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Observation of a reactive resonance in the integral cross section of a six-atom reaction: F+CHD₃

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The title reaction was investigated under crossed-beam conditions at collisional energies ranging from about 0.4 to 7.5 kcal/mol. Product velocity distributions were measured by a time-sliced, velocity-map imaging technique to explicitly account for the density-to-flux transformation factors. Both the state-resolved, pair-correlated excitation functions and vibrational branching ratios are presented for the two isotopic product channels. An intriguing resonance tunneling mechanism occurring near the reaction threshold for the $HF+CD_3$ product channel is surmized, which echoes the reactive resonances found previously for the $F+HD \rightarrow HF+D$ reaction and more recently for the $F+CH_4$ reaction. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1761051]

I. INTRODUCTION

One of the most fascinating subject in reaction dynamics has been the role of dynamical trapping in the vicinity of the transition state of the reaction.[1–4] This trapping can be traced to the existence of reactive or Feshbach resonances,[2–5] or to the slowing down of motion along the reaction coordinate near the top of an adiabatic barrier—a phenomenon normally associated with the vibrational threshold with large angular momenta in the transition state region.[1,6–8] The underlying physics of these two trapping mechanisms are different (see for example Fig. 2 of Ref. 2),[8] though their distinctions are often blurred. There are a number of well-established theoretical methods, such as L^2-stabilization techniques,[9,10] time-delay analysis,[11–13] and the spectral quantization method,[14] etc., which can be used to decipher the existence of a reactive resonance or not. The experimental observation of the resonance is, however, much more challenging. The main obstacle is not merely a technical experimental issue, but rather the lack of the knowledge of a unique and identifiable resonance fingerprint in experimental observables. To state it in simple terms, the dynamics of a full collision reaction will inevitably involve many partial waves corresponding classically to a range of impact parameters. Owing to the short-lived nature of resonance states, any resonance, which always occurs as a rotational progression of many partial waves, will generally be spaced by energies far less than the resonance widths—thus, sometimes referred to as "broad resonance."[15] Consequently, even in an experiment with a well-defined collision energy, E_c, the resonance feature could be smeared out over a broad energy range making it difficult to unambiguously identify resonance fingerprints in the integral cross section (ICS) measurements.[15,16] Although this impact parameter averaging will be partly lifted when the state- and angle-resolved quantity is examined, the aforementioned adiabatic threshold effect[6–8] could also yield structures in this highly resolved quantity,[17–22] masking the resonance imprints in experimental observations.

At this point in time, the only unequivocal evidence for a reactive resonance in a full collision experiment is that for the $F+HD \rightarrow HF+D$ reaction.[5,14,23–26] In these reports, several identifiable resonance imprints in experimental observables were suggested and elucidated. Concurrent theoretical simulations and analyses not only confirmed the experimental conjectures, but also provided deeper insights into the nature of this resonance state. For the integral cross sections, a distinct step for $E_c \lesssim 1$ kcal/mol was observed in the reactive excitation function for the $HF+D$ product channel, whereas it is entirely absent for the other $DF+H$ channel.[14] Anomalous collision energy dependence of the HF vibrational branching was also observed. In fact, the state-specific excitation function for $HF(v'=2)$ features a step-like structure span from 0.2 to 1 kcal/mol, while $HF(v'=3)$ is characterized by a broad peak starting from its energetic threshold ~1.16 to about 3 kcal/mol.[24] Two striking signatures for resonance were also identified in the total angular distribution. In the three dimensional plot of $\sigma(\theta,E_c)$-θ-E_c, a ridge structure is formed at low energy, and highly oscillatory forward-backward peaking appears at higher collision energy.[23] In terms of state- and angle-resolved quantity, it was found that in the resonant tunneling regime the $HF(v'=2, j')$ products are characterized by a bimodal rotation distribution which exhibits complicated, fast-evolving angular distributions with respect to both the final j' states and the initial collision energies.[25,26] All of these are unveiled from a single reaction system. Since every chemical reaction has its own characteristics, it is not clear how general those resonance signatures are—namely, will the similar features manifest in the other chemical reactions? Or are they just the resonance fingerprints for that particular reaction?

In a recent report the first experimental evidence for detecting reactive resonances in a polyatomic reaction was

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suggested.[27] Near the reaction threshold of $F+CH_4 \rightarrow HF +CH_3$, several remarkable observations were uncovered. A significant reactivity, occurring only near the threshold, for the formation of the high-frequency symmetric stretch mode of the $CH_3(v_1=1)$ product was discovered. Its coincident co-product is highly state specific of $HF(v'=2)$, and the angular distribution is characterized by a distinct forward scattered peak. Moreover, at low collision energies the concomitant $HF(v'=2,j')$ states to the vibrational ground state CH_3 $(v=0)$ product exhibit a bimodal rotation distribution up to the energetic limit, in sharp contrast to the low rotation excitation observed for this reaction at higher collision energies and for the isotopic reaction of $F+CD_4 \rightarrow DF+CD_3$.[28,29] And the angular distributions of those high j' states of the $HF(v'=2)+CH_3(v=0)$ product pairs also display a clear preference for forward scattering. A resonant tunneling mechanism analogous to the $F+HD \rightarrow HF+D$ reaction,[23,25] in conjunction with a competing intramolecular energy redistribution (IVR) within the transient resonant complex, was proposed to rationalize those anomalies.[27]

Reported here is the investigation of the $F+CHD_3$ reaction. Only the ICS aspects will be presented, the detailed analysis of the differential cross section is currently in progress. As will be shown, similar observations in ICS as those found previously for the $F+HD$ reaction[14,22] were discovered. We assert the existence of reactive resonances in the title reaction, which echoes our recent claim for the $F +CH_4$ reaction[27] although the resonance in the latter reaction manifests itself in very different dynamical attributes— rather than from the appearance of the excitation function as in the present reaction.

II. EXPERIMENT

The experiment was carried out using a rotating-sources, crossed-beam apparatus. The experimental details and procedures have been described previously,[30,31] therefore, only the relevant features are presented here. A double-skimmed F-atom beam was generated by discharging a F_2/rare-gas mixture at the nozzle of a pulsed valve. Typically, a 5% F_2 mixture in Ne or He was used in this work. The measured speeds of the F-atom beams are 1.13 and 1.62 km/s, respectively, which in turn can cover two ranges of collisional energies, 0.43–4.4 and 2.3–8.2 kcal/mol, for the present reaction. Fine tuning of the collision energy was achieved by rotating the source chambers to change the intersection angle of the two molecular beam velocity vectors. A double-skimmed CHD_3 beam was generated by expanding neat CHD_3 gas (Cambridge Isotope Inc., 99%) through a fast solenoid pulsed valve (Evan-Lavie valve).[32]

The product of methyl radicals was detected by using a $(2+1)$ resonance-enhanced multiphoton ionization scheme via the $3p_z$ intermediate state.[28,29,33] The Q branch of the 0_0^0 vibronic transition was used to select the ground vibrational state of CHD_2 or CD_3, for which the sampling of the rotational states is approximately averaged by scanning the laser frequency back and forth over the Q branch spectral profile. This rotational averaging is weighted by the transition line strengths, and the results will be somewhat different from those by the partial rotational selection (i.e., laser frequency fixed) in previous studies.[28–30,34]

The velocity distribution of the ground vibrational state of the methyl products was measured by a time-sliced, ion-velocity imaging technique.[30] The recorded image corresponds to the central slice of the velocity Newton sphere, which represents the product velocity distribution as $d^3\sigma/dv_x dv_y dv_z$. As detailed previously,[31] to normalize the relative signals at different collisional energies, a series of ion images without time slice were also independently recorded using a sufficiently wide time gate of the detector. This mode of operation requires only several minutes of accumulation for each image, thus minimizes the possible long-term drift problems. The apparent reaction cross sections were then obtained by dividing the total ion counts of the wide-gated images by the relative velocity of the two reactants. A density-to-flux correction[30] was then performed for the time-sliced image at each collisional energy to recover the true excitation function. Several efforts were taken to make the density-to-flux transformation more robust, including the use of an artificial laser sheet,[30] proper selection of the time-slicing gatewidth,[31] etc. The errors of raw images from repeated measurements were typically within 5%. Considering the possible uncertainties in the density-to-flux transformation and from the partition of the ring structures, we estimated the overall errors in the reported ICS are within $\pm 10\%$, which is also evidenced from the scatterings of the data points to be presented later.

III. RESULTS AND DISCUSSION

A. Pair-correlated excitation functions— resonance signatures

Exemplified in Figs. 1 and 2 are a few raw ion velocity images of the two isotopic product channels. The images recorded with and without time slicing in a back-to-back manner are presented. By conservations of energy and momentum, the ring-like features in the images of Figs. 1 or 2 can readily be assigned to the coincidently formed vibration states of the HF or DF products, respectively. Clear separations of the vibrational rings allow us to partition the correlated vibrational states without ambiguity. At low collisional energies, even the rotational levels of the HF coproducts can be resolved from the velocity images of CD_3^+, as demonstrated in Fig. 1(c). The raw images display a slight asymmetry around the initial relative velocity vector that lies horizontally in the figures. It reflects the effect of the nonuniform sensitivity of detecting the reactive events. With the density-to-flux correction, the cylindrical symmetry about the relative velocity is recovered. Nonetheless, as is evident from Figs. 1 and 2, even a casual inspection of the raw images can qualitatively reveal the angular distributions of the correlated product pairs. (The relative velocity lies horizontally and the forward direction is to the left.) The more detailed analysis of DCSs and possible interpretations are in progress. Figures 1(f) and 2(f) summarize the collisional energy dependences of the apparent cross sections of the two isotopic channels.

With the density-to-flux correction to each image, the "true" excitation functions of the two isotopic channels can
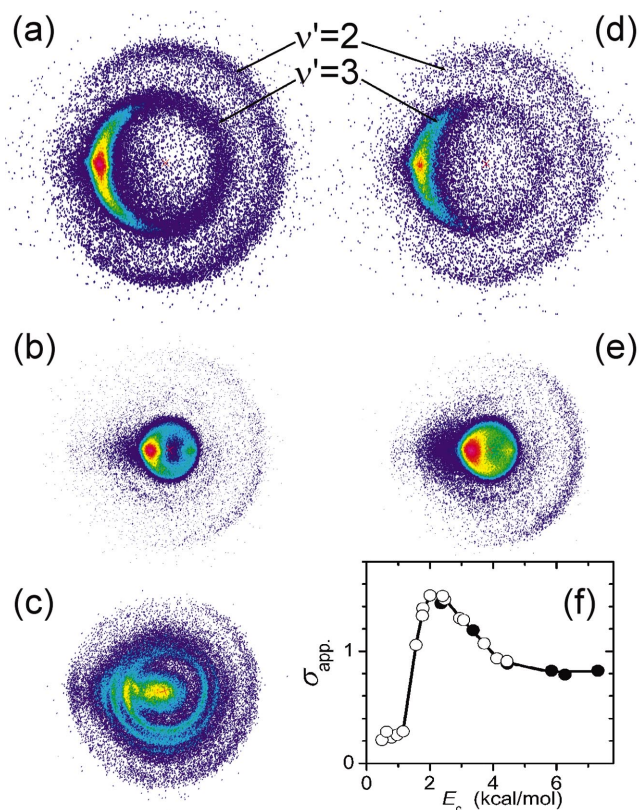
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FIG. 1. (Color) Exemplified in (a)–(c) are the time-sliced raw images for probing the CD$_3$(v=0) state at E_c=6.3, 2.0, and 0.97 kcal/mol, respectively. A gatewidth of 30 ns was used. Shown in (d) and (e) are the same as (a) and (b), respectively, but without time slicing (230 ns gatewidth). The apparent excitation function for the F+CHD$_3$→HF+CD$_3$(v=0) reaction is summarized in (f). The symbols are: ○ for Ne as the carrier gas of the F-atom beam source, and ● for He as the carrier gas. The line is to guide the eyes.
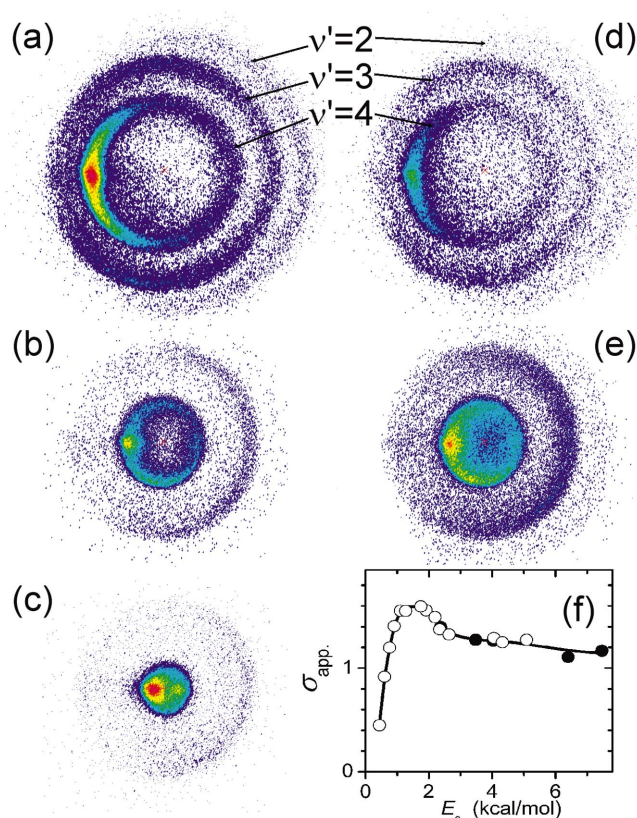
FIG. 2. (Color) Similar to Fig. 1, except for probing the CHD$_2$(v=0) state at E_c=6.4, 2.2, and 0.91 kcal/mol, respectively. Note that the apparent cross sections of this isotopic channel of F+CHD$_3$→DF+CHD$_2$(v=0) are scaled to Fig. 1(f) according to their relative signal strengths under otherwise identical conditions.

then be obtained[31] and the results are shown in Fig. 3. Compared to the apparent excitation functions shown in Figs. 1(f) and 2(f), the effects of the density-to-flux correction are discernible. For the HF+CD$_3$ channel the effect is noticeable, albeit relatively minor. On the other hand, the correction factor becomes quite significant for the DF+CHD$_2$ channel— changing the excitation function into an entirely different shape [see Fig. 2(f) versus Fig. 3(b)]. The two product channels display significantly different features. For the DF +CHD$_2$(v=0) product channel, the excitation function rises almost linearly after the reaction threshold, followed by an intriguing change in slope. Its appearance is somewhat at variance with the previous report on the F+CD$_4$→DF +CD$_3$(v=0) reaction.[30]

As to the HF+CD$_3$(v=0) channel, the excitation function is characterized by a distinct finite step at low collisional energies, which followed by an abrupt rise near 1.2 kcal/mol. It is interesting to note that the onset of the finite step in the HF+CD$_3$ channel occurs around the same energy as where the excitation function for the DF+CHD$_2$ channel displays a kink in shape. The behavior of the HF+CD$_3$ channel, particularly near the threshold region, is very different from the DF+CHD$_2$ channel, as well as from the reactions of F +CH$_4$→HF+CH$_3$[31] and F+CD$_4$→DF+CD$_3$.[33] Instead, the step-like feature near threshold is strongly reminiscent of

the F+HD→HF+D reaction,[14] for which the resonance tunneling has been shown to be the sole contribution at low collision energies of 0.4–1.2 kcal/mol.[14,25] In an early theoretical investigation of the Cl+HCl→ClH+Cl reaction,
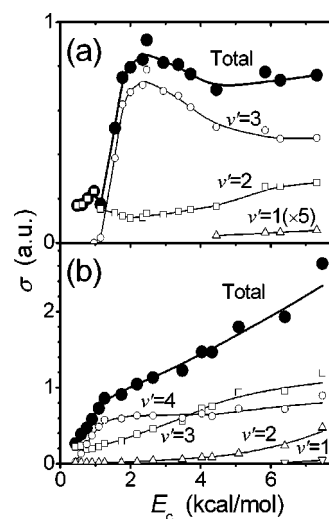

FIG. 3. Depicted in (a) and (b) are the excitation functions of F+CHD$_3$ →HF(v')+CD$_3$(v=0) and F+CHD$_3$→DF(v')+CHD$_2$(v=0), respectively. The vibrational state-specific excitation functions for the HF or DF coproducts are also shown. The lines are to guide the eyes. The relative cross sections of the two isotopic channels have been normalized to each other, except the unknown detection sensitivity factors.

Schatz *et al.* also observed the step-like behavior in the integral cross sections and attributed it to the influence of transition state resonances in that reaction.[35] In retrospect, the connection from an isolated resonance to a step-like feature, rather than a peak or a dip, in the reactive excitation function is not difficult to comprehend. In the absence of the direct scattering component, the reactivity originates from many resonance partial waves—each is characterized by a resonant Lorentzian-like peak—that form a rotational progression. It is then the overlaps of those Lorentzian profiles giving rise to the step-like feature in ICS.[14]

Similar mechanism is proposed here. Energetically, the endothermic $HF(v'=3)+CD_3(v=0)$ channel becomes accessible for $E_c \gtrsim 1.14$ kcal/mol. From the vibrational state resolved excitation functions shown in Fig. 3(a), it is clear that once the $HF(v'=3)+CD_3(v=0)$ channel opens up energetically, its formation rises very rapidly—indicating no exit channel barrier, while that of $HF(v'=2)+CD_3(v=0)$ displays small variations. A closer inspection suggests that the energy dependence of the $v'=2$ channel appears to consist of two parts: the resonant scattering component at lower E_c and predominantly the direct over-the-barrier mechanism for $E_c \gtrsim 2$ kcal/mol. By comparison, the reactivity to form $HF(v'=3)$ in the present reaction is much more significant than the F+HD reaction, for which the $HF(v'=2)$ product has a higher yield than $HF(v'=3)$ over the entire energy range of the investigation (0.4–4.6 kcal/mol).[24] Apparently, the substitution of the D atom of the HD reactant by a CD_3 moiety makes the reaction more heavy-light-heavy alike, and causes a dramatic change in the vibrational branchings of the newly formed HF products. The exact nature of this difference is, however, unclear: Either from the relative contributions of the resonant mechanism versus the direct scattering component or from the different partial widths of the intricate resonance decays into product vibration states, or both.

Examining the images for the $HF+CD_3$ channel at low energies [for example, Fig. 1(c) for one E_c] revealed that the product velocity distributions are strikingly similar to those of $F+CH_4 \rightarrow HF(v')+CH_3(v=0)$ for $E_c \lesssim 1$ kcal/mol.[27] In both cases, high rotation states, up to the energetic limit, of $HF(v'=2)$ are formed with strong preference toward the forward direction, which is distinctly different from those at higher E_c.[28,29,31,34] By analogy to the $F+CH_4$ case,[27] the resonance state in the present reaction is tentatively assigned as three quanta in the H–F stretching mode and zero quanta for all other modes in the local mode representation.

One of the most surprising and remarkable findings in the studies of the $F+CH_4$ reaction is the observation of symmetric stretching excited CH_3 products, the $v_1=1$ state,[27] near the reaction threshold. Searching for the stretching excitations of CD_3 and CHD_2 products from the present reaction failed. This negative result is not totally unexpected from the proposed resonance scenario. The formation of the $CH_3(v_1=1)+HF(v'=2)$ product pairs from the $F+CH_4$ reaction was previously interpreted as a result of the combination of a resonance state formation ($F\cdots H\cdots CH_3$, with 3 quanta in the F–H stretch and zeros for all other modes) and a restricted IVR process in competition to the resonance decay of the transient collision complex.[27] Replacing the CH_3

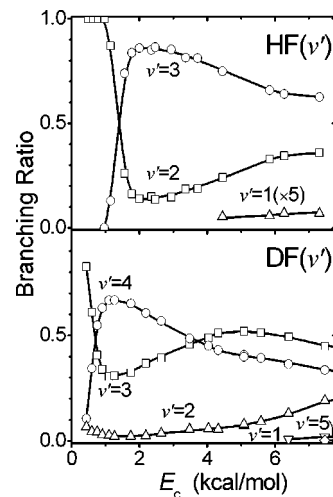FIG. 4. The correlated vibrational branching ratios as a function of collisional energy for the $HF(v')+CD_3(v=0)$ and $DF(v')+CHD_2(v=0)$ product channels in the upper and lower panels, respectively.

moiety by either CD_3 or CHD_2 pushes the vibrationally adiabatic surface, which leads to the $v_1=1$ methyl products, significantly away from that correlated to the resonance state, thus, reducing the coupling strength between the two adiabatic surfaces and making the competing IVR unfavorable.

Another quantity of considerable interests is the isotopic branching ratio of the two product channels. Unfortunately, the spectroscopic detection efficiencies of $CD_3(v=0)$ and $CHD_2(v=0)$, which depend on the unknown Franck–Condon factors and the isotope-dependent predissociation of the intermediate states, are difficult to be quantified. Aside from the uncalibrated detection efficiency factors, the excitation functions shown in Fig. 3 have, nonetheless, been scaled according to their relative signal strengths for future comparisons.

B. Correlated vibrational branching ratios

Figure 4 depicts the collisional energy dependences of the correlated vibrational branching ratios of the two isotopic product channels. Both channels exhibit strong preference for high vibrational states of HF and DF, which is expected from either the proposed resonance mechanism[24,27] or the direct scattering mechanism of a highly exoergic reaction with an early barrier.[36] Because of the dominance of the two highest vibrational states for both isotopic channels over the entire energy range of this study, the product vibrational branching ratios are overwhelmed by the behaviors of these two states, forming a mirror image as seen in Fig. 4. The lower vibrational states, i.e., the minor channels of $HF(v'=1)$ and $DF(v'=1)$, can only be observed at higher collisional energies, and their contributions increase slightly as the collisional energy increases. As seen from Figs. 1 and 2, these lower vibrational states are formed preferentially in the backward hemisphere, for which collisions with small impact parameters should dominate in a direct reaction. The combination of the collisional energy dependence and the angular distribution will then suggest that the lower HF/DF vibrational states are produced mainly through a direct re-
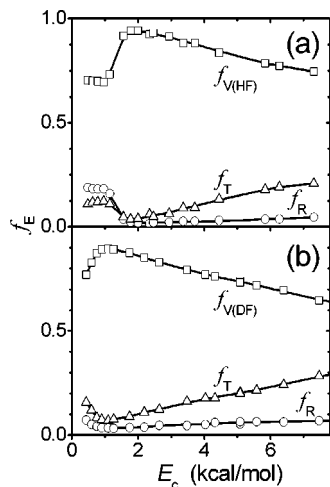
FIG. 5. Summary of the collisional energy dependencies of the fractional energy disposals of correlated product pairs for (a) HF(v')+CD$_3$($v=0$) and (b) DF(v')+CHD$_2$($v=0$) channels. Note that f_R is deduced from the energy conservation relationship, $f_R=1-f_V-f_T$, and contains the rotational energies of both product rotors in this report.

bound mechanism, for which the line-of-center forces are stronger. This is a general trend observed in the F-atom reactions with methane and its isotopic variants.[28–31,34]

As to the CHD$_2$($v=0$)+DF($v'=2$) product pair, its branching ratio for $E_c \gtrsim 1.5$ kcal/mol displays a mild increase as E_c increases—similar to the behaviors for DF($v'=1$) and CD$_3$($v=0$)+HF($v'=1$). The amount of this increase is at the expense of the adjacent higher vibrational state, DF($v'=3$). For $E_c \lesssim 1.2$ kcal/mol, however, its branching ratio exhibits an opposite energy dependency. And the onset of this low-energy behavior coincides with the abrupt changes in branching ratios for DF($v'=3$) and DF($v'=4$). Interestingly, this onset energy is also where the total excitation function shows a change in slopes [see Fig. 3(b)]. Energetically, there is nothing special around $E_c \sim 1.2$ kcal/mol for the CHD$_2$+DF channel. On the other hand, it is near the energetic threshold for CD$_3$($v=0$)+HF($v'=3$) that is, however, a chemically different channel. The exact origin of those observations, fortuitous or not, is yet unclear at the present time.

C. Correlated energy disposals

Figure 5 shows the collisional energy dependences of the fractional energy disposals of the correlated HF/DF vibrational energy, the product translational energy, and the rotational energy. Both f_V and f_T are obtained directly from the image analysis, whereas f_R is deduced from energy conservation, $f_R=1-f_V-f_T$. Since the CD$_3$ or CHD$_2$ rotational distributions are approximately sampled in this study, the quantity of f_R is best regarded as the sum of the two product rotors. For these averaged quantities, similarity between the two channels is noted. In particular, except near thresholds, f_R always remains small and nearly invariant to collisional energies. As a consequence, the two remaining degrees of freedom, f_V and f_T, display an anticorrelated behavior.

As shown previously for the F+CD$_4$ reaction, the propensity of $\Delta E_c \sim \Delta E_T$ holds.[37] Similar behavior is seen here

for both product channels at higher collisional energies, which results in a roughly linear rise of f_T for $E_c \gtrsim 2$ kcal/mol. Higher vibrational energy disposals are observed at lower collisional energies unless the highest vibrational levels become energetically closed. For example, as shown in Fig. 3(a), $\sigma_{HF(v'=3)}$ drops sharply for $E_c \lesssim 2$ kcal/mol, while $\sigma_{HF(v'=2)}$ remains about flat. The step shape of $f_{V(HF)}$ simply reflects the particular shapes of the vibrational state resolved excitation functions. Upon the drop of f_V, both f_T and f_R rise, at different rates, to balance the energy conservation. The rotational distribution of the HF($v'=2$) products at low collision energies is always quite broad and bimodal, as can be seen from the raw image shown in Fig. 1(c), which then boosts f_R to a higher plateau for $E_c \lesssim 1.2$ kcal/mol.

As to the DF product channel, f_R also rises for $E_c \lesssim 1.0$ kcal/mol, though to less extent. We note again that it is over the same energy range as where the branching ratio of DF($v'=2$) displays an unusual energy dependence, as alluded to early. Whether this rise in f_R comes from a warmer rotational excitation of DF products and if it can also be regarded as a resonance imprint or just a threshold anomaly require deeper scrutiny because of the contributions from both product rotors in this study. Further experiments with either N-state tagged or partially rotational selection of the CHD$_2$ coproduct will be needed to clarify it.

IV. SUMMARY

In this work, several dynamical aspects of the integral cross sections of the title reactions are presented. As elucidated here, examining the collisional energy evolutions of those attributes not only provides a global view of dynamics of this particular reaction, but contains rich information that, in conjunction with future theoretical investigations, can deepen our general understanding about chemical reactivity of more complex systems. Perhaps, the most significant contribution of the present study is the observation of a step-like structure in the excitation function of the HF+CD$_3$ product channel. In many respects this unusual feature is entirely in analog to that discovered previously for the F+HD→HF +D reaction,[14] and is suggestive of the existence of a reactive resonance in this six-atom reaction. From the behaviors of the vibrational state-specific excitation functions, it appears that the resonant contribution to the present reaction might be more significant than in the previous F+HD reaction. Future theoretical confirmation is warranted.

The step-like behavior in reactive excitation function has now been reported in the literature for three chemical reactions: F+HD,[14] the theoretical study of Cl+HCl,[35] and the present F+CHD$_3$ reaction. It appears that the resonance fingerprints can after all survive the impact parameter averagings in ICS in favorable cases. And we may very well encounter more examples in the future than what we have previously conceived.[14–16]

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