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Communication: Experimental and theoretical investigations of the effects of the reactant bending excitations in the F+CHD$_3$ reaction

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The effects of the reactant bending excitations in the F+CHD$_3$ reaction are investigated by crossed molecular beam experiments and quasiclassical trajectory (QCT) calculations using a high-quality *ab initio* potential energy surface. The collision energy (E_c) dependence of the cross sections of the F+CHD$_3$(v_b=0,1) reactions for the correlated product pairs HF(v')+CD$_3$(v_2=0,1) and DF(v')+CHD$_2$(v_4=0,1) is obtained. Both experiment and theory show that the bending excitation activates the reaction at low E_c and begins to inactivate at higher E_c. The experimental F+CHD$_3$(v_b=1) excitation functions display surprising peak features, especially for the HF(v'=3)+CD$_3$(v_2=0,1) channels, indicating reactive resonances (quantum effects), which cannot be captured by quasiclassical calculations. The reactant state-specific QCT calculations predict that the $v_5(e)$ bending mode excitation is the most efficient to drive the reaction and the $v_6(e)$ and $v_5(e)$ modes enhance the DF and HF channels, respectively. © *2010 American Institute of Physics*. [doi:10.1063/1.3490795]

The control of chemical reactions by activating specific bonds/vibrational modes in the reactant molecules is a dream of chemists.[1] This dream has become reality for a few fundamental chemical reactions. As early experimental[2,3] and theoretical[4,5] studies showed, OH stretching excitation in the H+HOD reaction enhances production of the H$_2$ products, whereas the excitation of the OD stretch mode significantly promotes the OD bond cleavage, thereby controlling the outcome of this prototypical bimolecular reaction. However, a recent experiment found that the CH stretching excitation in the F+CHD$_3$ reaction inhibits the breaking of the excited bond,[6] which questions our predictive chemical knowledge about mode-selective polyatomic reactivity. This surprising experimental result was recently confirmed by quasiclassical trajectory (QCT) computations showing that the CH stretching excitation steers the F atom to one of the CD bonds, thereby promoting the D-abstraction channel especially at low collision energies (E_c).[7,8]

Although most of the previous studies focused on the reactant stretching excitations, there are a few investigations of the effects of the bending mode excitations of the polyatomic reactants. For example, Zare and co-workers[9] measured an enhancement factor of 200 (80) in the late-barrier Cl+CH$_4$ (Cl+CD$_4$) reaction. Similar qualitative conclusion, albeit not quantitatively, was also drawn by Liu and co-workers.[10] The observed modest enhancement factor of about 3 was later confirmed in a reinvestigation that prepared CH$_4$(v_4=1) by direct infrared excitation.[11] This enhancement upon bending excitation was previously predicted by several theoretical studies.[12–17] There have also been studies on bend-excitation in the O+CH$_4$ reaction.[18–20] However, apart from very recent computational studies on the F+CH$_4$(v_4=1) and F+CH$_2$D$_2$(v_9=1) reactions,[21,22] the previous work usually focused on the late-barrier polyatomic reactions (the transition state has a product-like structure) and there is almost no prior study on bending-excited early-barrier reactions, such as the F+methane reaction. Indeed the Polanyi rules[23] predict that the translational energy is more efficient to activate early-barrier reactions than vibrational excitation (and the reverse is true for the late-barrier reactions). These qualitative rules have been shown to work well for atom +diatom reactions. Is this simple picture valid for polyatomic early-barrier reactions? Does the reactant bending mode excitation increase the rate of an early-barrier reaction? Do the specific excited bending modes promote different product channels? Can we/chemists predict the effect of bending mode excitations based on simple chemical intuition?

In this study we seek answers for these questions in the case of the F+CHD$_3$ reaction using state-of-the-art experimental and theoretical techniques. The preparation of a specific bend-excited state of CHD$_3$ in the laboratory is an extremely challenging task; therefore, the present experiment provides reactant bending-state averaged results only. In a reaction dynamics simulation, it is straightforward to prepare initial conditions for specific excited bending states; thus, our computations provide state-specific results as well. On the other hand, full(12)-dimensional quantum dynamics is cur-

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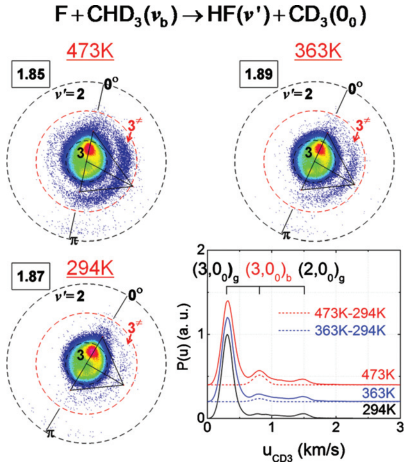

FIG. 1. Typical raw images of the $CD_3(v=0)$ product under three different methane source temperatures at the same $E_c \sim 1.9$ kcal/mol as well as product speed distribution $P(u)$ and their differences (dashed lines). $HF(v')$ states are labeled as black $v'=2,3$ and red $3^{\#}$ for the ground state and bend-excited reactions, respectively. The red circles represent the largest possible recoil speed from bend-excited reactions.

rently not feasible; thus, we perform QCT calculations on a high-quality *ab initio* full-dimensional potential energy surface (PES).[24] Obviously, QCT cannot capture possible quantum effects, such as reactive resonances. In the experiment the dynamics are exact; thus, measurement shows the quantum features of the reaction.

The experiment was performed using a crossed-beam apparatus as described previously,[25,26] except that the CHD_3 beam was heated thermally. Three source temperatures (T_s)—473, 363, and 294 K—were used to vary the initial populations of bend-excited CHD_3.[10,20] Through careful analysis of the speed distribution of the supersonic beam and by energy balance, the vibrational energy content of CHD_3 in the beam and thus the corresponding vibration temperature (T_v) can be deduced. We found that over the range of $T_s = 294-473$ K, T_v was approximately 45 K (±10 K) lower than T_s, from which the relative populations of bend-excited CHD_3 reactants were estimated. Product methyl radicals were detected by using a (2+1) resonance-enhanced multiphoton ionization (REMPI) scheme near 333 nm. The state-tagged product velocity distribution was measured by a time-sliced, velocity map imaging technique of the REMPI ions. The Q-head of the 0_0^0 and 2_1^1 [0_0^0 and 4_1^1] transitions were used to probe the $CD_3(v_2=0,1)$ [$CHD_2(v_4=0,1)$] ground and umbrella states.[27,28] The laser frequency was fixed at the peak of the Q-head, thus only the low N-states, which dominate the total reactivity, were sampled. To isolate the effects of the initial bending excitation, the intersection angles of the two molecular beams were adjusted so that the experiments under different T_s yield nearly the same E_c.

Figure 1 exemplifies three typical raw images of $CD_3(v=0)$ products from the $F+CHD_3$ reaction at $E_c = 1.9$ kcal/mol, under different methane source temperatures. All three images are dominated by an intense forward-scattered feature with small recoil velocity. On energetic grounds, this intense feature is identified as the $HF(v'=3) + CD_3(v=0)$ product pair, or $(3,0_0)_g$ with the subscript "g" denoting the ground-state reaction. Adjacent to this intense feature is a sideways scattered, ringlike structure. Its intensity displays a marked dependence on the source temperature. Energetically, it can be ascribed to the same product pair from the bend-excited reaction, i.e., $F+CHD_3(v_b=1)$, and labeled as $(3,0_0)_b$. The CD_3 product speed distributions $P(u)$ presented in Fig. 1 show three distinct peaks: the relative intensities of the first (or the slowest) and the third peaks appear invariant to the change in T_s, in contrast to the behavior of the second peak. By normalizing the three distributions with the same intensities of the first peak and subtracting from each other, the resultant dashed lines indeed show a single $(3,0_0)_b$ peak. The relative intensities of the two difference-signals correlate well with the calculated population differences of the bend-excited CHD_3 reactants based on the deduced T_v. To quantify the relative reactivity of the bend-excited reactant is, however, not without ambiguity. CHD_3 have several low-lying vibration modes, $v_3(a_1)$ (the umbrella mode of 1003 cm^{-1}), $v_6(e)$ (the CD_3 rock of 1036 cm^{-1}) and $v_5(e)$ (the CD_3 deformation of 1291 cm^{-1}). The energy spacing is too close for the present experimental resolution. We then adopt the approach used previously to quantify the reactivity.[10,20] In this approach, a Boltzmann distribution at a given T_v was assumed and the sum of the normalized populations of all low-lying modes was taken to be the concentration of the bend-excited CHD_3, $n_b(T_v)$, from which the relative cross section of σ_b/σ_g can then be obtained from analyzing the respective $P(u)$ distributions. Thus, the experimental σ_b is best viewed as the average cross section of the above three bending modes.

QCT calculations were performed for the $F+CHD_3(v=0)$ and $CHD_3(v_b=1)$ [$b=3,6,5$] reactions using a recent *ab initio* full-dimensional PES from Ref. 24. The initial quasiclassical vibrational states of the reactant were prepared by standard normal-mode sampling[29] and we have verified that the initial mode-specific bending excitation energy does not leak to the other modes prior to the collision [see Fig. S1 in the Supplementary Material (SM) (Ref. 30)]. We consider roughly 4×10^6 trajectories computed at five different E_c. The quantum number assignment and the Gaussian weighting procedure for the correlated product pairs were done based on Ref. 8. In order to make the comparison between experiment and theory possible, we calculate a thermally averaged cross section obtained as $\sigma_b = 0.28\sigma_{3_1} + 0.51\sigma_{6_1} + 0.21\sigma_{5_1}$ at 430 K. For more computational details see the SM.[30]

Measured and computed cross sections of the $F+CHD_3(v_b=0,1)$ reactions versus E_c for the correlated product states $HF(v') + CD_3(v_2=0,1)$ are given in Fig. 2. Both experiment and theory show that $\sigma_g(0_0)$ remain small at low E_c and rise rapidly as soon as the energetic threshold of $HF(v'=3)$ is reached at $E_c = 1.14$ kcal/mol—a similar behavior to the previous report when all rotational states of $CD_3(v=0)$ were probed.[31] For the bend-excited reaction, the measured formation of $(3,0_0)_b$ shows a significant enhancement at lower energies, followed by a distinct bump superimposed over an E_c-independent behavior. Intriguingly, the location of this bump is in the vicinity of the threshold of the $(3,0_0)_g$ pair. As a result, the cross section ratios σ_b/σ_g exhibit a very sharp decline from a value of ~4 to less than

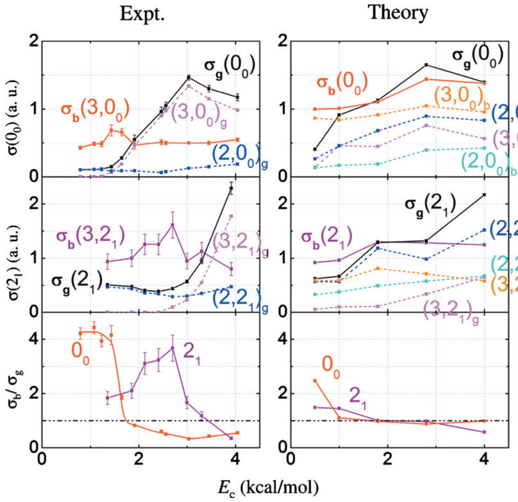

FIG. 2. Experimental and theoretical excitation functions of the F+CHD$_3$(v_b=0,1) reactions for the HF(v')+CD$_3$(v=0) (top) and the HF(v')+CD$_3$(v_2=1) (middle) product states. The experimental scales of these two panels have been normalized to each other (see Ref. 27), with an estimated uncertainty of about 2. To compare with theory, a single scaling factor was used. The pair-correlated cross sections within each panel are also normalized to one another. ($\sigma_g(0_0)$ and $\sigma_b(0_0)$ denote the sum over HF(v')+CD$_3$(v=0); $\sigma_b(3,0_0)\equiv(3,0_0)_b$; and similarly for CD$_3$($v_2$=1) $\equiv 2_1$.) The lower panels show the E_c-dependence of rate-enhancement factor induced by bend-excited CHD$_3$(v_b=1) for the CD$_3$(v_2=0,1) states.

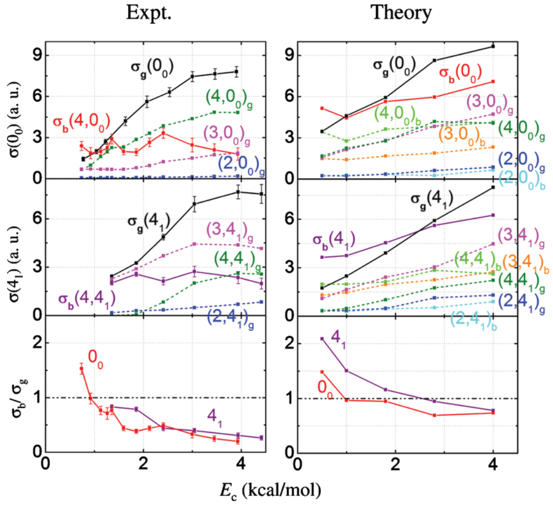

FIG. 3. As Fig. 2, except for the DF(v')+CHD$_2$(v=0) and the DF(v')+CHD$_2$(v_4=1) product states. Experimentally, while the relative cross sections of the two CHD$_2$ states are normalized to each other, they are not normalized to the CD$_3$ channel. See caption of Fig. 2.

unity near $E_c\sim1.7$ kcal/mol. Similar behavior is seen for $\sigma_b(3,2_1)$, where superimposed over a more-or-less flat excitation function is a peak feature occurring again near the energetic threshold of the $(3,2_1)_g$ channel. The QCT results agree with experiment that $\sigma_g(0_0)$ increases with E_c, whereas $\sigma_b(3,0_0)$ has only a slight E_c dependence and HF(v'=3) is the major product state in the F+CHD$_3$(v_b=1) reaction. However, QCT does not show the experimental bump features indicating quantum effects (reactive resonances), which cannot be described in a quasiclassical simulation. Because of those "resonance" features, the disparity in comparing the cross section ratios between theory and experiment (the lower panels of Fig. 2) are greatly amplified. Nonetheless, both agree on a positive (and negative) influence in reactivity by reactant bending excitations at lower (and higher) E_c. Note that a recent five-dimensional quantum dynamics study found similar resonance signatures when the umbrella mode in F+CH$_4$ was initially excited.[21]

The excitation functions for the DF(v')+CHD$_2$(v_4=0,1) states are presented in Fig. 3. Again, both experiment and theory show that the ground-state reaction cross sections feature the typical behavior of activated reactions, whereas the bend-excited ones display more-or-less flat excitation functions overlaid by some less-pronounced peaking features shown by experiment. The measured as well as the computed σ_b/σ_g ratios are above 1 at low E_c and decreases below 1 as the E_c increases.

The reactant CHD$_3$ has three bending modes with harmonic frequencies in the 1000–1350 cm^{-1} range; thus, one could ask whether the nearly degenerate modes have specific effects on the dynamics? Figure 4 shows the computed reactant-bending-state-specific total cross-section ratios σ_b/σ_g. All the reactant bending-excitations activate the reaction at low E_c and the σ_b/σ_g ratios decrease with increasing E_c. The $v_5(e)$ mode excitation increases the cross sections most especially for the HF+CD$_3$ channel, where the other two modes have only slight effects on the cross sections. For the DF channel the bending-mode specificity is not as pronounced as in the HF channel and the $v_3(a_1)$ and $v_6(e)$ modes activate the DF channel more efficiently than the HF channel.

Figure 4 also shows the DF/HF product ratios as function of E_c. As we mentioned above, the $v_5(e)$ mode appears

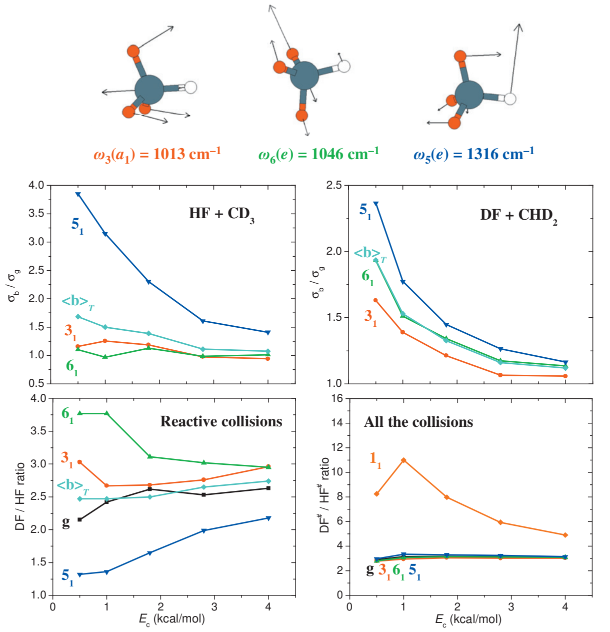

FIG. 4. Computed reactant-bending-state-specific ratios of the total cross sections of the F+CHD$_3$(v_b=1) and F+CHD$_3$(v=0) reactions for the channels HF+CD$_3$ and DF+CHD$_2$ (upper panels) as well as branching ratios of the reactive collisions forming the DF and HF products and ratios of trajectories (including the nonreactive ones as well) in which the F atom approaches either the D or H atom in the saddle-point region (lower panels) as a function of E_c. The ratios denoted $\langle b\rangle_T$ show the Boltzmann averaged bending-state-specific results at 430 K and (1_1) denotes the CH-stretch-excited reaction.

special among the bending modes in the HF channel; thus, the DF/HF ratio in the $v_5(e)$ mode excited reaction is significantly below the ratio in the ground-state reaction. The normal-mode vectors shown in Fig. 4 indicate that the $v_5(e)$ bending mode exhibits a relatively large amplitude H-atom motion, suggesting that this mode may have an effect on the H-abstraction channel. Since the saddle-point has a noncollinear C–H–F arrangement ($\angle \sim 150°$),[24] the $v_5(e)$ mode may help to maintain the $D_3CH—F$ saddle-point structure, thereby promoting the HF channel in the $F+CHD_3(v_5=1)$ reaction. In the $v_3(a_1)$ umbrella-mode-excited reaction the DF/HF ratio only slightly increases relative to the ratio in the ground-state reaction, whereas the $v_6(e)$ mode excitation significantly enhances the DF products and increases the DF/HF ratio well above 3 especially at low E_c. It is generally true that at higher E_c, the reactant vibrational excitation effects in the $F+CHD_3$ reaction become less significant and the DF/HF ratios show less pronounced mode selectivity.

We have found a bending mode, $v_6(e)$, whose excitation promotes the DF product channel; however, this DF enhancement is less significant than that in the $F+CHD_3(v_1=1)$ reaction.[6] This unexpected CH stretching effect was explained by a long-range interaction, which steers the slow F atom away from the stretching excited CH bond.[7] Does this stereodynamical "steering effect" play a role in the dynamics of the bending-excited reactions as well? In order to answer this question we followed the pathway of the F atom in the case of all the trajectories (including nonreactive ones) and monitored the H—F and D—F distances as functions of time. On the basis of the distance of the closest approach, we obtained the ratios of the trajectories in which the F atom attacks either the D or H atom in the saddle-point region (denoted as $DF^{\#}/HF^{\#}$) as shown in Fig. 4. It is interesting to see that only the CH stretch excited reaction shows significant stereodynamical effect, e.g., a $DF^{\#}/HF^{\#}$ ratio of about 11 at $E_c=1.0$ kcal/mol, whereas this ratio is close to 3 for the ground-state and bending-excited reactions. The enhancement of the HF product upon the excitation of the $v_5(e)$ mode cannot be explained by a long-range interaction, since the F atom rather attacks the D atoms with $DF^{\#}/HF^{\#} \cong 3.2$. Therefore, the HF enhancement may be due to the facts that the $v_5(e)$ bending excitation (a) facilitates attaining the bent D_3CH---F transition-state geometry, as alluded to early, and (b) promotes the CH bond cleavage by decreasing the vibrationally adiabatic barrier height.[32]

Based on simple chemical intuition, it is not straightforward to predict the effects of the bending (and torsional) motions, which involve nonlocalized and concerted motions of three or more atoms, on the dynamics of chemical reactions. In this paper we have reported the first joint experimental and theoretical investigations of the bending excitation effects in the $F+CHD_3$ reaction. Contrary to the CH stretch excited reaction, the present QCTs show that the long-range stereodynamical interactions are not significant in the bending-excited reactions. Theory further predicts that the $v_6(e)$ and $v_5(e)$ bending mode excitations promote the DF and HF channels, respectively, and among all bending modes, the $v_5(e)$ excitation increases the reactivity most efficiently. These predictions on the bending mode-selective dynamics await future experimental confirmations. It is also important to emphasize that the experimental cross sections of the bending-excited reaction show peak features especially for $HF(v'=3)+CD_3(v_2=0,1)$, which occur near the thresholds of the same product pairs of the $F+CHD_3(v=0)$ reaction. These peak features cannot be captured by the QCT simulation, indicating possible quantum effects (reactive resonances).

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[32] The harmonic frequency of the reactant ($\omega_5(e)=1316$ cm^{-1}) and the corresponding nondegenerate frequencies,[8] in cm^{-1}, at the saddle-point configurations $D_3\mathbf{CH}$---$\mathbf{F}(C_s)$ (1212, 1230) and $D_2HC\mathbf{D}$---$\mathbf{F}$ (C_s or C_1) (1300, 1331) or (1269, 1343) indicate that the excitation of the $v_5(e)$ fundamental of CHD_3 changes the ground-state vibrationally adiabatic barrier height of the HF channel by (−104, −86), whereas the change is only (−16, +15) or (−47, +27) for the DF channel. Note that the CH stretching excitation decreases the vibrationally adiabatic barrier height for the HF channel even more significantly (by 517 cm^{-1});[7] however, at low E_c, this cannot compensate the long-range steering effect, which strongly favors the CD bonds.