated (in cm ^{–1})	Experiment (in cm ^{–1}) ^a
(0,0,0)	3616 (ZPE) ^b	
(1,0,0)	2985	2993
(0,1,0)	2175	2142
(0,0,1)	1011	1003

^aThe experimental data are taken from <http://webbook.nist.gov/chemistry/>.

^bZero-point energy (ZPE).

functions of r were used in the asymptotic and interaction regions, respectively. For the vibration of the CD₃ group, 3 and 9 basis functions were used for coordinates q and γ , respectively. The size of the rotational basis functions is controlled by the parameters, $J_{max} = 60$, $l_{max} = 33$, $j_{max} = 27$, and $k_{max} = 6$. After considering parity and C_{3v} symmetry, the size of rotational basis functions was 47 394 and the size of the total basis functions was 3.6×10^9 . The vibrational states of CHD₃ for $J = 0$ were also solved with the same basis set. As the PWEM-SO PES has multiple bound and resonance states supported by the pre-reaction channel, the convergence of the reaction probabilities requires long propagations (170 000–200 000 a.u., depending on the initial vibrational state selected).

In our calculations, excitations in three of the six vibrational modes of CHD₃ were considered. They are labeled by (v_1, v_2, v_3) for the CH stretch, CD₃ s-stretch, and CD₃ s-deform (umbrella). The H–CD₃ rock mode (v_5) is not well described in the 8D model because it necessarily distorts the C_{3v} symmetry. Thus, it is not discussed in this work. The other two modes, CD₃ d-stretch (v_4) and CD₃ d-deform (v_6), are not included in this 8D model due to the C_{3v} symmetry constraint. The first, and sometimes the second, excited states of the v_1, v_2 , and v_3 modes are investigated and the vibrational energy levels of CHD₃ within the 8D model are listed in Table I.

Figure 1(a) shows the $J_{tot} = 0$ reaction probabilities with the reactant CHD₃ from the ground state (0,0,0) and the fundamental of the CH stretching mode (1,0,0). The most striking feature of the reaction probabilities is the absence of a reaction threshold. Given the classical barrier of 0.77 kcal/mol, this observation strongly suggests that tunneling is facile in this system, possibly enhanced by the pre-reaction well. The QCT study on the same PES has, however, indicated a clear threshold for the ground state CHD₃, near the classical barrier.³⁸ Such tunneling facilitated reactivity below the classical barrier has been reported for the F + H₂ and F + H₂O reactions,^{51–53} both having low barriers. On the other hand, there are many peaks at low collision energies, which are apparently due to resonances supported by the pre-reaction well. The resonances are generally very sensitive to the shape and depth of the associated well. Different values of the well depth, ranging from 45 to 363 cm^{–1}, were reported for different global PESs.^{15,21,38} The PWEM-SO PES employed in this work is considered to be more reliable as good agreement was found between experimental and theoretical transition-state spectra. These resonances in the transition-state spectra have been investigated extensively in full dimensionality using the multiconfiguration time-dependent Hartree method,^{4,31,32,35,40}

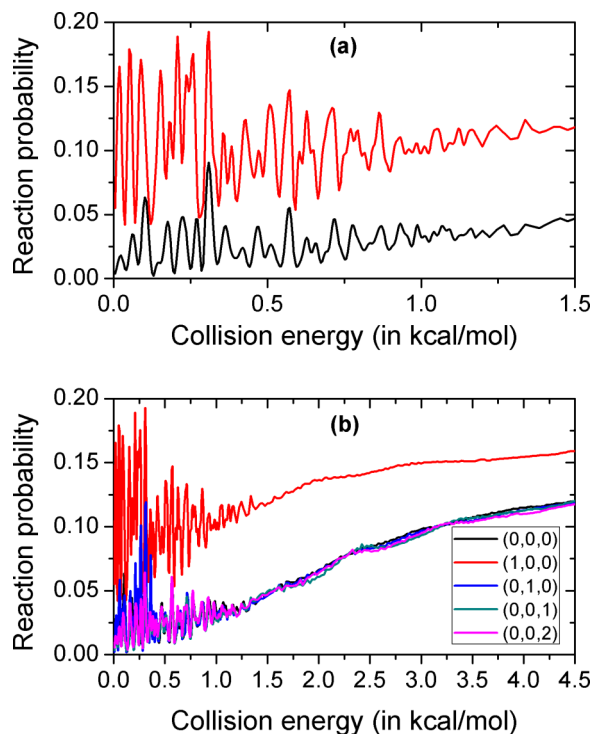


FIG. 1. Calculated ($J_{tot}=0$) reaction probabilities as a function of the collision energy for the reaction $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$. (a) The reactant CHD_3 in the ground and the fundamental states of the CH stretch mode. (b) The reactant CHD_3 in five selected vibrational states.

because of their importance in photodetachment of FCH_4^- . Comparison with these full-dimensional results is not attempted because the 8D model does not offer a comparable characterization of the pre-transition state dynamics.

In Figure 1(b), the reaction probabilities are compared for various initial vibrational states of CHD_3 . Clearly, they all present similar features, which oscillate strongly at low collision energies while become subdued at high collision energies. The probabilities are close to each other except for the fundamental of the CH stretch mode, for which the probability is remarkably larger than from the others.

In Figure 2, the calculated ICSs obtained from J -shifting are compared for different vibrational states of CHD_3 . To

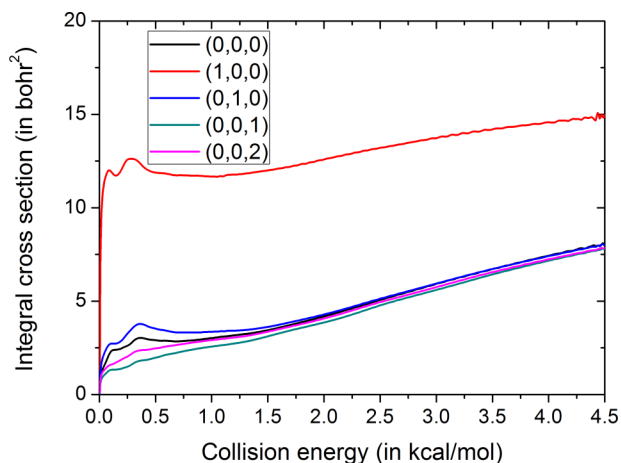


FIG. 2. Integral cross sections as a function of the collision energy for the reaction $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ for CHD_3 in five vibrational states.

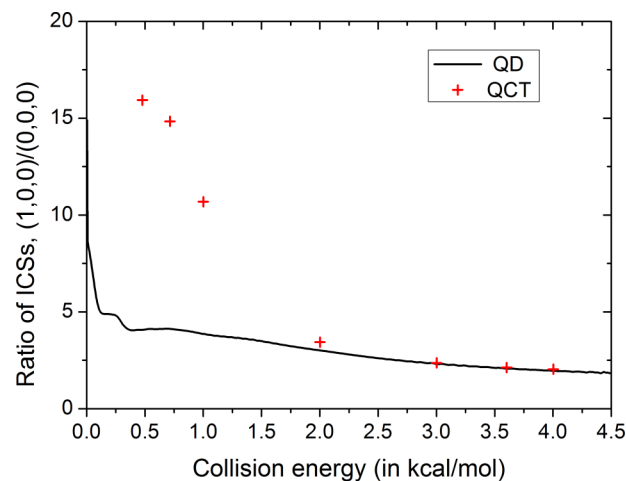


FIG. 3. Comparison of the QD and QCT ratios between the (1,0,0) and (0,0,0) state integral cross sections. The QCT results are adapted from Ref. 38.

give a better view of mode specificity in this reaction, the ICSs are smoothed to suppress the oscillations in the J -shift probabilities. This is done by averaging the J -shift probabilities over two neighbor energy points with several cycles. From the figure, it is clear that excitations in the umbrella mode of $\text{CHD}_3(v_3)$ inhibit the reaction slightly, while the excitation of the s -stretching mode of $\text{CD}_3(v_2)$ enhances the reaction somewhat. On the other hand, the excitation of the C-H vibration (v_1) significantly enhances the reactivity of the title reaction.

The enhancement ratio between the (1,0,0) and (0,0,0) states of CHD_3 is compared with the earlier QCT results³⁸ on the PWEM-SO PES in Fig. 3. At low collision energies, the ratios for both the QD and QCT results are always larger than unity, indicating that the vibrational excitation in the v_1 mode enhances the $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ reaction. The QCT ratios are, however, significantly larger than the QD counterparts in this energy range, largely because of the absence of the tunneling contributions for the ground state of CHD_3 . At higher energies, the agreement is particularly good as the calculated ratios approach each other. They both predict a significant enhancement by the vibrational excitation.

Recently, the Sudden Vector Projection (SVP) model was proposed to rationalize and predict mode specificity in bimolecular reactions.⁵⁴ While the SVP model has been generally successful in this respect,⁵⁵ including the $X + \text{CH}_4/\text{CHD}_3$ reactions,⁵⁶ it fails to predict the observed vibrational enhancement in the title reaction. As shown in Table II, the projection of the CH (v_1) mode is merely 0.08 on the PWEM-SO PES, which is very close to that on the CSBB

TABLE II. SVP values for the $F + \text{CHD}_3$ reaction.

CH stretch, v_1	0.079
CD_3 s -stretch, v_2	0.004
CD_3 s -deform, v_3	0.094
CD_3 d -stretch, v_4	0.012
Rock, v_5	0.041
CD_3 d -deform v_6, v_5, v_6	0.021
Translation	0.650

PES (0.07),⁵⁶ suggesting very weak coupling with the reaction coordinate at the transition state, and thus small enhancement. The most likely reason for this failure is that the sudden model on which the SVP model is based does not hold in this system, due to the strong stereodynamic forces in the entrance channel and the low barrier.

In conclusion, our 8D QD model suggests that the CH excitation promotes the title reaction, in agreement with QCT results. However, we emphasize that the 8D QD result reported here is not conclusive as it does not consider the DF + CHD₂ channel. As a result, it does not give the full picture of the reaction dynamics as in the full-dimensional QCT calculations. Nevertheless, the enhancement of reactivity for the title reaction by exciting the ν_1 mode of CHD₃ concluded by both QCT and reduced-dimensional QD calculations deepens the controversy concerning the theory-experiment disagreement. The possible sources of the discrepancy can be from either the experimental or theoretical side. On the experimental side, the REMPI method is state-selective and may miss some states that contribute to the reactivity. Indeed, in the recent studies of the Cl + CHD₃ reaction, the reactivity for the vibrationally excited reactant was found to increase when more rotational states of the products were included in the experiment,^{57,58} bringing the vibrational enhancement factor closer to theoretical prediction.⁵⁹ Theoretically, the 8D QD model still contains large uncertainties concerning approximations introduced by the reduced dimensionality. In addition, the rotational state of the CHD₃ reactant in our calculations ($|J, K\rangle = 0, 0$) is different from the experiment ($|J, K\rangle = 2, 0$ and ± 1). Although rotational effects are typically small, recent work has shown that this might not necessarily be true.^{46,60–64} Furthermore, significant errors might still exist in the PES, especially in the reactant well and product regions. Finally, our model ignores the non-adiabatic dynamics on the low-lying spin-orbit states. It is hoped that further investigations in both experimental and theoretical sides will be stimulated to resolve this discrepancy.

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