# CH Stretching Excitation Steers the F Atom to the CD Bond in the F + CHD₃ Reaction

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The investigation of the details of chemical reactivity is an active area at the heart of chemistry. One well-established probe of reactivity is the dependence of aspects of the reaction (e.g., rate, branching ratios, final-state distributions, etc.) on the vibrational excitation of the reactants.[1-10] In general, such excitation activates the reaction and, more specifically, the reaction pathway associated with the bond that is excited. Thus, it was quite surprising that vibrational excitation of the CH stretch in the F + CHD₃ reaction, which was recently studied by Liu and co-workers in a crossed molecular beam experiment,[11] suppressed the HF + CD₃ channel. This was of course noted by the authors, who presented a very detailed and thorough investigation of this unexpected result. We investigate this finding theoretically in this communication by performing quasiclassical trajectory (QCT) calculations for the ground state and the CH-stretch-excited F + CHD₃($\nu_1 = 0, 1$) reactions using a recent ab initio full-dimensional potential energy surface (PES).[12] The effect is seen, but it depends sensitively on the initial relative kinetic energy. This dependence is elucidated by examining the details of relevant trajectories, which are governed by the PES and the time scales of the molecular motions.
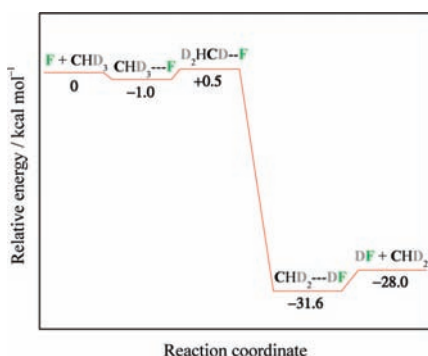
**Figure 1.** Energetics of the F + CHD₃ → DF + CHD₂ reaction relative to F + CHD₃(eq).

A schematic diagram showing the relevant energetics of the PES is given in Figure 1. It contains two van der Waals minima and a low-energy first-order saddle point separating the reactants from the products. Of particular relevance for the present study are the unique arrangements of the H and three D atoms at the saddle points for various channels and the corresponding CH stretch harmonic frequencies (ω_{CH}), which are given in Figure 2. For the HF channel saddle point, ω_{CH} is 2603 cm⁻¹, which is 517 cm⁻¹ smaller than the harmonic CH stretch fundamental ($\nu_1 = 1$) of CHD₃ (3120 cm⁻¹). In contrast, for the arrangements leading to the DF channel, ω_{CH} is larger by 17 and 47 cm⁻¹. Thus, exciting the CH stretch fundamental of CHD₃ decreases the ground-state vibrationally adiabatic barrier height of the HF + CD₃ channel by 517 cm⁻¹ but increases it slightly for the DF + CHD₂ channel. Thus, conventional

transition-state theory would predict an enhancement of H abstraction over D abstraction for the F + CHD₃($\nu_1 = 1$) reaction, in disagreement with the experimental results.[11] Thus, it appears that a dynamical approach to these reactions is necessary to elucidate the experimental finding.

$\omega(CH) = 2603$ cm⁻¹ $\omega(CH) = 3137$ cm⁻¹ $\omega(CH) = 3167$ cm⁻¹
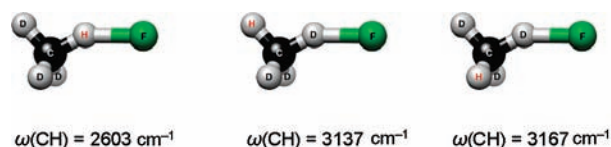
Figure 2. Saddle-point structures of (D₃CH···F)_SP [C_s symmetry] and (D₂HCD···F)_SP [C_s and C_1 symmetry].

Here we report the results of such an approach obtained by performing roughly 6 million trajectories at 10 different collision energies in the range 0.5−7.0 kcal/mol. The initial conditions for these trajectories were the standard ones,[13] and details are given in the Supporting Information (SI). The preparation of the excited vibrational state was based on the harmonic normal mode approximation, and we verified that the CH excitation energy did not leak into the CD mode prior to the collision (Figure S1 in the SI). The first set of results is the DF/HF ratio for the F + CHD₃($\nu_1 = 0, 1$) reactions as a function of collision energy (E_{coll}), shown in Figure 3a. The ratio is for all DF + CHD₂ and HF + CD₃ products obtained by summing over Gaussian-weighted trajectories[14] (details of this weighting procedure as well as results obtained using standard histogram binning are given in the SI). The ratio is significantly greater for the vibrationally excited reaction at low E_{coll} than for the ground-state reaction, in agreement with experiment. As a simple probe of the change in dynamics upon vibrational excitation and the dependence on E_{coll}, we considered the distance of closest approach of the H or D atom to the F atom. This distance was typically close to the HF or DF saddle-point value, and on this basis we could assign nonreactive trajectories to either the
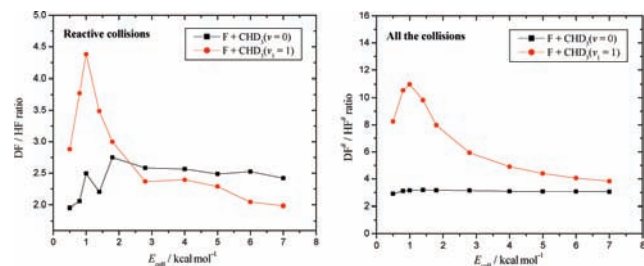
Figure 3. (a) Branching ratios of the reactive collisions forming DF + CHD₂ and HF + CD₃ products as a function of collision energy. (b) Ratios of the F + CHD₃($\nu_1 = 0, 1$) trajectories in which the F atom approaches either the D or H atom in the saddle-point region (indicated by superscript #) as a function of collision energy.

$D_3CH\cdots F$ or $D_2HCD\cdots F$ saddle point configuration. As shown in Figure 3b, in the case of the $F + CHD_3(v = 0)$ reaction, the F atom approaches the D and H atoms as statistically expected, i.e., the ratio is close to 3 and shows only a slight dependence on collision energy. It should be noted from Figure 3a that the DF/HF product ratio is roughly 15% less than this value because of the slightly enhanced probability to abstract the H atom. The picture is substantially different when the reactant CH stretching mode is excited. As shown in Figure 3b, in roughly only 8% of the trajectories does the F atom attack the excited CH bond at $E_{coll} = 1.0$ kcal/mol. The $DF^\#/HF^\#$ ratio decreases with increasing collision energy and appears to approach the statistical ratio at $E_{coll} = 7.0$ kcal/mol (Figure 3b). Therefore, the molecular dynamics simulation clearly shows that the excited CH stretching steers the F atom to one of the CD bonds at low E_{coll} (this is shown in an animation given in the SI, and histogram distributions of the closest HF and DF distances are also given there). We also note that at the lowest E_{coll} (0.5 kcal/mol), the enhancement, while still present for the vibrationally excited reaction, is less than the value at 1.0 kcal/mol. Examination of relevant trajectories indicates significant complex formation at 0.5 kcal/mol due to the van der Waals well in the entrance channel (an animation of a representative trajectory is shown in the SI), and this complex formation undermines the steering effect somewhat.

Another indicator of the change in reaction mechanism with E_{coll} is the $CHD_2(v_1 = 1)/CHD_2(v = 0)$ cross-section ratio for the $F + CHD_3(v_1 = 1)$ reaction, shown in Figure S5. This ratio is greater than 1 (except at the lowest E_{coll}) and increases substantially with E_{coll}. The dominance of the $CHD_2(v_1 = 1)$ channel agrees with experiment.[11] The results described thus far indicate that two effects must be considered in order to understand the bond selectivity of the $F + CHD_3$ reaction. First, a stereodynamical effect steers the trajectories away from the excited CH bond, but second, if the F atom is able to approach the excited CH bond, formation of the $HF + CD_3$ products is promoted.
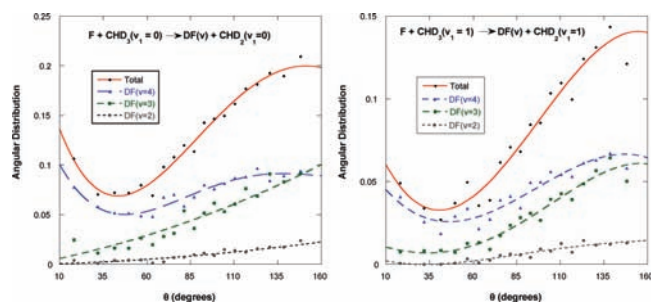
Figure 4. Correlated angular distributions for the $F + CHD_3(v = 0) \rightarrow DF(v) + CHD_2(v = 0)$ and $F + CHD_3(v_1 = 1) \rightarrow DF(v) + CHD_2(v_1 = 1)$ reactions at $E_{coll} = 1.0$ kcal/mol.

The crossed molecular beam experiments also reported the angular distributions of the correlated $DF(v) + CHD_2(v)$ products for the reactions in the ground and vibrationally excited states.[11] We computed these distributions for the $F + CHD_3(v = 0) \rightarrow DF(v) + CHD_2(v = 0)$ and $F + CHD_3(v_1 = 1) \rightarrow DF(v) + CHD_2(v_1 = 1)$ reactions at $E_{coll} = 1.0$ kcal/mol.[15] The results, shown in Figure 4, can be compared to the measured angular distributions at $E_{coll} = 1.2$ kcal/mol (Figure 2 of ref 11). Theory and experiment agree that the angular distributions of the two reactions are very similar. The $DF(v = 2)$ and $DF(v = 3)$ molecules are mainly backward-scattered, whereas $DF(v = 4)$ has significant distributions in the forward direction (this forward scattering is more pronounced in the experiment[11]).

Another direct comparison between simulation and experiment involves the ratio of cross sections of the $F + CHD_3(v_1 = 1) \rightarrow DF + CHD_2(v_1 = 1)$ and $F + CHD_3(v = 0) \rightarrow DF + CHD_2(v = 0)$ reactions. The present computations found this ratio to be $0.3-0.6$ (i.e., less than 1), depending on the binning method (see Figure S6), with a slight E_{coll} dependence. This agrees with the experiment, which reported a ratio of $0.1-0.2$, also with a slight E_{coll} dependence.[11] Therefore, in the case of these specific product channels, the reaction is slower if the reactant CH stretching mode is excited.

We have presented a brief description of a detailed quasiclassical trajectory study of the effect of the CH stretching excitation in the $F + CHD_3$ reaction. The qualitative agreement between the measured and computed correlated angular distributions and state-specific cross-section ratios validates the theoretical approach (i.e., the quasiclassical treatment of the nuclear dynamics and the accuracy of the global PES). Furthermore, theory is able to provide deeper insight into the dynamics by following the pathway of the F atom even in the case of a nonreactive collision. We have found that the CH stretching excitation steers the F atom to the CD bond, which explains the unexpected bond selectivity in the $F + CHD_3(v_1 = 1)$ reaction. This effect is seen especially at low collision energies, where the entrance-channel van der Waals well plays a significant role in the dynamics. Thus, the present QCT study confirms the speculation of Liu and co-workers[11] that "the mechanism is reminiscent of the stereodynamical effect, induced by the anisotropic van der Waals forces in the reactant valley, that was proposed previously for a preferential formation of DCl over HCl in the Cl + HD ground state reaction."[16]

Supporting Information Available: Vibrational frequencies, details of QCT calculations, cross sections, and trajectory animations. This material is available free of charge via the Internet at http://pubs.acs.org.

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