Electronic supplementary information

for

"CH Stretching Excitation Promotes its Cleavage in F + CHD$_3$(ν_1=1) → HF + CD$_3$ Reaction at Low Collision Energies"

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The CH stretching excitation effects on the CD$_3$ products translational energy and angular distributions.

Integrating the images (Fig. 2) for the ground- and excited-state reactions over the scattering angle or along the radial direction weighted by the appropriate Jacobians, after density-to-flux correction,[1] we obtained product translational energy and angular distributions for the ground- and excited-state reactions at collision energy of 1.21 kcal/mol, as shown in Fig. S1 and S2 respectively. The energetic limits for HF coproducts in different vibrational states are calculated and depicted, by employing conservation of energy and momentum. From Fig. S1 and S2 it is clear that the CD$_3$ translational energy and angular distributions are largely similar for the ground- and excited-state reactions, as suggested by the visual inspection of the images. While in the ground-state reaction, the HF products are mainly produced at v=2, with minor contributions from lower vibrational states. In the excited-state reaction, the HF products are mainly produced at v=3. In another word, the HF products from the excited-state reaction are about one vibrational quantum hotter than those from the ground-state reaction, suggesting 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, leaving the recoiling speed of the reaction products largely unaffected. This total transfer of the vibrational energy of the excited reagent exclusively into the vibrational excitation of one of reaction products was also observed in the title reaction at collision energy of 9.0 kcal/mol and other reaction systems.[2,3]
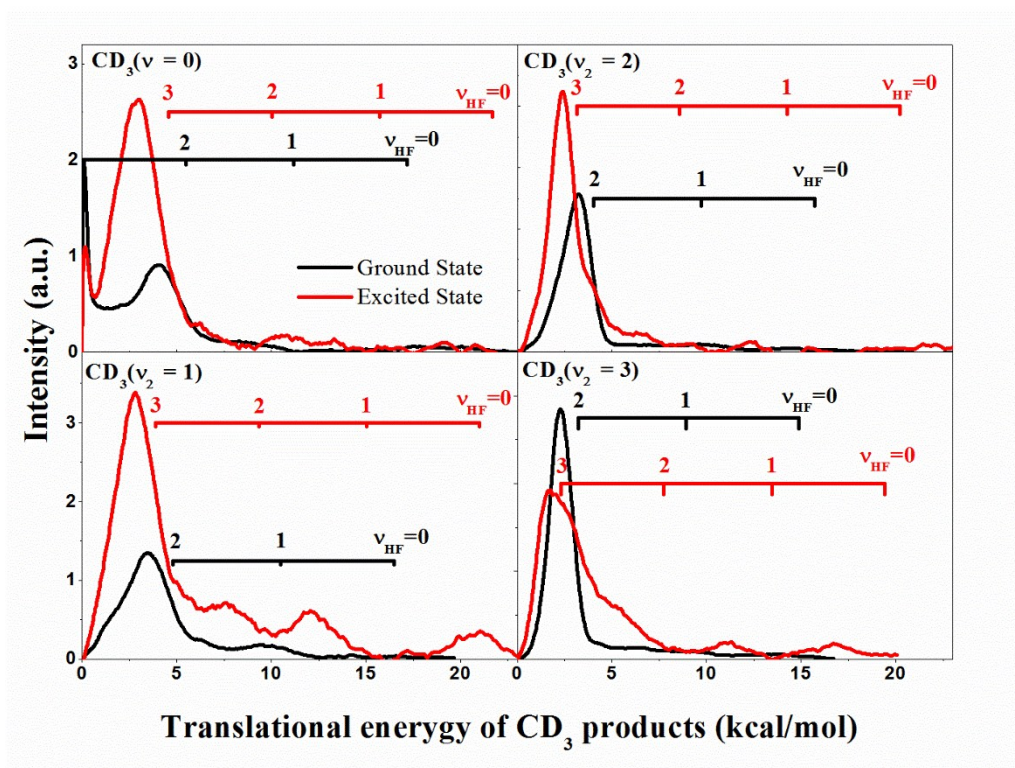
Figure S1. The translational energy distributions of CD_3 products at different vibrational states for both ground- and excited-state reaction at 1.21 kcal/mol. The relative intensities between the ground- and excited-state reactions are scaled for each specific vibrational state of the CD_3 products, according to the relative reactivities (Table 1). The energetic limits for the production of HF coproducts in different vibrational states are also depicted.
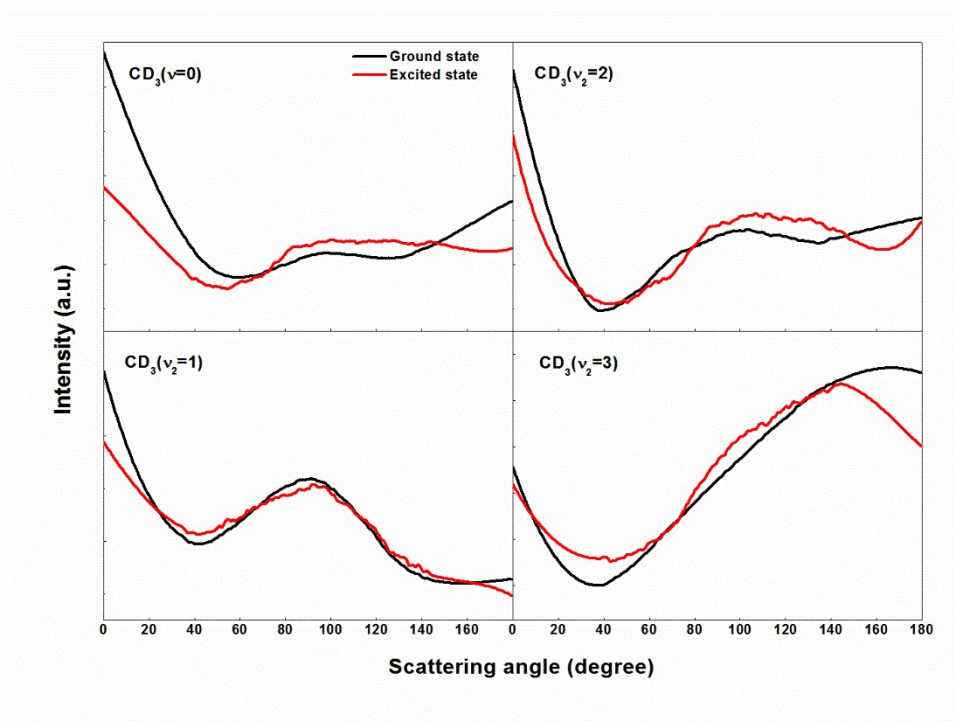
Figure S2. The angular distributions of CD_3 products at different vibrational states for both ground- and excited-state reaction at 1.21 kcal/mol. All the curves are scaled to have the integral cross section of 1.

The CD$_3$ product vibrational state-specific excitation functions for the ground-state reaction.

The state-specific excitation functions for the formation of CD$_3$(v_2=0-3) products in the ground-state reaction were measured over the collision energy range between 1.21 and 10.75 kcal/mol. In order to cover such a broad collision energy range, both F atom and CHD$_3$ molecular beams were operated in two different ways: the F atom beam of two different speeds was generated by discharge of the expanding gas mixture of F$_2$ with helium or neon (5% seeded in helium or neon at 5 atm, Spectra Gases, Inc.) using a double-stage discharge setup;[4] the CHD$_3$ beam was generated from the supersonic expansion of neat CHD$_3$ gas or a gas mixture of 20% CHD$_3$ seeded in helium (Cambridge Isotope Laboratories, Inc.) at 6 atm using an Even-Lavie valve. The fine tuning of the collision energy was achieved by changing the crossing angle between two beams. Four different combinations of two molecular beams were used to cover the whole collision energy range investigated, each covering a short collision energy range. There was at least one overlapped collision energy between neighboring collision energy ranges in order to link them together. At each collision energy range, images at different collision energies were taken by changing the crossing angles back and forth a few times in order to minimize the short term fluctuation and long term drift. The resonance-enhanced multiphoton ionization (REMPI) laser wavelength was fixed at the peak of each corresponding vibronic bands during image acquisition. A density-to-flux transformation was then performed for the image at each collision energy to correct the inhomogeneous detection issue. The excitation functions derived in such way are shown in Fig. S2 for each of the four vibrational states of the CD$_3$ products observed in the experiment. The four excitation functions have been normalized to one another by setting the values at 8.7 kcal/mol

matching with the relative reaction cross sections of these four vibrational states of CD_3 products at this collision energy. The shapes of the excitation functions show a clear dependence on the vibrational state of CD_3 products. While the reaction cross section for the ground state rises rapidly from threshold and then decreases slowly at higher collision energies. The vibrationally excited CD_3 products display a more gradual increase with the increase of collision energy and then the reaction cross-sections start to decrease at a much higher collision energy.
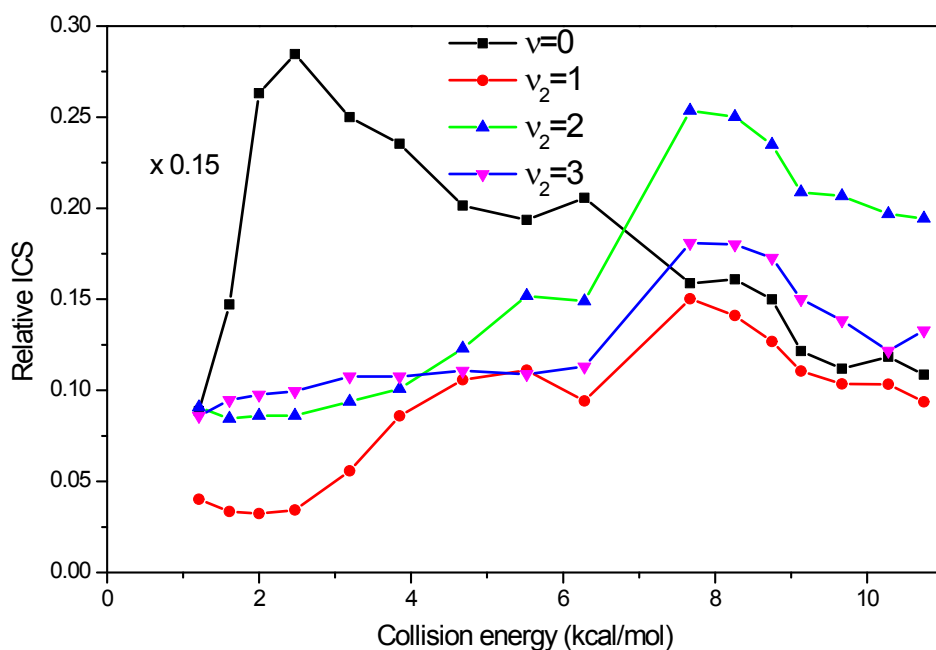

Figure S2. Vibrational state-specific excitation function for formation of $CD_3(v_2=0-3)$. The relative values between different vibrational states are scaled according to the relative image intensities.

References

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