Dynamics of the F₂ reaction with the simplest σ-bonding molecule
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I. INTRODUCTION

Regarding the fluorination in organic chemistry, $\text{F}_2 + \text{C}_2\text{H}_4$ reaction is an important benchmark as it is the simplest reaction of $\text{F}_2$ with $\pi$-bonding systems. If this simple reaction can be understood, the mechanism may be extended to larger systems. Due to the small number of participating atoms, it should be feasible to study this reaction with high level ab initio calculations to reach a precision of the so-called chemical accuracy. Definitive experimental results of this reaction are also extremely desirable as to provide a test of the theories. Although there have been quite a number of experimental $^{2-11}$ and theoretical $^{12-19}$ investigations on the reaction of fluorine with ethylene, the reaction mechanism remains unclear. For convenience of discussion, we list three most likely primary product channels together with the calculated $^{20}$ reaction enthalpies:

$\text{F}_2 + \text{C}_2\text{H}_4$

$\rightarrow \text{C}_2\text{H}_4\text{F} + \text{F}, \quad \Delta H_{\text{vib}}^0 = -7.8$ kcal/mol (R1),

$\rightarrow \text{C}_2\text{H}_3\text{F} + \text{HF}, \quad \Delta H_{\text{vib}}^0 = -100.4$ kcal/mol (R2),

$\rightarrow \text{C}_2\text{H}_2\text{F}_2, \quad \Delta H_{\text{vib}}^0 = -118.5$ kcal/mol (R3).

R1 has been observed in the gas phase. $^{2-4}$ The released F atom can initiate a series of exothermic chain reactions, which may lead to explosion. Kapralova et al. $^{5}$ reported the temperature dependence for R1 and showed the rate constant of reaction (1) can be expressed as follows:

$k_1 = 8.0 \times 10^{-14} \exp(-E_a/RT)$ cm$^3$ molecule$^{-1}$ s$^{-1}$,

and

$E_a = 4.6$ kcal/mol.

Farrar and Lee $^{5}$ studied the decomposition of chemically activated $\text{C}_2\text{H}_2\text{F}$ from $\text{F} + \text{C}_2\text{H}_4$ reaction in a crossed molecular beam setup. They employed a pyrolysis method to generate the F atom source from a $\text{F}_2$ gas mixture. The reactive signal of R1 was observed as a by-product from the reaction of $\text{C}_2\text{H}_4$ with the residue $\text{F}_2$ in their beam source.

For the $\text{F}_2 + \text{C}_2\text{H}_4$ reaction in the condensed phase, investigations using the matrix isolation technique have provided some important results. Hauge et al. $^{6}$ studied the reactions of $\text{F}_2$ with a series of small hydrocarbons in $\text{F}_2$ or Ar matrices at 15 K. They concluded that propylene, butadiene, and cyclohexene reacted spontaneously with $\text{F}_2$ even at this low temperature; ethylene and allene reacted with $\text{F}_2$ when the matrix was exposed to infrared light in the wavelength range from 1 to 4 $\mu$m. For ethylene, the observed products were 1,2-difluoroethane (R3), vinyl fluoride and HF (R2). Neither the small alkane nor alkylene reacted, even exposed to the infrared light for a long time. Their results suggest that the activation energies of the $\text{F}_2$ reactions with these hydrocarbons may be in the order of propylene $\approx$ butadiene $\approx$ cyclohexene $\approx$ ethylene $\approx$ allene $\approx$ alkylene, alkane.

Frei and co-workers $^{7-10}$ investigated the infrared photoinduced reaction of $\text{F}_2 - \text{C}_2\text{H}_4$ complex in $\text{N}_2$ or Ar matrices at 12 K. They excited various vibrational levels of $\text{C}_2\text{H}_4$ in the complex and monitored the reaction with Fourier-transform infrared absorption spectroscopy. Products of both R2 and R3 have been observed. The lowest excitation frequency which leads to the product formation is 1896 cm$^{-1}$ (5.4 kcal/mol), indicating a reaction threshold. For vibra-
tional transitions between 1896 and 4209 cm\(^{-1}\), deviations from a smooth rise of the quantum yield with energy have been attributed, in part, to mode selectivity. Similar HF/DF branching ratios close to 1.1 were found for the reactions of \(\text{F}_2\) with three different isomers of \(\text{C}_2\text{H}_3\text{D}\). Based on this observation, the contribution of an abstraction reaction of \(\text{F} + \text{C}_2\text{H}_2\text{D}\) to the HF(DF) formation was ruled out because at such a low temperature, the author expected significant isotope effect for the \(\text{F}\) atom attacking back on the \(\text{CH}\) or \(\text{CD}\) bond.\(^{12}\) They concluded\(^7\)-\(^{10}\) that the \(\text{F}_2 + \text{C}_2\text{H}_4\) reaction under the cryogenic matrix-isolation conditions involves a vibrationally hot 1,2-difluoroethane intermediate, followed by a decomposition via either R2 or R3; the product branching ratio originates in a competition between the HF(DF) elimination and the thermal stabilization of the vibrational excited intermediate. The later process can be enhanced by two orders of magnitude with the addition of a second \(\text{C}_2\text{H}_4\) in the matrix cage. It is less conclusive, however, for how the 1,2-difluoroethane intermediate is formed. Two possibilities have been mentioned: (i) a one-step four-center addition of \(\text{F}_2\) to the \(\text{C}==\text{C}\) \(\pi\)-bond and (ii) a rapid sequential process within the same matrix cage, \(\text{F}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{F} + \text{F} \rightarrow \text{C}_2\text{H}_4\text{F}_2\).

Grover et al.\(^{11}\) studied the reaction of \(\text{F}_2\) with benzene in a crossed molecular beam experiment and determined the energy threshold of generating \(\text{C}_6\text{H}_6\text{F}+\text{F}\) products to be \(13.9 \pm 0.5\) kcal/mol. The angular distribution of the \(\text{C}_2\text{H}_6\text{F}\) product was observed to be slightly backward with respect to the \(\text{F}_2\) beam direction. The \(\pi\) electron system of benzene is more stable than that of \(\text{C}_2\text{H}_4\) due to the resonance effect. Thus, a larger threshold for \(\text{F}_2 + \text{C}_6\text{H}_6\) reaction may be expected.

When reliable \textit{ab initio} calculations were lacking, Raff\(^{12}\) reported a semiempirical potential energy surface (PES) with the central structure being 1,2-difluoroethane, in which the barrier height of R3 was set to be 12.3 kcal/mol for the concerted, planar, four-center addition of \(\text{F}_2\) across the ethylene double bond. A series of dynamic studies\(^{13\text{-}15}\) have been performed on this PES for reactions in the gas phase and matrix-isolation conditions. Although this empirical PES yielded equilibrium geometries, reaction enthalpies, and fundamental vibrational frequencies in fair-to-good accord with experimental values, there was no reliable input for the properties of the transition states at that time.\(^{12}\) Therefore, the results should be used with caution.

There have been some earlier \textit{ab initio} investigations on \(\text{F}_2 + \text{C}_2\text{H}_4\) reaction but the employed calculation levels are probably not high enough to describe the reaction. Yamabe et al.\(^{16}\) proposed a four-center transition state for a concerted \(\alpha\beta\)-addition using the Hartree–Fock and third-order Møller–Plesset calculations with 3-21G basis sets. The reported barrier is about 51 kcal/mol, which is even higher than the bond dissociation energy of \(\text{F}_2\) (\(D_{\text{b}}=37\) kcal/mol). Iwaoa et al.\(^{17}\) suggested a nonconcerted mechanism with the MP2/6-31 +G calculation, in which one C—F bond is formed first at the transition state structure. The calculated reaction barrier is 23 kcal/mol.

Recently, Wang et al.\(^{18}\) investigated the mechanism for the addition of \(\text{F}_2\) to \(\text{C}_2\text{H}_4\) using density functional theory (DFT) with large basis sets. They proposed a two-step diradical mechanism: the first step is low-barrier attack of \(\text{F}_2\) on \(\text{C}_2\text{H}_4\) to produce a diradical intermediate of \(\text{F}==\text{F}—\text{CH}_2==\text{CH}_2\) structure; the second step is the complete dissociation of the \(\text{F}==\text{F}—\text{CH}_2==\text{CH}_2\) (R1). For the first step, the obtained barrier height differs with the used functional; 1.8 kcal/mol using B3LYP and 6.3 kcal/mol with BHH (half-and-half functional). Qi et al.\(^{19}\) studied this reaction with calculations of direct dynamics based on DFT and plane-wave basis sets. The authors found all three channels (R1, R2, and R3) in their simulations.

The abovementioned experimental and theoretical results in literature give rise to an immediate question as to why this reaction leads to totally different products in the gas phase than in the matrices which simulate a condensed phase surrounding. The chosen matrices consisted of \(\text{N}_2\) or \(\text{Ar}\), which should be inert enough in order to neglect chemical effects induced by the matrix itself. However, sterical caging effect in the condensed phase may be an important factor. Another arising question is: are the present theoretical calculations able to account for all the experimental observations? With this contribution, we would like to answer the above questions with crossed molecular beam experiments and high level \textit{ab initio} calculations.

In our crossed molecular beam experiments, R1 was observed to be the only product channel for a wide range of collision energy up to 11 kcal/mol. The translational energy and angular distributions of the corresponding products were recorded. The collision energy threshold for the reaction was determined. In addition, possible reaction paths have been searched with high level \textit{ab initio} calculations. Among the three possible primary channels, only a reaction path corresponding to R1 could be found under modest energy range. Energetics of R1 was determined using the CCSD(T) calculation extrapolated to the complete basis set limit (CBSL). The results obtained from various \textit{ab initio} methods were compared and discussed. Combining the experimental and computational results, an unambiguous mechanism is given in this paper.

II. METHODS

A. Experimental

The experimental setup was similar to our previous works.\(^{21\text{-}22}\) Therefore, only the essential parts of this experiment are given here. The \(\text{F}_2\) molecular beam was generated by expanding 5% \(\text{F}_2/\text{He}\) mixture or neat \(\text{F}_2\) gas (Spectra Gases, Inc.) through a fast pulsed valve\(^{23}\) (Even-Lavie valve, high repetition rate model, \(\approx 1000\) Hz). The nozzle temperature was controlled to be at room temperature or a cryogenic temperature (\(\approx 150\) K) to generate different beam velocities. The mean speed of the neat \(\text{F}_2\) beam was 700 m/s from the room temperature nozzle and 535 m/s from the cryogenic nozzle. The expansion of the seeded 5% \(\text{F}_2/\text{He}\) gas through the room temperature nozzle leads to a mean velocity of 1530 m/s.

The \(\text{C}_2\text{H}_4\) gas (Linde, >99.99%) was seeded in He with two different concentrations of 4% and 10%. The gas mixtures were expanded through a similar pulsed valve to form
the molecular beams. To increase the beam speed, the respective nozzle is heated. The C$_2$H$_4$ beam speed was tuned between 1500 and 1860 m/s by varying the seeding ratio and nozzle temperature. Both molecular beams were collimated by sharp-edge skimmers (Beam Dynamics, Inc.) to an angular divergence of about ±1.3° [full width at half maximum (FWHM)].

Both molecular beams passed through further collimators cooled by a helium refrigerator and collided with each other under 90°. Following the reaction, the neutral products traveled a fixed distance to an ionizer. After ionization, the charged products were selected by a quadrupole mass filter and entered a Daly detector coupled with a multichannel scalar (MCS) (EG&G ORTEC) to do ion counting. The time-of-flight (TOF) spectra accumulated by the MCS were recorded and transferred into the product velocity distributions. The laboratory (LAB) frame angular distribution was obtained by integrating the TOF data for each given LAB angle. Scattering experiments of Ar+C$_2$H$_4$ and F$_2$+N$_2$ were performed to confirm that the observed signals in the F$_2$+C$_2$H$_4$ crossed beam experiments were not affected by the impurities in the F$_2$ and C$_2$H$_4$ samples.

To transform the data taken at the LAB frame to the center-of-mass (CM) frame, a forward convolution program was applied to simulate all TOF spectra and angular distribution. We input the experimental parameters (spreads of the beam velocities and flight distance, etc.) and iteratively adjusted the CM-frame translational energy distribution $P(E_T)$ and angular distribution $P(\theta_{CM})$ until a best fit was obtained. The Jacobian factor of the LAB-CM transformation has been included in the program.

The experimental studies were performed using two different apparatuses. The majority of the results presented here were obtained with the apparatus equipped with an electron-impact ionizer in the detector. For measuring photoionization efficiency spectra, a second crossed molecular beam apparatus coupled with the synchrotron radiation facility was employed. The product flight distance is 10.1 cm in the synchrotron apparatus and 24.2 cm in the electron-impact apparatus. For a better velocity resolution, the TOF analysis was based on the electron-impact results.

For determination of the relative reaction cross section as a function of collision energy, the C$_2$H$_4$ and F$_2$ beam intensities need to be known. The C$_2$H$_4$ beam intensity was measured using a fast ionization gauge (Beam Dynamics, Inc.) operated at a reduced electron-impact energy (=23 eV) at which the He buffer gas produced no signal while C$_2$H$_4$ can still be efficiently ionized. The F$_2$ beam intensity could be deduced from the attenuation measurements, in which the C$_2$H$_4$ beam intensity was obtained with the apparatus equipped with an electron-impact ionizer at 70 eV.

FIG. 1. (Color online) (a) A comparison of typical TOF spectra at m/z =47 and 46. The data were recorded with the electron-impact ionizer at 70 eV; (b) LAB-frame angular distributions of the reactive signals at m/z =47 and 46. The experimental data are connected with a spline fit for visualization. The corresponding LAB angle of the center of mass is shown as a vertical dashed line. The data were recorded with the photoionization detector at 11 eV photon energy. The collision energy is 11.4 kcal/mol in both cases.

B. Ab initio calculation

In this work, the complete active space self-consistent field (CASSCF) calculation with the second-order multireference perturbation theory (CASPT2) corrections was used to explore the PES. It has been found that the CASPT2 calculation is computationally efficient to predict not only the geometries of stable species but also transient structures along the reaction path. We believe that it is important to use a multireference method to check the calculation of a reactive PES, especially when breaking/formation of a chemical bond is involved.

All calculations have been performed without setting the molecular symmetry, i.e., using the C$_1$ point group. This allows us to avoid unnecessary bias in choosing active orbitals. All employed active spaces have been carefully chosen and tested. The geometry optimization and zero point energy (ZPE) calculations were obtained mainly using the CASPT2 methods. Dunning basis sets (cc-pVNZ and aug-cc-pVNZ, N=T, Q, 5) were employed. The barrier height and reaction enthalpy were obtained using single-point CCSD(T) calculations based on the respective CASPT2 optimized geometries. The CCSD(T) energy was extrapolated to CBSL using the following scheme: the Hartree–Fock energy was extrapolated with an exponential function, $\exp(-c \cdot N^3)$; the CCSD(T) correlation energy was extrapolated with a function of $\gamma_2 N^{-3}$. Whenever the QCISD(T) analytical gradients were available, the QCISD(T) approach was used to double-check the geometry optimization. All calculations were performed with the MOLPRO 2006.1 quantum chemistry package.
III. RESULTS

A. Crossed beam experiments

The first goal of this study is to identify the primary product channel(s) among the three possible ones: R1, R2, and R3. In the crossed molecular beam reaction of \( \text{F}_2 + \text{C}_2\text{H}_4 \), we have searched for signals with the mass-to-charge ratios \( m/z = 47 \), 46, and 66, which correspond to the parent masses of the possible products, \( \text{C}_2\text{H}_3\text{F} \) (R1), \( \text{C}_3\text{H}_4\text{F} \) (R2), and \( \text{C}_2\text{H}_3\text{F}_2 \) (R3), respectively. In the experiments, signals of reactive scattering could be observed at \( m/z = 46 \). The existence of R1 can be verified with the observation of the \( m/z = 47 \) signal. On the other hand, there are two likely contributions to the \( m/z = 46 \) signal. One is from the \( \text{C}_2\text{H}_3\text{F} \) products of R2; the other is from dissociative ionization of the \( \text{C}_2\text{H}_4\text{F} \) (R1) product. For the latter case, the signal of the daughter ion usually has the same arrival time and angular distribution as its parent ion. Therefore, the recoil velocity of the \( \text{C}_2\text{H}_3\text{F} \) product of R2 should be much larger than that of the \( \text{C}_2\text{H}_4\text{F} \) product of R1. The noise at earlier arrival times in the experimental TOF spectra is quite low, thus we can be sure that there is no faster product observed at \( m/z = 46 \). Hence, the observed \( m/z = 46 \) signal should stem from the dissociative ionization of the \( \text{C}_2\text{H}_4\text{F} \) product. Regarding the possibility of R3, its product angular distribution in the LAB frame will be very narrow because the recoil velocity is zero. Such hypothetical signal has not been observed in the crossed beam experiments. Again, energetically, the R3 product is unlikely to be observed in the gas phase because its exothermicity is larger than the energy required to break a chemical bond or to eliminate a HF molecule.

Figure 2 shows the experimental TOF spectra of the \( \text{C}_2\text{H}_4\text{F} \) product from the \( \text{F}_2 + \text{C}_2\text{H}_4 \) crossed beam reaction at 11.0 kcal/mol collision energy. The ion of \( m/z = 46 \), which is a daughter ion of \( \text{C}_2\text{H}_4\text{F} \), was chosen because of its higher signal-to-noise ratio. Figures 1 and 2 show the product distributions in the LAB frame. In order to comprehend the underlying reaction dynamics, the experimental TOF data and angular distribution were transformed to the CM frame using the forward convolution method described in Sec. II A. The best-fit results in the CM frame are plotted in Fig. 3(a). Initially, one single \( P(E_T) \) distribution was assumed to describe the entire dataset. However, the product scattered in the backward direction was consistently slower than at other CM angles. Therefore, a slower \( P(E_T) \) for the backward direction \( (\theta_{CM}=180^\circ) \) and a faster \( P(E_T) \) for CM angles between 0° and 110° were used, connected by a linearly interpolated \( P(E_T) \) distribution for the region between 110° and 180°. The resulting best fit for a collision energy of 6.6 kcal/mol is shown in Fig. 3(b).
behavior is consistent with the previous gas-phase kinetic 
been observed at higher collision energies. This threshold 
below that of the CM. Checking the LAB-frame angular dis-
product at 11.0 and 6.6 kcal 
6.6 kcal/mol is shown in Fig. 3(b). At this collision energy,
we used only one $P(E_T)$ distribution to fit all of the TOF spectra recorded.

Figure 4 shows a comparison between the experimental 
simulated LAB-frame angular distributions of the C$_2$H$_4$F 
product at 11.0 and 6.6 kcal/mol collision energies. Figure 4 
clearly shows a highly asymmetric product angular distribution 
with a pronounced bias toward the LAB angles larger 
than that of the CM. Checking the LAB-frame angular distri-
butions at several collision energies in the range of 
5.3 to 11 kcal/mol always gave a similar trend. It is obvious 
from Figs. 3 and 4 that the CM-frame angular distributions 
are peaking preferentially in the backward direction.

No reactive signal could be found at collision energies 
smaller than 5.0 kcal/mol, while significant signals have 
been observed at higher collision energies. This threshold 
behavior is consistent with the previous gas-phase kinetic study\cite{2} and matrix-isolation infrared-excitation investigations.\cite{7-10} To determine the reaction threshold, the excitation 
function of R1, i.e., the relative reaction cross section as 
a function of collision energy was measured. The result is 
shown in Fig. 5, which was determined by the following procedure: (i) the LAB-frame angular distribution was measured 
at every selected collision energy; (ii) the peak height of the angular distribution was normalized with respect to 
both F$_2$ and C$_2$H$_4$ beam intensities. Then, the normalized peak height was plotted as a function of collision energy to 
give the data points in Fig. 5. This approach neglects the Jacobian factor of the LAB-CM transformation. However, we 
found that this factor varies very little within the collision
energy range in Fig. 5. The resulting error of not including 
the Jacobian factor is less than 5%, thereby smaller than other experimental uncertainties. A more significant influ-
ence is the width of the collision energy. From the measured 
spreads of the molecular beam speeds, the width of the collision energy can be deduced. It is indicated as a horizontal 
error bar in Fig. 5. The experimental excitation function was 
fit with two simple forms, a linear form $\sigma(E_c) \propto (E_c - E_0)$ or a quadratic form $\sigma(E_c) \propto (E_c - E_0)^2$, for the collision energy $E_c$ higher than the threshold energy $E_0$. Both func-
tions have been convoluted with the derived collision energy spread. The $E_0$ obtained are 5.8 ± 0.2 and 5.3 ± 0.3 kcal/mol 
for the linear and quadratic functions, respectively. Account-
ing for both results, we suggest the collision energy threshold 
for R1 to be 5.5 ± 0.5 kcal/mol.

To vary the molecular beam speed, we could heat the 
C$_2$H$_4$ nozzle to 413 K or cool the F$_2$ nozzle to 150 K. In 
order to check the influence of the nozzle temperature and 
the resulting change in vibrational distributions of the react-
ants, the experiment was designed to have conditions of 
different nozzle temperatures distributed in a narrow range of 
collision energy. In Fig. 5, the nozzle temperature combina-
tions are indicated with different symbols as open/closed 
symbols for heated/RT C$_2$H$_4$ nozzle; square/circle symbols for cryo/RT F$_2$ nozzle (heated=413 K; RT=300 K; cryo=150 K).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{The relative reaction cross section of R1 as a function of collision energy. Two functions convoluted with the collision energy spread are shown as the solid and dashed lines. The horizontal error bar indicates the width (FWHM) of the collision energy spread. Different symbols of the data points indicate the nozzle temperature used in the experiments: open/closed symbols for heated/RT C$_2$H$_4$ nozzle; square/circle symbols for cryo/RT F$_2$ nozzle (heated=413 K; RT=300 K; cryo=150 K).}
\end{figure}

\section{B. Calculations}

To further investigate the reaction mechanism of R1, the 
transition state was searched with the CASPT2 and 
QCISD(T) methods. For all CASPT2 results presented here,
the active spaces have been carefully chosen to ensure that there is no orbital switching along the reaction paths and that the chemically important molecular orbitals such as the π/π* orbitals of C2H4 and σ/σ* orbitals of F2 are included in the active spaces. Although we did not constrain the symmetry in the calculation (C1 point group was used in all input files), two kinds of transition state (TS1) geometries were found for R1. The point groups of the two TS1 structures can be assigned as C2v and Cs. The optimized geometries are shown in Fig. 6. Both C2v and Cs structures of TS1 have been verified as a first-order saddle point on the PES. The vibrational frequency analysis for both structures shows that there is one imaginary frequency, of which the normal-mode displacement vector corresponds to the motions of the F—F bond dissociation and C—F bond formation.

Both C2v and Cs geometries of TS1 can be located using CASPT2 calculations with different initial guess geometries. We have checked a few active spaces from [4(6e, 8o)] to [6(6e, 6o)]. Selected results with important geometry parameters are listed in Table I. It can be seen in Table I that the active spaces have only little effect on the transition state geometry. For example, TS1a and TS1b are almost the same, and so are TS1c and TS1d. The QCISD(T) calculation predicts a C2v transition state (TS1 g) with a slightly longer r1 and slightly shorter r2, r3.

To check the effect of the augmented basis sets on the geometry calculation, a CASPT2(6e, 6o) calculation was performed to locate the transition state with the basis sets: H = cc-pVDZ; C, F = aug-cc-pVTZ. The resulting geometry TS1e is very similar to TS1d with the largest difference in bond length to be only 0.04 Å. In addition, TS1f was obtained with larger basis sets on H. The resultant geometry is again very similar to TS1e. These results indicate that the type and size of the basis sets used have only minor effects on the TS1 geometry.

To clarify these C2v and Cs structures of TS1, we performed single-point CCSD(T) calculations with the same basis sets. The results (see Table I) indicate practically no energy difference for these structures at the CCSD(T) level, independent of being of C2v or Cs symmetry. We have also checked the single-point CCSD(T) energy for a few interpolated geometries between the C2v and Cs structures. A smooth path connecting these two structures without any barrier could be obtained. These results indicate the PES is very flat in the region between the C2v and Cs structures of TS1. It is important to mention that the product valley of R1 has to be a lower symmetry than C2v. For the C2v transition state, symmetry lowering is inevitable for product formation. We believe that the actual path of R1 may go though anyone of the C2v and Cs transition state structures or any geometry between/near them. With the above argument of symmetry lowering, we have chosen the Cs structure of TS1 for the following discussions.

From TS1e, an intrinsic reaction coordinate (IRC) which connects TS1e to both reactant valley and product valley was obtained with a CASPT2 calculation [active space: (6e, 6o); basis sets: H = cc-pVDZ; C, F = aug-cc-pVTZ]. At each structure on the IRC, single-point energy calculations were performed. A single-point energy calculated with CCSD(T)/cc-pVTZ(C2H4); aug-cc-pVTZ(C). Unit: hartree. 1 hartree = 627.5096 kcal/mol.

### Table I. Comparison among TS1 geometries obtained with selected methods. Method of the geometry optimization: TS1a and TS1d: CAS-PT2(6e, 6o)/cc-pVDZ (H), cc-pVTZ(C,F) with different initial guess geometries; TS1b: CAS-PT2(6e, 6o)/cc-pVDZ (H), cc-pVTZ (C,F); TS1c: CAS-PT2(6e, 6o)/cc-pVTZ (H), aug-cc-pVTZ (C,F); TS1e: CAS-PT2(6e, 6o)/cc-pVTZ (H), aug-cc-pVTZ (C,F); and TS1f: CAS-PT2(6e, 6o)/cc-pVTZ (H), aug-cc-pVTZ (C,F).

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*aUnit: Å and deg.

*aSingle-point energy calculated with CCSD(T)/cc-pVTZ (C2H4); aug-cc-pVTZ (C,F).
formed with larger active spaces up to (12e,12o). The results are shown in Fig. 7. All relative energy curves in Fig. 7 have a similar shape but the barrier heights are slightly different. The lowest barrier height (ZPE not included) is about 4.6 kcal/mol for the CASPT2 calculations using (8e,10o) and (12e,12o) active spaces. The higher values are 5.6 and 6.2 kcal/mol for (10e,12o) and (10e,10o) active spaces, respectively.

With the results shown in Figs. 6 and 7, the reaction path of R1 can be described as a simple rebound type, in which one fluorine atom transfer is the major atomic motion along the reaction coordinate. A single barrier separates the products from the reactants. It can be anticipated that the flux of the reaction is controlled by the TS1 barrier, acting as a kinetic bottleneck. To overcome this barrier, the favorable orientation of the approaching F2 is roughly normal to the C2H4 molecular plane. The structure of the C2H4 subsystem varies little from the reactant valley to TS1, with a slightly elongated C—C bond distance for TS1. The analysis of the CASSCF molecular orbitals suggests the coupling of the π/π* orbitals of C2H4 with the σ/σ* orbitals of F2 to be the most important interaction for the TS1 structure. On the IRC, there are van der Waals wells in both entrance and exit valleys. The well depths are about 1 kcal/mol, which is in the range of typical van der Waals interactions. The reaction is exothermic, i.e., the newly formed C—F bond is stronger than the F—F bond of F2.

Figure 8 shows the effect of the basis sets on the TS1 barrier height (ZPE not included) at the CCSD(T) level. Five families of basis sets were tested. As can be seen in Fig. 8, the use of the augmented basis sets on fluorine has the most significant effect. For TS1, partial charge transfer to the F atoms was observed in the calculation. In this situation, the augmented basis sets are required to adequately describe the diffuse character of the atoms with (partially) negative charge. The quality of the basis sets is less crucial for the rest of atoms, especially for the H atoms as the CH bonding character varies only slightly along the IRC. In order to perform more efficient computation, relatively smaller basis sets were selected for the H atoms. If an extrapolation scheme is performed on the size of the basis sets for C and F atoms, the calculated potential energy barriers converge to about 6.8 kcal/mol (without ZPE correction) at all basis set selections.

The results of the ZPE calculations and CCSD(T) energies are summarized in Table II. The ZPE-corrected CBSL barrier height for TS1 is 7.8 kcal/mol or 7.1 kcal/mol using the individual CASPT2 or the QCISD(T) frequencies (not scaled), respectively. The lower value of 7.1 kcal/mol is still 1.6 kcal/mol higher than the experimental threshold of 5.5 ± 0.5 kcal/mol. This discrepancy seems significant and may locate on the borderline of the statistical CCSD(T) accuracy. A possible source of error to account for this discrepancy lies in the ZPE calculation. The structure of the C2H4 subsystem of TS1 is quite similar to that of the reactant, suggesting the ZPE correction should be small. It is possible that the ZPE of TS1 is overestimated especially for the CASPT2 calculation, and/or that the harmonic approximation is not very good for TS1. As for the CCSD(T) energy, CCSD(T) is a single-reference based calculation, which may be less reliable if the electronic wave function of the studied system is of significant multireference character. For examining this issue, we have checked the value of the T1 diagnostic of the CCSD(T) calculation. It has been recommended that if T1 is larger than 0.02, the results from single-reference electron correlation methods limited to single- and double-excitations should be viewed with caution, i.e., the CCSD calculation may be less reliable. For the studied structures, T1 is about 0.017 for TS1; 0.013 and 0.011 for F2 and C2H4, respectively. The T1 values are all small, suggesting that the single-reference methods such as CCSD, CCSD(T), and MP2 may be applicable. Nevertheless, although the discrepancy between the calculated and experimental reaction threshold seems significant, it is still in the reasonable range of statistical errors of CCSD(T) calculations. Other corrections, e.g., for core/valence and scalar relativistic effects and higher order correlation may improve the energy calculation at higher computational expense. Moreover, for transitions states, the error estimation of an ab initio calculation is not well established yet.

Figure 9 shows the result of a two-state CASSCF calcula-
lution along the same IRC in Fig. 7. Although the energy calculation at the CASSCF level is not very accurate, Fig. 9 provides qualitative potential energy curves of the ground state and the first excited state. The energy gap between these two electronic states is quite large at the reactant valley and becomes smaller for the product side. It is expected that there are degenerate electronic states at the product valley which are stable structures separated by a high barrier. Energy of the CH₂CH₂F product should be less than 20 kcal/mol, which is not enough for this H-atom migration process.

C. H-atome migration and photoionization efficiency spectrum

With the synchrotron facility, the photoionization efficiency (PIE) spectrum of the CH₂HF product was measured at 9 kcal/mol collision energy. The corresponding ionization threshold was determined to be 8.9 eV from the abrupt rise of the PIE curve. Additionally, the PIE spectrum of CH₄ was also measured and the ionization threshold determined is in good accord with the literature value of 10.5 eV. However, it is less straightforward to compare the experimental photoionization threshold of CH₂HF to the result from a conventional \textit{ab initio} calculation. We found that the ionic form of CH₂HF is not a stable structure on the PES, which can isomerize to a more stable structure of CH₃CHF⁺ without any barrier. The experimental PIE signal usually corresponds to a photoionization process with a good Franck–Condon factor. A simple model of harmonic oscillators is not applicable in this case because the considered structure is very far from the equilibrium geometry. A fair description of the Franck–Condon factor and the interpretation of the PIE spectrum therefore require further theoretical investigation. On the neutral PES both isomers CH₂HF and CH₃CHF are stable structures separated by a high barrier (see Fig. 10 for details). In our experimental conditions, the internal energy of the CH₂HF product should be less than 20 kcal/mol, which is not enough for this H-atom migration process.

<table>
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aCalculated at the TS1f geometry.
bNotation for the basis sets: H=cc-pV_NZ; C=cc-pV_NZ; F=aug-cc-pV_NZ; CBSL=complete basis set limit. The Hartree–Fock energies were extrapolated with a function of \exp(-\gamma_N). The CCSD(T) correlation energies were extrapolated with a function of \gamma_N.\(^{-3}\)
cZPE=vibrational zero-point energy, which is calculated using the basis sets: H=cc-pVDZ; C=cc-pVTZ; F=aug-cc-pVTZ. The active spaces used for the CASPT2 calculations are (6e,6o) for singlet species, and (5e,5o) for doublet species. Experimental data are from Ref. 43.\(^{d}\)
d\(\Delta\)ZPE\(_{\text{CASPT2}}\) is included in TS1 barrier; \(\Delta\)ZPE\(_{\text{CASPT2}}\) is used in \(\Delta\)H\(_{\text{ex}}\)K.
IV. DISCUSSION

The average kinetic energy release ($E_T$) can be obtained from the product translational energy distribution $P(E_T)$. The total available energy $E_{av}$ for the R1 products is given by the sum of the collision energy and the reaction exothermicity of 7.8 kcal/mol. The fraction of the excess energy released as translation ($f_T=(E_T/E_{av})$) was determined to be $f_T=0.27$ and $f_T=0.29$ for the collision energies of 6.6 and 11 kcal/mol, respectively. This means that more than 70% of the available energy is deposited into the product’s internal degrees of freedom. In this reaction, the structure of TS1 was found to be more similar to the reactants than to the products. Thus, according to Polanyi’s rule, TS1 can be classified as an early barrier and the available energy is likely to excite the vibrational motion of the products. Polanyi’s rule also suggests that a translational excitation of the reactants is more efficient in promoting the reaction than vibrational excitations. Although Polanyi’s rule was initially proposed for a triatomic A + BC reaction, it seems applicable to the F$_2$ + C$_2$H$_4$ reaction because that the reaction path of R1 is very similar to a simple atom transfer reaction and the C$_2$H$_4$ sub-system is spectatorlike along the reaction path from the reactant valley to TS1. In addition, the equilibrium structure of the CH$_2$CH$_2$F product is quite different from the TS1 structure, also suggesting vibrational excitation of the products induced by the structure change in the exit valley.

The experimental angular distribution is highly asymmetric, indicating the reaction time scale is much shorter than the rotational period of the collision complex. This observation can clearly rule out the contribution of any long lived reactive events; and

(i) the reaction time scale is much shorter than the complex rotation period;  
(ii) collisions at small impact parameters dominate in the reactive events; and  
(iii) the interaction between the three subunits, F, F, and (C$_2$H$_4$), is approximately linear.

Our reaction threshold of R1 is slightly higher than the reported activation energy of 4.6 kcal/mol obtained from a kinetic study in the temperature range of 300 to 430 K. Under these comparably hot conditions, however, a thermal excitation of the F$_2$ vibration is possible to promote the reaction leading to the observed lower threshold. The fundamental vibrational frequency of F$_2$ is 894 cm$^{-1}$, corresponding to an energy gap of 2.55 kcal/mol. From the Boltzmann distribution, the ratio of $F_2(v=1)/F_2(v=0)$ can be estimated to be 5.0% at 430 K and 1.4% at 300 K. The increase in F$_2(v=1)$ population is quite significant when the temperature is raised above room temperature. It is very likely that the F$_2$($v=1$)+C$_2$H$_4$ reaction has a significant lower threshold than the F$_2$(v=0)+C$_2$H$_4$ reaction. Therefore, the amount of thermal excitation of the reactants may have significant contribution to the empirical activation energy.

Wang et al.\textsuperscript{18} studied the reaction with DFT calculations and proposed a diradical intermediate, which can be formed through a low barrier. The corresponding transition state has C$_2v$ symmetry and its geometry ($r_1$=1.794 Å; $r_2$, $r_3$ =1.975 Å; and $r_4$=1.330 Å) is quite similar to our TS1a and TS1b. However, in the crossed beam experiments, we have observed highly asymmetric product angular distribution, indicating the reaction time scale is substantially shorter than rotation. This finding does not support the mechanism of a stable intermediate. The stability of the diradical may be too small to have a significant effect. In Fig. 7, a van der Waals well can be seen in the product valley but the well depth is quite shallow in comparison with the DFT results\textsuperscript{18} of 5.6 kcal/mol (B3LYP) or 4.0 kcal/mol (BHH). We believe that the multireference CASPT2 calculation should provide a better description than the DFT calculations for the exit valley which has significant diradical character. On the other hand, from the product valley, it is quite feasible to form the structure of 1,2-difluoroethane if the ejected F atom is let to attack back to the radical site (the unpaired electron on the carbon atom) of the CH$_2$CH$_2$F. In the gas phase, there is essentially very little probability for this process but it should be quite likely in the condensed phase. Cage effect in high density environments, such as a cryogenic matrix, effectively hinders the escape of the F atom. The F + CH$_3$CH$_2$F reaction is a typical process of radical-radical recombination which is usually barrierless. Therefore, R3 product may be formed through this sequential process following R1. The initially produced 1,2-difluoroethane is highly vibrationally excited. It can decompose to HF+CH$_2$CHF or be stabilized through efficient energy transfer in the condensed phase. In this study, a detailed computational search for a direct reaction path related to either concerted addition (R3) or HF formation (R2) led to no results. Combining these theoretical efforts with the experimental observation that only R1 is observed in the gas phase, we strongly suggest that R2 and R3 observed in the condensed phase are most likely due to the cage effect and fast sequential reactions following R1.

V. SUMMARY

The F$_2$+C$_2$H$_4$ reaction has been investigated with crossed molecular beam experiments and high level ab initio calculations in detail. R1 has been found to be the only primary product channel in the gas phase. The experimental reaction threshold has been determined to be $5.5 \pm 0.5$ kcal/mol. The translational energy and angular distributions of R1 products have been recorded. The strongly backward angular distribution indicates a typical rebound reaction mechanism discriminating mechanisms involving a stable intermediate. The calculated transition state of R1 can be classified as an earlier barrier, which is consistent with the
small fraction of product translational energy release \((f_T \approx 0.28)\) observed in the experiments. The reaction path of R1 has been calculated while other concerted-addition paths could not be found. The previous condensed-phase results can be explained by secondary reactions following R1 due to the cage effect.

Our ongoing research includes \(F_2\) reactions with other unsaturated hydrocarbons such as \(C_2H_6\), \(C_2H_8\), and \(C_2H_2\). Preliminary results show that the barriers for the \(F_2\) reactions with \(C_2H_6\) and \(C_2H_8\) are significantly lower than that of \(F_2 + C_2H_4\) reaction, while the \(F_2 + C_2H_2\) reaction has a much higher barrier. A direct formation of HF could not been observed in either of these reactions.

**ACKNOWLEDGMENTS**

National Science Council (Grant No. NSC95-2113-M-001-041-MY3) and Academia Sinica, Taiwan supported this work. We thank Professor Yuan T. Lee and Dr. Jens Riedel for valuable comments and National Synchrotron Radiation Research Center, Taiwan for the use of facilities.

20. The electronic energy \(U\) is calculated with the CCSD(T) method at the complete basis set limit for R1 (see Table II) and at the basis sets: \(\text{H} = \text{cc-pVTZ}; \text{C} = \text{cc-pVQZ}; \text{F} = \text{aug-cc-pVQZ}\) for R2 and R3. The vibrational zero-point energy is calculated with the CASPT2 methods. \(\Delta E_{\text{vibr}} = \Delta E + \Delta E_{\text{ZPE}}\). See Table II for details.
37. H.-J. Werner, P. J. Knowles, R. Lindh et al., MOLPRO, Version 2006.1, a package of *ab initio* programs (see http://www.molpro.net).
42. For CCSD(T), \(T_1\) slightly larger than 0.02 may be acceptable, but there is no recommended critical value of \(T_1\) for CCSD(T) calculations in the literature.
43. See: http://webbook.nist.gov/cgi/cbook.cgi?ID=C74851&Units=SI&Mask=20#Ion-Energetics.
44. Calculated with B3LYP, MP2, QCISD, and CASPT2 methods using cc-pVTZ basis sets.
45. Experimental adiabatic ionization energy of CH\(_2\)CF is 7.93 eV; See: http://webbook.nist.gov/cgi/cbook.cgi?ID=C52067193&Units=SI&Mask=20#Ion-Energetics.