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Dynamically Hidden Reaction Paths in the Reaction of CF$_3^+$ + CO

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1. INTRODUCTION

Under the Born-Oppenheimer approximation, a chemical reaction can be described using reaction paths on the potential energy surface (PES). The intrinsic reaction coordinate (IRC)$^{1,2}$ is a reaction path inherent to an elementary reaction that connects the structures of reactants, a transition state (TS), and products and provides an intuitive picture of the structural changes during the reaction. Recently, automated reaction path search methods such as the anharmonic downward distortion following (ADDF)$^{3,4}$ and the artificial force induced reaction$^5$ have emerged, making it possible to determine the reaction path without prior knowledge of the target reaction. These methods have led to a powerful concept called the global reaction route mapping (GRRM) strategy, which comprehensively finds numerous IRCs and dissociation paths on the PES. GRRM has elucidated various chemical reaction mechanisms.$^6$ In combination with TS theory, a method for efficient kinetic simulation based on the reaction route map obtained by GRRM has also been developed.$^7$ In these methods, assuming the validity of statistical approximations, chemical reactions are expected to proceed along multiple reaction paths that constitute the reaction route map.

It should be noted that the reaction path is determined solely on the basis of the shape of the PES. In other words, the reaction path does not take into account the dynamical effects of finite atomic momenta. Several early studies analyzed the dynamical effects on the basis of the reaction path curvature.$^8,9$ Nowadays, on-the-fly molecular dynamics (MD) is a powerful tool to study the dynamical effects of reaction processes by following the time evolution of nuclei with sequential electronic structure calculations. In 2002, Hase and co-workers proposed the concept of non-IRC dynamics from their observations that 90% of the trajectories of the OH$^+$ + CH$_3$F reaction do not form the direct reaction path.$^{10}$ It has been experimentally and theoretically confirmed that the reaction of F$^-$ + CH$_2$OOH led to HF + CH$_2$O + OH$^-$ and HF + CH$_3$OO$^-$.
which are different products compared to those from the terminus of the IRC, the CH$_2$(OH)$_2$−F$^+$ complex. This is probably a result of the large curvature of the IRC. Another important factor in the dynamical effects is bifurcation of the reaction path. In organic and chemical reactions, there are sometimes unusual TSs, called ambimodal TSs, from which the diverging reaction path leads to multiple products. In reactions involving an ambimodal TS, the reaction dynamics can significantly affect the branching ratio of the products. Recently, Tsutsumi et al. proposed the idea of mapping on-the-fly MD trajectories on the reaction route map. They applied this idea to the isomerization reaction of Au$_5$ clusters and found “IRC jumps” corresponding to molecular transitions from one IRC to another. Furthermore, studies with reference to experiments are needed to explore the dynamical effects based on the reaction route map.

In this study, we performed automated reaction path search calculations and guided ion beam tandem mass spectrometry (GIBMS) experiments for the CF$_3^+$ + CO reaction to validate the reaction route map with reference to experimental data. Proper data analysis of the GIBMS experimental results allows measurements of the reaction thresholds of all ionic products formed in gas-phase ion–molecule collisions, which can be directly compared with the reaction route map. Note that in the CF$_3^+$ + CO system, the charge transfer excited state (CF$_3^+$ + CO$^+$) has sufficiently high energy compared to that of the ground state that one can eliminate involvement of the excited state. Nevertheless, we observe a clear discrepancy between the experimental GIBMS results and the theoretical predictions based on the reaction route map. More specifically, among the various product channels, the CF$^+$ + F$_2$CO channel is not observed experimentally even above the GRRM-predicted energy threshold of $E_0 = 2.3$ eV. This indicates a significant dynamical effect resulting from the non-statistical nature of the reaction dynamics. We therefore perform on-the-fly MD simulations in order to understand the experimental observations and rationalize the dynamical origins of this discrepancy.

2. RESULTS AND DISCUSSION

2.1. Guided Ion Beam Experiment and Data Analysis

Detailed descriptions of the guided ion beam apparatus used in this study and the experimental procedures are given elsewhere. Less than 0.3% hexafluoroorane (C$_6$F$_{18}$, 99.999%, Matheson) mixed with 90% He and 10% Ar was supplied to a dc discharge/flow tube source at a total pressure of 44 Pa and at ambient temperature. The produced CF$_3^+$ ions underwent $\sim 10^5$ collisions with He and $\sim 10^4$ collisions with Ar in a meter-long flow tube. Subsequently, they were mass-selected, decelerated to a desired kinetic energy, and focused into an octopole ion guide that radially trapped the ions using radiofrequency electric fields. While in the octopole, the ions passed through a static gas cell that contained CO or N$_2$ at a pressure less than 0.02 Pa to ensure that multiple ion–molecule collisions did not occur. This was verified by examining the pressure dependence of the reaction cross-sections in the range of 0.007–0.02 Pa. The remaining reactant and product ions were confined in the radial direction in the guide until they drifted to the end of the octopole where they were extracted and focused into a quadrupole mass filter for mass analysis. The ions were then detected using a secondary electron scintillation ion detector, and the signal was processed using standard pulse counting techniques. After correcting for background signals, ion intensities were converted to absolute reaction cross-sections, as described previously. The uncertainties in absolute cross-sections were estimated to be $\pm 20\%$.

The kinetic energy was varied in the laboratory frame by scanning the dc bias on the octopole rods with regard to the potential of the ion source region. Translational energies in the laboratory frame of reference are related to energies in the center-of-mass (CM) frame using $E_{\text{CM}} = E_{\text{lab}} (M + m)/(M + m)$, where $M$ and $m$ are the masses of the incident ion and neutral reactants, respectively. The kinetic energy distribution of the reactant ions and the thermal motion of the neutral reactant gas (Doppler broadening) both contributed to broadening of the cross-sections. The octopole beam guide was used as a retarding potential analyzer, as described previously, to determine both the absolute zero of the energy scale and the full width at half-maximum (fwhm) of the kinetic energy distribution of the ions. This distribution was nearly Gaussian and independent of energy, with a fwhm of 0.05–0.12 eV (CM). Uncertainties in the absolute energy scale are $\pm 0.02$ eV (CM).

The energy dependence and thresholds for the endothermic reactions were analyzed in the following way. Theory and experiments show that cross-sections can be parameterized in the threshold region using

$$\sigma(E) = \sigma_0 \sum g_i (E + E_i - E_0)^n / E$$

where the sum is over all rovibrational states of the reactants denoted by $i$, $g_i$ is the population of these states ($\sum g_i = 1$), $E_i$ is the excitation energy of each rovibrational state of the reactants, $\sigma_0$ is an energy-independent scaling factor, $E$ is the relative (CM) translational energy of the reactants, $E_0$ is the 0 K threshold for reaction of the ground rovibrational and electronic state of the reactants, and $n$ is an adjustable parameter. In the absence of evidence to the contrary, it is assumed that $n$ and $\sigma_0$ are the same for all reactant rovibrational states. Before comparison with the data, the model of eq 1 is convolved with the kinetic energy distributions of the reactants, as described previously. This form is expected to be appropriate for translationally driven reactions and has been found to reproduce the cross-sections for endothermic reactions in a number of previous studies of both atom–diatom and polyatomic reactions.

Figure 1 shows the cross-sections as a function of the collision energy for reactions of CF$_3^+$ with both CO and N$_2$. Note that a supplementary experiment for the CF$_3^+$ + N$_2$ reaction was carried out to investigate the origin of the products observed in the CF$_3^+$ + CO reaction. The curves in the figure are the models of eq 1 with the resulting optimized parameters summarized in Table 1. In the CF$_3^+$ + CO collision, FCO$^+$, CF$_2^+$, and CF$^+$ were observed, whereas CF$_2^+$ was the only product ion observed in the CF$_3^+$ + N$_2$ collision. In the latter reaction, the presence of CF$^+$ was carefully looked for but could not be observed.

The threshold energies obtained from the CO system can be compared with the known literature thermochemistry for the following possible reactions.

$$\text{CF}_3^+ + \text{CO} \rightarrow \text{FCO}^+ + \text{CF}_2^+ \quad \Delta H_0 = 2.44 \pm 0.01 \text{ eV}$$

$$\rightarrow \text{CF}_2^+ + \text{FCO} \quad \Delta H_0 = 4.52 \pm 0.01 \text{ eV}$$

$$\rightarrow \text{CF}_2^+ + \text{F} + \text{CO} \quad \Delta H_0 = 5.97 \pm 0.01 \text{ eV}$$

$$\rightarrow \text{CF}^+ + \text{F}_2\text{CO} \quad \Delta H_0 = 2.31 \pm 0.01 \text{ eV}$$
It can be seen that the measured threshold for generation of FCO\(^+\) is in good agreement with the 0 K energy needed for reaction 2; hence, this reaction clearly corresponds to the transfer of F\(^+\) from CF\(_3\)^+ to CO. The complementary channel in which the charges of the two products are exchanged, reaction 3a, is much lower in energy than the observed threshold for CF\(_2^+\) formation. Here, it can also be realized that reaction 2 corresponds to heterolytic bond cleavage of a [FCO−CF\(_2^+\)] intermediate. As a consequence, the alternative CF\(_2^+\) + FCO asymptote, the homolytic bond cleavage, actually correlates with an unstable excited state (triplet or singlet spin) of the same intermediate.\(^{31}\) Hence, experimental formation of CF\(_2^+\) appears to correspond to the collision-induced dissociation (CID) reaction 3b, consistent with the similarity with the reaction of CF\(_3^+\) with N\(_2\), Figure 1. We believe that the difference in the thresholds obtained for these two CID reactions can be traced to a stronger interaction with CO, which allows more efficient energy transfer. The observation of reaction 2 is clear evidence for this stronger interaction.

Four possible reactions are available to generate CF\(^+\) with the literature thermochemistry for reaction 4a lying much lower than the observed threshold energy. In contrast, reactions 4b and 4c are consistent with the observed threshold energy, whereas the enthalpy of reaction 4d lies too high to explain the experimental observations. Note that reaction 4d corresponds to the subsequent dissociation of an initially formed CF\(_3^+\) product in reaction 3b. The experiment suggests that the observation of CF\(^+\) probably corresponds to reaction 4c because reaction 4b must be preceded by either reactions 3a or 4a, neither of which is obviously observed in the experiment. The failure to see CF\(^+\) in the reaction with N\(_2\) indicates that the CID reaction 4c is also not expected to occur in the collision reaction between CF\(_3^+\) and CO; however, given the relative magnitudes of the cross-sections for CF\(_2^+\) (about half as large in the N\(_2\) system), it is possible that observation of CF\(^+\) in reactions with N\(_2\) near the noise level. It is also possible that CF\(^+\) is formed in reaction 4a with a threshold shifted to high energies by a barrier or dynamic constraints. Thus, it is difficult to clarify the collision energy dependence of the reaction mechanism from experimental studies alone.

### 2.2. Reaction Route Map for CF\(_3^+\) + CO

To understand the reaction mechanism for the reaction of CF\(_3^+\) and CO investigated by the GIBMS experiment, we carried out automated reaction path search calculations by employing the ADDF method\(^{32}\) at the UB3LYP/6-31+G(d) level with singlet spin multiplicity. The stable = opt\(^{32,33}\) option was specified to describe the doublet–doublet dissociation. To verify the accuracy of the computed reaction route map, we performed geometry optimization of the stationary points using the aug-cc-pVTZ basis set at the coupled-cluster single, double, and perturbative triple [CCSD(T)] level (see S1 in Supporting Information). Consequently, we confirmed that the UB3LYP results are in qualitative agreement with the CCSD(T) results with a root mean square error of 0.15 eV. More importantly, comparison of the UB3LYP and CCSD(T) theoretical results with the literature thermochemistry shown in reactions 2−3b shows deviations of less than 0.2 eV for all five product asymptotes, with a mean absolute deviation of 0.12 ± 0.07 eV. The energy of the dissociation products was calculated as the sum of the energies of the isolated fragments. The electronic structure

![Figure 1. Cross-sections for the CF\(_3^+\)/CO (part a) and N\(_2\) (part b) reactions as a function of collision energy in the CM frame (lower x-axis) and laboratory frame (upper x-axis). Symbols indicate the experimental results. Solid (dashed) lines show their model cross-sections obtained using eq 1 with (without) convolution over the x-axis.](https://doi.org/10.1021/acsphyschemau.2c00012)
calculations were performed using Gaussian09 Revision D.01, and the ADDF calculations were performed using GRRM14.33

The ADDF calculations yielded 172 equilibrium structures, 417 TS structures, and 66 dissociation structures for the CF3+/CO collision reaction. From these structures, we extracted low-energy regions that are relevant to the experimental observations. Figure 2a shows the energy diagram of the stationary points along the reaction paths from the CF3+/CO reactants to the low-energy dissociation channels FCO+/CF2 (denoted as PFCO+) and CF2+/F2CO (denoted as PCF+). The calculated energies of the high-energy channels containing the ions observed in the experiment, CF3+/F2CO, CF2+/F2CO, and CF2+/F2/CO, are also shown. The initial interaction of CF3+/CO reactants leads to the formation of two complexes, [F3CCO]+ and [F2CCOCF]+ (I1CO and I1CC). The structures of I1CC and I1CO are shown in Figures 2b and c, respectively. In addition, Figure 2a shows the energies of the relevant TSs (TS1CC, TS2CC, and TS3CC) and the planar structure intermediates, [F3CCO]+ (I1CC) and [F2CCOCF]+ (I2), that lie on the reaction path from the complex I1CC or the complex I1CO to the dissociation products. In addition, Figures 2b and c shows three TS structures TS-1CC (−0.11 eV), TS-I2 (1.20 eV), and TS-I2′ (1.39 eV) as auxiliary TSs leading to the planar intermediates of interest. As shown, intermediates I1CC and I2 are planar versions of TS-I1CC and TS-I2, respectively. Our calculations indicate that TS-I1CC corresponds to the TS of CF3 rotation of the complex I1CC (−0.14 eV). Similarly, TS-I2 and TS-I2′ correspond to the TSs of CF3 rotation of the intermediate I2 (1.04 eV). According to the IRC calculations, TS1CC is connected to the TS-I1CC whereas TS2CC is connected to TS-I1CC and TS-I2, and TS3CC is connected to TS-I2’. Note that the connection of the IRC such as TS1CC and TS-I1CC indicates the appearance of a valley–ridge inflection point along the IRC.

Figure 2. (a) Energy diagram of the CF3+/CO reaction determined from the reaction route map at the UB3LYP/6-31+G(d) level. Energies are given in eV relative to the reactants. The equilibrium structures and the TS structures are depicted by solid and dashed lines, respectively. (b) Structural change from I1CC to I2 via TS1CC and from I1CC to I2 via TS2CC. (c) Structural change from ICO to I2 via TSCO. Note that the dashed line for TS-I1CC (−0.11 eV) is too close to the line for I1CC (−0.14 eV) to be displayed.

We now summarize the key structural changes that are predicted to occur along the various pathways leading to the different product channels. Figure 2b shows the structural change from I1CC to I2. Upon isomerization, the complex I1CC isomerizes to I1CC via TS1CC with the migration of a F atom, and the system proceeds along the PFCO+ channel to produce FCO+/CF2 via C–C bond cleavage over a loose TS. Alternatively, the system can further isomerize to I2 via TS2CC with the migration of an O atom to produce CF2 via C–O bond cleavage over a loose TS. In contrast, Figure 2c shows the structural change from I1CC to I2 after the simultaneous migration of F and O atoms via TSCO. Note that the reaction paths for the dissociation of I1CC to FCO+ via the PFCO+ channel and from I2 to CF2 via the PCF+ channel are uphill, and there is no tight TS. We also found the TS structure of the reaction path in which CF3+/CO collide from the F-atom side (F3C,F,C···CO), leading to PFCO+; however, the activation barrier for this path is significantly higher (3.56 eV) than that of the I1CC → TS1CC → I1CC → TS2CC → I2 → CF2 pathway. Therefore, we do not consider the collision from CO to the F-atom side in the following discussion.

As shown in the previous section (cf. Figure 1 and Table 1), the energy thresholds for the product ions obtained from the GIBMS experiments are 2.39 ± 0.05 eV for FCO+, 6.40 ± 0.20 eV for CF2+, and 7.48 ± 0.15 eV for CF+. In comparison, the ADDF calculations show that the relevant thresholds are 2.35 eV for FCO+/CF2, 5.81 eV for CF2+/F/CO, and 2.30 eV for CF2+/F2CO. Thus, the ADDF results are in relatively good agreement with the GIBMS results for the FCO+/CF2 and CF2+/F/CO product channels. However, and perhaps surprisingly, there is a large difference between the GIBMS-observed and ADDF-predicted threshold for the CF2+ channel. In this regard, it can be realized that the intermediate I1CC can undergo further reaction either by dissociation over the loose TS leading to FCO+/CF2
The same experiment was also performed for the collision of disfavored tight TS2CC. Higher energy dissociation channels favored because it does not require passing over the entropically observed threshold for CF+ shown in Table 1. 

These values quantitatively agree with the relative energies calculated to be 7.40 and 7.58 eV, respectively due to dissociation to CF+/F2CO (at 2.30 eV). Because the overall energetics are similar, the dissociation to FCO+/CF will be favored because it does not require passing over the entropically disfavored tight TS2CC. Higher energy dissociation channels producing CF+ include CF+/F/FCO and CF+/F2/CO, with relative energies calculated to be 7.40 and 7.58 eV, respectively (cf. Figure 2a). These values quantitatively agree with the experimentally observed threshold for CF+ shown in Table 1. 

The same experiment was also performed for the collision of CF3+ with CO. Because of its high energy, the reaction of CF3+ with CO (or N2), whereas FCO+ originates from more complicated rearrangements in the reaction of CF3 with CO. Of course, in GIBMS experiments, the relative orientation similar to the structure of the optimized TS. This model was proposed by generalizing Polanyi’s rule, which is well known for atom–diatom collisions, to polyatomic bimolecular reactions. 

In the CF3+/CO system, the reaction route map shows that a collision energy of at least 2.3 eV is required to reach CF+/F2CO. If the reactant molecules have enough translational energy to reach the PCF+ channel upon collision, the reactants are expected to reach the initial TS directly without being trapped in the pre-reaction complex. Of course, in GIBMS experiments, the relative orientation of the reactant molecules may change before reaching this TS because of molecular vibrations or rotational motion, but here, we assume a direct collision mechanism that leads to the vicinity of the TS without changing the orientation. Here, we consider the two TSs that correspond to the first TS of the reactions leading to PCF+. CF3+ + CO reactions can occur via TS1CC or TS2CC, and are assumed to occur via a relative orientation similar to the structure of the optimized TS. This assumption allows for proper sampling that defines the initial collision conditions to obtain the reactive trajectories.

First, we define the ideal atomic coordinates of the reactant molecules just before the collision. Reactant molecules are placed in mass-weighted Cartesian coordinates to maximize their structural overlap with the TS geometry using the Kabsch algorithm, keeping the center of mass of each reactant

Figure 3. (a-1) Structure of TS1CC in F3C−→CO collisions, (a-2) the structure of the corresponding sudden complex, and (a-3) SVP-based parameter $\eta_{RC}(\theta)$ as a function of collision angle; (b-1) structure of TS2CC in F3C−→OC collisions, (b-2) structure of the corresponding sudden complex, and (b-3) SVP-based parameter $\eta_{RC}(\theta)$ as a function of collision angle. The RC mode $L_{RC}$ at the TS and the collision mode $L_{coll}$ at the sudden complex are indicated by arrows in each panel. In each molecular structure, the solid circle and the open circle indicate the center of mass of the entire molecular system and the center of masses of the reactant molecules, respectively.

2.3. On-the-Fly MD for CF3+ + CO

2.3.1 Initial Conditions for Promoting the Collision Reaction. In order to resolve the discrepancy between the GIBMS experiment and the reaction route map and to gain a better understanding of the reaction dynamics, we performed on-the-fly MD simulations for the CF3+ + CO reaction. First, we ran 100 trajectories under random initial conditions and found that the colliding molecules passed each other, and no chemical reaction occurred. This result is reasonable considering that the reaction cross-section is very small (less than 0.01 Å² at 5 eV collision energy), as shown in Figure 1. This magnitude is about 1000 times smaller than other collision reactions studied in MD simulations.46,47 Therefore, the dynamics simulation of this collision reaction requires an efficient selection of the initial conditions for the chemical reaction to occur.

In ion–molecule reactions, a pre-reaction complex is usually formed by the reactants. Previous experimental and theoretical studies have shown that when the translational energy of the reactant molecules is relatively high, most of the trajectories are not trapped in the pre-reaction complex and can directly reach the TS region.38–41 In such bimolecular reactions with direct collision processes, the sudden vector projection (SVP) model proposed by Jiang and Guo provides a good approximation to elucidate the reaction mechanism.42 Assuming a direct collision mechanism, the reactant molecules will probably collide in the same relative orientation as the TS during any collision that leads to products. In the SVP model, the reactant molecules are placed in this relative orientation, and the inner product between the basis vectors of the translational, rotational, and vibrational modes of the reactant molecules and the reaction-coordinate (RC) mode at the TS is calculated to estimate the effect of each mode in promoting the reaction. This model was proposed by generalizing Polanyi’s rule, which is well known for atom–diatom collisions, to polyatomic bimolecular reactions.43–46

In the CF3+/CO system, the reaction route map shows that a collision energy of at least 2.3 eV is required to reach CF+/F2CO. If the reactant molecules have enough translational energy to reach the PCF+ channel upon collision, the reactants are expected to reach the initial TS directly without being trapped in the pre-reaction complex. Of course, in GIBMS experiments, the relative orientation of the reactant molecules may change before reaching this TS because of molecular vibrations or rotational motion, but here, we assume a direct collision mechanism that leads to the vicinity of the TS without changing the orientation. Here, we consider the two TSs that correspond to the first TS of the reactions leading to PCF+. CF3+ + CO reactions can occur via TS1CC or TS2CC, and are assumed to occur via a relative orientation similar to the structure of the optimized TS. This assumption allows for proper sampling that defines the initial collision conditions to obtain the reactive trajectories.
molecule fixed at the corresponding position in the TS geometry. We call this structure a sudden complex in which the reactant molecules suddenly approach the TS region without changing their respective geometries. Figure 3 shows the geometry of TS1CC, the corresponding sudden complex for F3C+···CO collisions, the geometry of the TS_CC, and the corresponding sudden complex for F3C+···OC collisions. Note that the center of mass of the entire molecular system is located on the line connecting the centers of mass of the reactants (hereafter referred to as the collision line).

Next, we introduce the collision mode \( L_{\text{coll}} \), which is represented by a linear combination of the translational modes of each of the reacting molecules superimposed so that they approach each other. In the collision mode, the center of mass of the entire system is fixed at the origin, so the kinetic energy given in this mode corresponds to the collision energy in the CM frame. Consider the case where the motion of the atoms in the reactant molecules determined in the collision mode is parallel to the collision line. The collision mode obtained by rotating the translational mode of each reactant molecule by an angle \( \theta \) (called the collision angle) counterclockwise in the C, symmetry plane with respect to the collision line is called \( L_{\text{coll}}(\theta) \).

Furthermore, we introduce the SVP-based parameter \( \eta_{\text{RC}}(\theta) \) as \( \eta_{\text{RC}}(\theta) \eta_{\text{RC}}(\theta) \in [0,1] \), which is the inner product of the collision mode \( L_{\text{coll}} \) and the RC mode \( L_{\text{RC}} \) at a TS, as an index to evaluate how efficiently the collisional momenta contribute to the crossing of the specific TS of interest. The optimal collision angle \( \theta_{\text{opt}} \) that maximizes \( \eta_{\text{RC}} \) allows the molecular system to traverse the TS region in the most efficient way. Figures 3a-3 and b-3 show \( \eta_{\text{RC}}(\theta) \) as a function of collision angle in the range of \(-90^\circ \leq \theta \leq 90^\circ \) for TS1CC and TS_CC, respectively. The maximum \( \eta_{\text{RC}}(\theta) \) is 0.56 (\( \theta_{\text{opt}} = 49^\circ \)) for TS1CC and 0.47 (\( \theta_{\text{opt}} = 30^\circ \)) for TS_CC. In Figures 3a-2 and b-2, the collision modes with collision angles \( \theta = 0^\circ \) and \( \theta_{\text{opt}} \) for the sudden complexes are indicated by arrows. The collision mode with the optimal collision angle is in relatively good agreement with the RC mode in Figures 3a-1 and b-1.

### 2.3.2 Trajectories for the F3C+···CO Collision

On the basis of the SVP analysis described in the previous section, initial conditions were prepared by separating the reactant molecules by 5 Å along the collision mode \( L_{\text{coll}} \) from the sudden complex structure of interest at 19 collision angles of \( \theta = 90^\circ, -90^\circ, \ldots, \) and \( 90^\circ \). In addition, the initial momenta along the collision mode corresponding to four different collision energies \( (E_{\text{coll}}) = 3, 5, 7, \) and 10 eV were considered. Starting from these 76 initial conditions for F3C+···CO collisions, we performed on-the-fly MD calculations at the UB3LYP/6-31+G(d) level using the in-house program SPRP \(^{34} \) linked to Gaussian09. \(^{34} \) We considered the case of singlet spin multiplicity for the entire molecular system and used the stable = opt option \(^{32,33} \) to deal with dissociation in open-shell electron configurations. The velocity-Verlet algorithm \(^{39} \) was used for the time evolution of Newton’s equation of motion, with a time step of 0.4 fs. The calculation for each trajectory was stopped when the C···C distance exceeded 6 Å.

Figure 4a shows a heat map of the 76 trajectory termination structures in the case of F3C+···CO collisions. (b) Snapshots of the molecular geometry along the trajectory resulting in FCO+, calculated for \( \theta = 70^\circ \) and \( E_{\text{coll}} = 5 \) eV. (c) Variation of \( \eta_{\text{RC}}(\theta) \) calculated for the collision mode and ith normal mode at TS1CC as a function of collision angle from \(-90^\circ \) to \( 90^\circ \). The number written next to each line indicates the corresponding mode vibrational frequency in cm\(^{-1} \) (0 corresponds to the rotational mode that preserves C, symmetry). (d) Oxygen migration mode \( L_{i} (v_1 = 337 \) cm\(^{-1} \)) at TS1CC, which is essential for reaching TS2CC.

Figure 3 shows the geometry of TS1CC, the corresponding sudden complex for F3C+···FO collisions, the geometry of the TS_CC, and the corresponding sudden complex for F3C+···OC collisions. We call this structure a sudden complex in which the reactant molecules suddenly approach the TS region without changing their respective geometries. Figure 3 shows the geometry of TS1CC, the corresponding sudden complex for F3C+···CO collisions, the geometry of the TS_CC, and the corresponding sudden complex for F3C+···OC collisions. Note that the center of mass of the entire molecular system is located on the line connecting the centers of mass of the reactants (hereafter referred to as the collision line).

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### 2.3.2 Trajectories for the F3C+···CO Collision

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Figure 4a shows a heat map of the 76 trajectory termination structures in the case of F3C+···CO collisions. (b) Snapshots of the molecular geometry along the trajectory resulting in FCO+, calculated for \( \theta = 70^\circ \) and \( E_{\text{coll}} = 5 \) eV. (c) Variation of \( \eta_{\text{RC}}(\theta) \) calculated for the collision mode and ith normal mode at TS1CC as a function of collision angle from \(-90^\circ \) to \( 90^\circ \). The number written next to each line indicates the corresponding mode vibrational frequency in cm\(^{-1} \) (0 corresponds to the rotational mode that preserves C, symmetry). (d) Oxygen migration mode \( L_{i} (v_1 = 337 \) cm\(^{-1} \)) at TS1CC, which is essential for reaching TS2CC.

### 2.3.2 Trajectories for the F3C+···CO Collision

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Figure 4a shows a heat map of the 76 trajectory termination structures in the case of F3C+···CO collisions. The product FCO+ (threshold energy = 2.35 eV) was observed only at collision
angles close to the optimum one, 49°. As collision energy increases, the collision angles leading to the product FCO⁺ become more dispersed. The product from the collision with θ = 20° and E_{coll} = 10 eV was assigned to a product of three-body dissociation (CF₂⁺/F/CO). Note that the PCF⁺ channel is not observed in any of the trajectories, which is consistent with the GIBMS experiment.

Before going into a detailed analysis of the dynamics, we mention additional simulations (see S2 in Supporting Information) that were performed to validate the restrictions we imposed on the atomic coordinates of the reactant molecules. In these additional simulations, the initial coordinates of the atoms were generated anew by rotating the reactant molecules in 30° increases from −90° to 90° around the CM point in the Cs symmetry plane to change their relative orientation. At collision angles θ = 60° and 70°, corresponding to a majority of the reactive trajectories in Figure 4a, on-the-fly MD simulations were performed again for these new initial coordinates and for several collision energies. The results showed that some trajectories with slightly altered initial coordinates undergo non-reactive collisions. This result supports the assumption that the CF₃⁺/CO reaction occurs at least through the direct collision process via the atomic coordinates near the sudden complex.

Figure 4b shows a snapshot of the structural change of the reactive trajectories starting from θ = 70° and E_{coll} = 5 eV as an example. From this figure, we can understand how one fluorine atom moves between a molecule and a dissociating fragment. In this case, there is not enough time for intramolecular vibrational energy redistribution (IVR) to occur around TS-I₁CC, where CO associates with CF₃⁺, so CO smoothly removes F⁺ and proceeds to the dissociation channel P_{FCO⁺}. The fate of the trajectory after crossing TS₁CC depends on the energy distribution to the molecular degrees of freedom at TS₁CC. In order to understand why this reaction system reaches the product P_{FCO⁺} and not TS₂CC, it will be important to consider the very fast intramolecular energy redistribution that occurs during the process of reaching TS₁CC through molecular collisions.

We now extend the SVP analysis to modes other than the RC mode and introduce \( \eta_i(\theta) = L_i \cdot L_{coll}(\theta) \), where \( L_i \) is the \( i \)-th normal mode of the reactive molecular system defined for the TS structure and represents one of the RC modes, vibrational modes, and rotational modes that preserve Cs symmetry. In the present analysis, we use the squared value, \( \eta_i(\theta)^2 \), to estimate how the collision energy is distributed among the molecular degrees of freedom after the molecular system passes near the TS structure (see S3 in Supporting Information for details). As shown in Figure 4c, the black dashed line corresponding to the rotational mode with frequency 0 cm⁻¹ shows a relatively large value compared to other modes around the collision angle of 50° where the RC mode shows its maximum, and this rotational mode is expected to be excited at this collision angle. In fact, the snapshot in Figure 4b shows that CO moving downward collides with CF₃⁺ at around 100 fs, leading to the TS structure, and after receiving one F atom, it changes its direction of motion to the left by rotational motion and dissociates. This result suggests that the analysis using \( \eta_i(\theta)^2 \) is effective in predicting the energy redistribution associated with the collision.
According to the reaction diagram in Figure 2, in order to reach the P_{CF+} region, the molecular system needs to cross TS_{1CC} and then reach TS_{2CC}, which requires oxygen atoms to move between the two carbon atoms. The vibrational mode $L_1$ at TS_{1CC} shown in Figure 4d corresponds to such a movement of the oxygen atom. In fact, we performed a preliminary calculation of on-the-fly MD by starting from TS_{1CC} and giving large kinetic energy in the direction of $L_1$ and confirmed that some trajectories reach TS_{2CC}. However, as shown in Figure 4c, $\eta_1^2$ is small when the collision angle is around $\theta_{opt} = 49^\circ$, which means that energy will not flow into the vibrational mode leading to TS_{2CC} and the reaction leading to P_{CF+} production will not occur. On the other hand, when the collision angle is between $-45^\circ$ and $-30^\circ$, the $\eta_1$ is relatively large and the molecular system may reach TS_{2CC} after crossing TS_{1CC}, but the $\eta_2$ is small and the collision energy must be quite large for the molecular system to pass TS_{1CC} (the interpretation of $\eta_{RC}$ will be explained in the next section). Note that, with the collision angle being more negative than about $-45^\circ$, the reactants cannot reach TS_{1CC} because $\eta_{RC}$ is negative, as shown in Figure 3a-3. As a result, at low collision energies, molecular systems are not expected to pass through TS_{1CC} and TS_{2CC} to produce CF* via the P_{CF+} channel. This phenomenon, in which the momentum at the TS determines the outcome of the product, is called “dynamic matching” and has attracted much attention in the study of the dynamics of organic reactions.\(^{50,51}\)

We also calculated trajectories with collision angles near the optimum angle and collision energies of $E_{coll} = 3.5, 4.0,$ and $4.5$ eV, but no reaction occurred in any of the cases. In addition, we generated trajectories using 600 different initial conditions with zero-point vibrational energies in all the vibrational modes along with relatively small collision energies and found trajectories that followed the P_{CO} channel but not the P_{CF+} channel. The details can be found in Supporting Information (S4). Note that the initial conditions for a number of the on-the-fly MD calculations performed here were limited to collision conditions so that the FCO* + CF$_2$ channel could be realized. No simulations were performed specifically for the CID reaction in which energy is just transferred to the internal energy of CF$_3^+$ and bond dissociation occurs. Nevertheless, as shown in Figure 4a, dissociation to CF$_3^+$ + F which corresponds to the CID reaction was observed. Because CID does not require a specific reactant orientation to transfer energy from translation into internal degrees of freedom, it is clear that many collisions would lead to this process, consistent with the relatively larger magnitudes of the CF$_3^+$ cross-sections compared to those for FCO* in Figure 1.

2.3.3 Trajectories for the F$_2$C····OC Collision. We also performed on-the-fly MD simulations for F$_2$C····OC collisions, in which CO collides with F$_2$C$_2$ from the O atom side, using the same procedure as for F$_2$C····CO collisions. Figure 5a shows the heat map of the 76 trajectory-terminated structures: the relative energy of TS_{CO} is 2.55 eV, but the reaction only occurs at $E_{coll} = 10$ eV, the maximum collision energy considered in the present study. As in the case of F$_2$C····CO collisions, the reaction occurred near the corresponding optimal collision angle of $\theta_{opt} = 30^\circ$. Surprisingly, the dominant product was P_{CCO} (FO* + CF$_3$), which can be formed starting at the structure of TS_{CO} because the directions of the velocity vectors can lead to this thermodynamically favored process. Note that in the reactive trajectory with collision angle $\theta = 40^\circ$, CF$_3$ was produced (Figure 5b). This result suggests that the CF$_3$ observed starting at a collision energy of 7.48 eV in the GIBMS experiment may be produced not only in the three-body dissociation channel CF$_2$/

F$_2$/CO, reaction 4c, but also in the P_{CF+} (CF$/^+$F$_2$/CO) channel, reaction 4a.

The reason as to why it takes significantly more energy than the height of the barrier to cross TS_{CO} can be understood by considering the value of $\eta_{RC}(\theta)^2$. In the vicinity of the TS structure, the molecular system climbs the PES along the direction of the RC mode. Therefore, the collision energy in the RC direction is used to cross the TS. Here, $\eta_{RC}(\theta)^2$ represents the relative ratio of the effective energy allocated to the RC direction out of the collision energy. Of course, this interpretation is valid only in the very near vicinity of the TS structure, and in the actual chemical reaction, the collision energy in the RC direction can be distributed to the various degrees of freedom in the molecular system. Therefore, the values obtained here should be regarded as qualitative or semi-quantitative.

In the F$_2$C····OC collision reaction via TS_{CO} the maximum value of $\eta_{RC}$ is 0.22 (Figure 5c), which means that within the SVP model, less than a quarter of the collision energy contributes to the motion along the RC mode. In other words, if the SVP model is strictly applied, even if the collision energy is 10 eV, the effective energy available for the reaction (10 eV $\times$ 0.22 = 2.2 eV) is less than the TSCO barrier height of 2.55 eV. Therefore, significantly higher collision energies are required to efficiently access and cross the TSCO transition state. It has been reported in previous trajectory studies that the collision energy is not always effective in assisting the reaction.\(^{52,53}\) Note that the estimation scheme based on the SVP model is too simple to quantitatively evaluate an effective energy. Actually, the CF$^+$ ion observed in the GIBMS experiment, which could originate from the CF$/^+$F$_2$/CO channel, shows a threshold of $7.48 \pm 0.15$ eV which is significantly lower than 10 eV. Nevertheless, such an estimate provides a qualitative understanding for the different energetic behavior associated with the P_{FCO} or P_{CF+} channels. Unlike the P_{CF+} case, formation of FCO$^+$ via the P_{CCO} channel requires crossing of TS_{CCO} with a barrier height of 0.71 eV. The corresponding maximum $\eta_{RC}$ value of 0.33 in the case of F$_2$C····CO collisions (Figure 4c) therefore requires a minimum energy of (0.71 eV /0.33 =) 2.15 eV, which is below the required asymptotic energy of 2.35 eV. Thus, our analysis based on $\eta_{RC}$ explains the correspondence between the observed and calculated energetics for this channel.

3. CONCLUSIONS

In quantum chemical studies of chemical reactions, the IRC plays an important role in elucidating the reaction mechanism. The automated reaction path search methods have made it possible to determine the IRC network (the reaction route map) on the PES and to reveal the reaction mechanism without any assumptions. On the other hand, some studies have pointed out that the true reaction mechanism may differ from the one inferred from the reaction path picture because of dynamical effects caused by the atomic momenta of the molecular system. It is therefore important that such dynamical effects on the reaction route map be investigated with reference to experiments.

In this study, we performed GIBMS experiments and automated reaction path search calculations for the CF$_3^+$ + CO reaction. The formation of FCO$^+$ and CF$_3^+$ can be readily explained using reactions 2 and 3b, but for the formation of CF$_3^+$, there was a discrepancy between the dissociation threshold of 7.48 ± 0.15 eV obtained from the GIBMS experiment and the energy required along the CF$_3^+$ formation pathway of 2.30 eV.
from the theoretical calculation. This discrepancy between experimental and theoretical results suggests that the molecular system does not follow the theoretically predicted reaction path leading to CF$^+$ + F$_2$CO because of dynamical effects. It is also entropically disfavored compared to the reaction path leading to FCO$^+$ + CF$^+$. To investigate this further, we performed on-the-fly MD simulations of the collision process between CF$_3$ and CO with the aid of the SVP model, assuming that it goes through the TS$_{1CC}$ or the TS$_{SCO}$ transition states.

From the results of the on-the-fly MD calculations, the dynamics of the CF$^+$ + CO reaction can be interpreted as follows. In the GIBMS experiment, thermalized reactant molecules (Boltzmann distributed at a certain temperature with vibrational and rotational degrees of freedom) collide with a fairly large (variable) amount of translational energy. This large collision energy causes the reactant molecules to approach the TS regions directly without being trapped by the potential minimum of the pre-reaction complex, so that the energy distribution of the internal degrees of freedom of the molecules remains unrelaxed and biased. Clearly, the energy of the molecular system after crossing the TS deviates from a statistical distribution. For this reason, the trajectory after crossing TS$_{1CC}$ cannot follow the reaction path to TS$_{2CC}$ and crossing TS$_{SCO}$ requires much higher collision energy than the reaction barrier. As a result, at low collision energies, the system cannot dissociate into CF$^+$ + F$_2$CO via TS$_{1CC}$ or TS$_{SCO}$, leading to the discrepancy in the threshold for CF$^+$ production between the GIBMS experiment and the predicted reaction route map.

Conventional arguments based on reaction paths obtained by quantum chemical calculations do not take into account the possibility that a molecular system with enough energy to cross the reaction barrier cannot follow the reaction path. In this study, we discovered the existence of a “dynamically hidden reaction path” in which a molecular system cannot follow the reaction path because of dynamical effects, even though the energetically accessible reaction path exists, and clarified its mechanism. Recent theoretical and experimental studies have revealed that in various reactions, such as gas-phase, condensed-phase, and gas-surface interface reactions, the energy distribution can be non-statistical because of an incomplete redistribution of intramolecular vibrational energy. These observations suggest that dynamically hidden paths may be common in other reactions as well. With the advent of the concept of reaction route maps based on automated reaction path search methods, the role of reaction dynamics in determining the destination of chemical reactions will become increasingly clear.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphyschemau.2c00012.

- Animation file for on-the-fly trajectory, non-reactive_trajectory_CC_collision_Sev_0deg (MP4)
- Reactive_trajectory_CC_collision_Sev_70deg (MP4)
- Reactive_trajectory_CO_collision_10ev_40deg (MP4)

Comparison of relative energies of stationary points between UB3LYP and CCSD(T); derivation of coupling effects, even though the energetically accessible reaction path exists, and clarified its mechanism. Recent theoretical and experimental studies have revealed that in various reactions, such as gas-phase, condensed-phase, and gas-surface interface reactions, the energy distribution can be non-statistical because of an incomplete redistribution of intramolecular vibrational energy. These observations suggest that dynamically hidden paths may be common in other reactions as well. With the advent of the concept of reaction route maps based on automated reaction path search methods, the role of reaction dynamics in determining the destination of chemical reactions will become increasingly clear.

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Notes

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### ABBREVIATIONS

- PES — potential energy surface
- GRRM — global reaction route mapping

ADD: anharmonic downward distortion following
TS: transition state
GB: guided ion beam mass spectrometry
MD: molecular dynamics
SVP: sudden vector projection
RC: reaction coordinate.

REFERENCES


