

# How Is C–H Vibrational Energy Redistributed in $F + \text{CHD}_3(\nu_1 = 1) \rightarrow \text{HF} + \text{CD}_3$ ?

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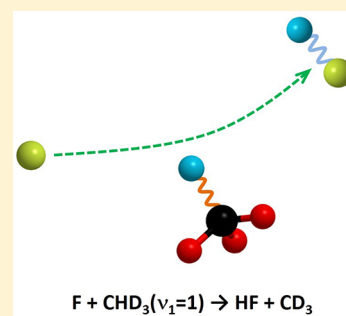
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## S Supporting Information

**ABSTRACT:** The effects of CH stretching excitation on the  $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$  reaction are studied experimentally using crossed-beam and time-sliced velocity map imaging techniques at the collision energy of 9.0 kcal/mol. The fraction of the vibrationally excited  $\text{CHD}_3$  reagent in the crossed-beam region was determined accurately, allowing us to investigate quantitatively the effects of CH stretching excitation on the title reaction. Experimental data show that the vibrational energy in the excited CH bond of  $\text{CHD}_3$  is almost exclusively deposited into the HF product vibration, and hence, the HF products from the excited-state reaction are about one vibrational quantum hotter than those of the ground-state reaction, while the vibrational state distribution of the  $\text{CD}_3$  products is only slightly affected. The reaction is suppressed by the CH stretching excitation, and the overall reactivity of the vibrationally excited reaction is  $74 \pm 4\%$  of that of the ground-state reaction for  $\text{CD}_3(\nu_2 = 0, 1, 2, 3)$  product channels.

**SECTION:** Kinetics and Dynamics



Since Polanyi proposed a set of rules<sup>1</sup> in 1972 on the effectiveness of vibrational and translational energies in promoting chemical reactivity for earlier and later barrier reactions, numerous studies on vibrational excitation effects on chemical reactions have been performed.<sup>2–30</sup> Most studies in the atom-plus-diatom systems confirmed Polanyi's conjecture.<sup>2–4</sup> The extension of Polanyi's rules to polyatomic reaction is, however, not very straightforward. In 2009, Zhang et al. performed a detailed experimental study on the effects of the CH stretching excitation in the early barrier  $F + \text{CHD}_3$  reaction at lower collision energies ( $<4$  kcal/mol).<sup>28</sup> A surprising and counterintuitive result was obtained that the vibrational excitation of the CH bond greatly suppresses the breaking of this bond, causing a much smaller cross section for the  $\text{HF} + \text{CD}_3$  channel. As for the  $\text{DF} + \text{CHD}_2$  channel, the  $\text{CHD}_2(\nu_1 = 1)$  product is enhanced and represents the only pronounced product channel. However, quantitative measurement of the reactivity suppression was not made in this study. This work also concluded that the excited CH bond acts largely as a spectator. A following quasiclassical trajectory study provided a qualitative picture on the dynamics of the CH excitation effect, that is, the CH stretching excitation steers the attacking F atom away to the CD bond, causing a smaller reaction possibility for a trajectory reaching the transition state region of the  $\text{HF} + \text{CD}_3$  channel.<sup>29</sup> According to Polanyi's rules, for an earlier barrier reaction such as  $F + \text{CHD}_3$ , the vibrational energy should be less efficient than the translational energy in promoting this chemical reaction (at the same total available

energy). Even though the vibrational energy is less efficient than the translational energy in promoting reactions with an earlier barrier, conventional wisdom tells us that extra vibrational energy should still help to promote rather than suppress reactions. Therefore, the observation of the strong suppression of the  $F + \text{CHD}_3$  reaction by the CH stretching excitation is truly surprising.

In an attempt to seek a quantitative understanding of this surprising phenomenon, we have carried out an experimental study on the  $F + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$  reaction and its CH stretching excitation effects using the crossed-beams sliced imaging technique. Detailed information on the vibrational excitation effects on the dynamics and reactivity is derived, with the help of the reliable estimation of the infrared (IR) excitation efficiency of the  $\text{CHD}_3$  reagent in the molecular beam, which has always been a challenge in quantitative studies of the vibrational excitation effect in polyatomic reactions. This quantitative study also provides a complete set of experimental results available for comparison with theoretical dynamics studies that are clearly needed to obtain deeper insights into the reaction dynamics of this interesting system.

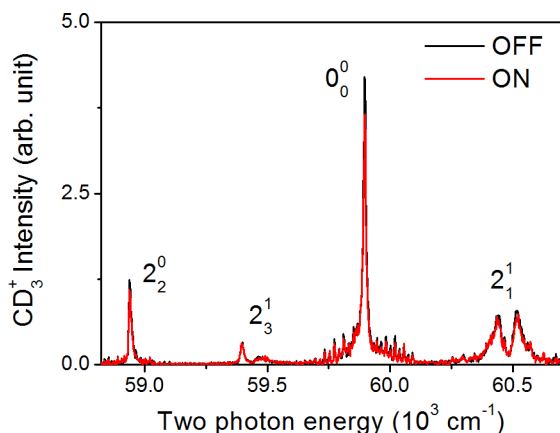
The experiment was carried out at the collision energy of 9.0 kcal/mol with a crossed-beam apparatus using the time-sliced

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velocity map ion imaging technique.<sup>31</sup> The CH stretching excited  $\text{CHD}_3$  reagent was prepared using direct IR absorption, and the nascent  $\text{CD}_3$  products were detected by the  $(2 + 1)$  resonance-enhanced multiphoton ionization (REMPI) method. Figure 1 shows the REMPI spectra of the  $\text{CD}_3$  products from



**Figure 1.** REMPI spectra of the  $\text{CD}_3$  products from the  $\text{F} + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$  reaction when the IR excitation laser was off (IR off) or on (IR on).

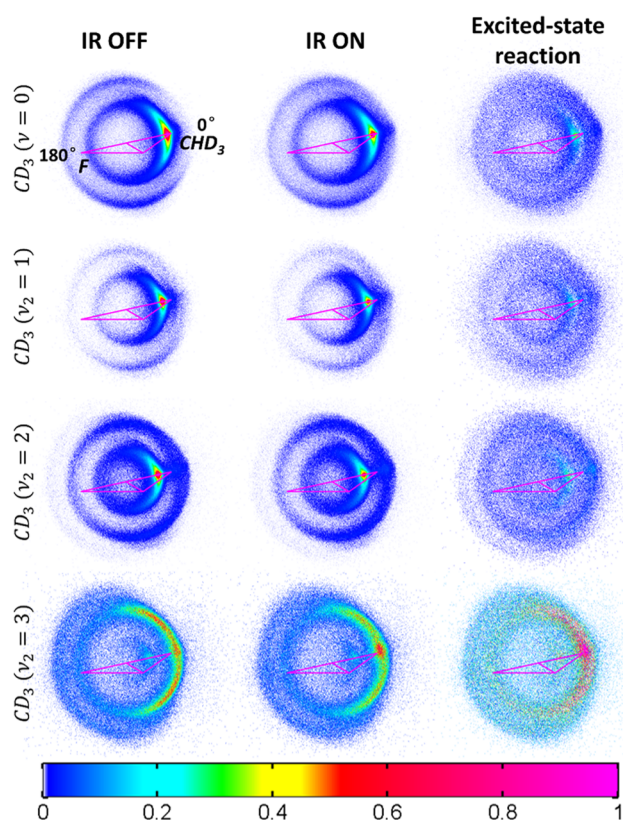
the title reaction when the IR vibrational excitation laser was on or off. The structures in the spectra are all identified and assigned according to previous spectroscopic studies.<sup>32,33</sup> For the ground-state reaction (IR off), only ground-state and umbrella-mode excited (up to  $\nu_2 = 3$ )  $\text{CD}_3$  products were observed. When the IR laser was on, the intensities of all transition bands decreased a certain amount, with no new transition band appearing, indicating overall suppression of the reactivity by the CH stretching excitation of the  $\text{CHD}_3$  reagent. The degree of intensity attenuation shows clear  $\text{CD}_3$  product vibrational state dependence.

More detailed information on the reaction dynamics can be obtained from the images of the  $\text{CD}_3$  products, which were taken by fixing the REMPI laser wavelengths at the peak of corresponding vibronic bands, as shown in Figure 2. The images with IR off represent the results of the ground-state reaction, while the ones with IR on contain contributions from both the ground- and excited-state reactions. The images with IR off and on are quite similar to each other, with only some noticeable differences in the forward direction and also in signal intensities. The similarity between the images with IR on and off indicates that the contributions from the ground- and excited-state reactions are heavily overlapped with each other, suggesting that the angular and translational distributions of the  $\text{CD}_3$  products are similar for the ground- and excited-state reactions. The images for IR on and off can be written as in the following equations

$$\text{IR off: } S_{\text{off}} = S^0 \quad (1)$$

$$\text{IR on: } S_{\text{on}} = (1 - P) \times S^0 + P \times S^\# \quad (2)$$

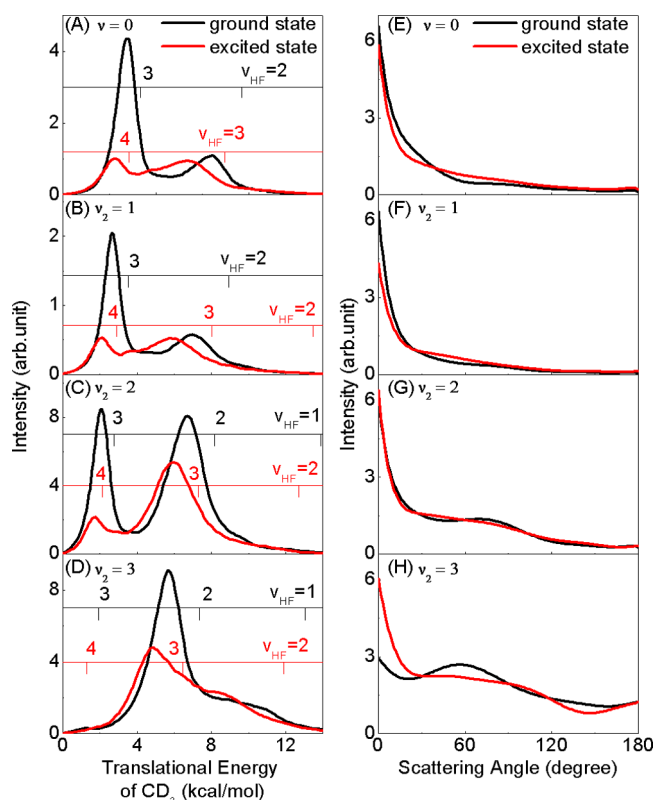
where  $S_{\text{off}}$  and  $S_{\text{on}}$  are the images with IR off and on, respectively.  $S^0$  and  $S^\#$  denote the contributions from the ground- and excited-state reactions, respectively, and  $P$  is the fraction of the excited  $\text{CHD}_3$  molecules in the crossed-beam region, which has been determined to be  $30.3 \pm 3.2\%$  (see details in the Supporting Information). Using eqs 1 and 2, the contributions solely from the excited-state reaction are readily



**Figure 2.** Raw images of the  $\text{CD}_3$  products with the IR laser off and on. The images for the excited-state reaction are derived from the IR off and on images, as shown in the last column. Superimposed on the images are the Newton diagrams.

derived, as shown in the last column of Figure 2. From the images of the ground- and excited-state reactions, detailed information on the dynamics and reactivity is further analyzed in the following paragraphs.

Integrating the images for the ground- and excited-state reactions over the scattering angle or along the radial direction, after the density-to-flux correction,<sup>31,34</sup> we obtained product translational energy and angular distributions for the ground- and excited-state reactions, as shown in Figure 3. The product translational energy and angular distributions for the excited-state reaction are very similar to those from the ground-state reaction, as we alluded to earlier. By conservation of energy and momentum, the translational energy limits of  $\text{CD}_3$  for forming HF coproducts in different vibrational states were calculated and are depicted in Figure 3A–D, for both the ground- and excited-state reactions. For the ground-state reaction, there are clearly two peaks in the translational energy distribution for each  $\text{CD}_3$  vibrational state that correspond to the vibrationally excited HF coproducts at  $\nu = 2$  and 3 for the  $\text{CD}_3(\nu_2 = 0, 1, 2)$  channels and at  $\nu = 1$  and 2 for the  $\text{CD}_3(\nu_2 = 3)$  channel. For the excited-state reaction, there is an extra energy of 8.59 kcal/mol from the CH vibrational excitation into the total available energy. However, the product translational energy distributions for the excited-state reaction are very similar to those from the ground-state reaction but slightly shifted toward the lower kinetic energy for all of the observed  $\text{CD}_3(\nu_2)$  channels. Similarly, the two peaks for the excited-state reaction are assigned to the HF coproducts at  $\nu = 3$  and 4 for the  $\text{CD}_3(\nu_2 = 0, 1, 2)$  channels and at  $\nu = 2$  and 3 for the  $\text{CD}_3(\nu_2 = 3)$  channel. These peaks also become marginally broader,



**Figure 3.** Translational energy distributions (A–D) and angular distributions (E–H) for the  $\text{CD}_3$  products in different vibrational states produced from the ground- and excited-state reactions. The energetic limits for the production of HF coproducts in different vibrational states are also depicted (A–D).

indicating that the rotational excitation of the HF products is slightly higher in the excited-state reaction. These observations lead to a very striking conclusion that the vibrational energy of the excited CH bond is deposited largely into the vibrational energy of the HF products in the excited-state reaction, and hence, the HF products from the excited-state reaction are about one vibrational quantum hotter. The shift of the two peaks toward to lower velocity is simply due to the energy mismatch between the CH and HF vibration energies, with the HF vibration energy larger than that of the CH vibration. This result is very different from the effect on the vibrational state distribution of the  $\text{CD}_3$  products by the CH stretching excitation, which shows very little change, as revealed by the REMPI spectra. Interestingly, the HF products are favorably populated at  $\nu = 3$  in both the ground- and excited-state reactions for all  $\text{CD}_3(\nu_2)$  product channels, except the  $\text{CD}_3(\nu_2 = 2, 3)$  channels of the ground-state reaction.

Using the  $\text{CD}_3$  images acquired for the ground- and excited-state reactions, we also obtained the relative reactivity of the vibrationally excited  $\text{CHD}_3(\nu_1 = 1)$  over the ground-state  $\text{CHD}_3$  by integrating the images after the density-to-flux correction, as summarized in Table 1 for each specific  $\text{CD}_3$  vibrational state. In Table 1, the values are derived by taking  $P$  as 30.3%, and the lower and upper limits of these values correspond to the lower and upper limits of  $P$ , respectively. The reactivity suppression by one quantum of CH stretching excitation of the  $\text{CHD}_3$  reagents is determined to be about 20–40% at the collision energy of 9.0 kcal/mol for different  $\text{CD}_3$  products. The suppression of reactivity is also dependent on the

**Table 1. Relative Reactivity of the Excited-State Reaction over the Ground-State One**

$\text{CD}_3$	relative reactivity (%)	
	from images	from REMPI spectra
$\nu = 0$	$59^{+4}_{-4}$	$69^{+3}_{-3}$
$\nu_2 = 1$	$63^{+4}_{-4}$	$75^{+3}_{-3}$
$\nu_2 = 2$	$64^{+4}_{-4}$	$68^{+3}_{-3}$
$\nu_2 = 3$	$81^{+2}_{-2}$	$84^{+2}_{-2}$

$\text{CD}_3$  product vibrational state, suggesting that the C–H stretching excited reaction produces a slightly different vibrational state distribution for  $\text{CD}_3$ .

The reactivity suppression by the CH stretching excitation obtained above is only valid for certain  $\text{CD}_3$  rotational levels in different vibrational states because the REMPI laser wavelengths were fixed at the peak of each vibronic band when these images were taken. Therefore, the REMPI detection only covers a few rotational states of the  $\text{CD}_3$  products within the bandwidth of the laser pulse. As a consequence, the reactivity of the excited-state reaction derived from these images only represents an average on a few rotational states of  $\text{CD}_3$ .

We now determine the relative reactivity from the REMPI spectra for all detected product channels. Because the images with IR on and IR off are quite similar, the relative integrated signal of the images for the excited- and ground-state reactions should not be affected considerably by the density-to-flux correction.<sup>35</sup> Therefore, we can also use the REMPI spectra with IR on and off to determine the reactivity of the excited-state reaction over the ground-state one. The estimation of relative reactivity averaged on all observed rotational states for a specific vibrational state  $\text{CD}_3$  was done by integrating the REMPI spectra over the whole vibronic band, as summarized in the last column of Table 1. These relative reactivities of the excited-state reaction over the ground-state reaction are all slightly higher than those derived from the images, suggesting that the reduction of excited-state reactivity is smaller for higher rotationally excited  $\text{CD}_3$  products. We have also obtained the overall reactivity of the excited-state reaction relative to the ground-state reaction by averaging over all observed vibrational states of the  $\text{CD}_3$  products. In this analysis, we assume that the REMPI detection efficiency is the same for all  $\text{CD}_3$  vibrational states. With this assumption, the overall reactivity of the CH stretching excited  $\text{CHD}_3$  reaction with the F atom is determined to be  $74 \pm 4\%$  of that of the ground-state reaction. This means that the overall suppression of the  $\text{F} + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$  reaction by the CH stretching excitation is only about 26%.

In conclusion, we have performed a detailed experimental study on the effect of the CH stretching excitation in the  $\text{F} + \text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$  reaction at the collision energy of 9.0 kcal/mol. Detailed information on the effect of the C–H stretching excitation of  $\text{CHD}_3$  on the dynamics and reactivity of the title reaction is derived by accurate determination of the fraction of the excited-state  $\text{CHD}_3$  reagent in the crossed-beam region. Experimental results show that the vibrational energy in the excited CH bond of  $\text{CHD}_3$  is mostly deposited into the HF product vibration, while the vibrational state distribution of the  $\text{CD}_3$  products is only slightly affected by the CH stretching excitation. It is also shown that the overall suppression of reactivity by the CH stretching excitation is about 26%, with a clear dependence on the specific  $\text{CD}_3$  product vibrational state.



## EXPERIMENTAL METHODS

The experiment was carried out on the crossed-beam apparatus<sup>31</sup> in combination with time-sliced velocity map ion imaging and (2 + 1) resonance-enhanced multiphoton ionization (REMPI) techniques. In brief, an intense F atom beam was generated by discharge of the expanding gas sample of F<sub>2</sub> in He (5% seeded in helium at 5 atm, Spectra Gases, Inc.) using a double-stage discharge setup.<sup>36</sup> The CHD<sub>3</sub> beam was generated from the supersonic expansion of neat CHD<sub>3</sub> gas at 5 atm (Cambridge Isotope Laboratories, Inc.). Both beams passed a skimmer before entering the reaction/detection chamber and crossed with each other at the center of the ion optics. The crossing angle between the two beams was fixed at 145°, corresponding to a collision energy of 9.0 kcal/mol. The CD<sub>3</sub> product was ionized by the (2 + 1) REMPI method via the 3p<sub>z</sub> Rydberg state<sup>32,33</sup> and recorded via the ion imaging system. The laser pulse used for the REMPI detection scheme was around 333 nm with a pulse energy of about 6 mJ, which was generated from the frequency-doubled dye laser output pumped by a Nd<sup>3+</sup>:yttrium aluminum garnet (YAG) laser at 532 nm and focused by an f/160 spherical focusing lens. A tunable IR laser pulse with a beam size of about 5 mm was guided into the CHD<sub>3</sub> source chamber to excite molecules from the ground vibrational state ( $\nu = 0, j = 1$ ) to the vibrationally excited state ( $\nu_1 = 1, j = 2$ ) via the R(1) rotational line.<sup>37</sup> In order to enhance the pumping efficiency, the IR laser was reflected many times by a polished copper ring, which was fixed just in the front of the skimmer.<sup>38</sup> The images were taken alternatively with IR off and on every 200 laser shots in order to minimize the statistical uncertainty and long-term drift. For the REMPI spectra measurements, the detector was operated in the “crushing imaging” mode, where the whole 3D distribution of ions was projected on the detector and recorded, while for imaging taking, the detector was operated in the time-sliced imaging mode while the REMPI laser wavelength was fixed at the peak of the corresponding vibronic band. About 0.5 million counting events were accumulated in each image. Background signals were also acquired and subtracted from these images.

## ASSOCIATED CONTENT

### Supporting Information

Detailed derivation of the fraction of CH stretching excited CHD<sub>3</sub> reagent in the crossed-beam region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

§J.Y. and D.Z. made similar contributions to this work.

### Notes

The authors declare no competing financial interest.

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