

Shock wave and modelling study of the dissociation kinetics of C₂F₅I

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ESI-I Modelling of the Unimolecular Dissociation of C₂F₅I

a. Computational details

Because only limited basis sets for I atoms are available, different basis sets were explored. The analysis indicated that the 6-311G(d) basis set as tabulated in <https://bse.pnl.gov/bse/portal> was most appropriate for the present calculations, see refs. [S1] and [S2].

Optimized structures and vibrational frequencies, derived with the functional M06-2X and combined with the 6-311+G(3df) basis set for C and F atoms and the 6-311G(d) basis set for I atoms given above, were employed to characterize the potential energy surface (PES) of dissociating C₂F₅I. Thermochemistry data and Morse parameters β were obtained from single-point CCSD(T) calculations with the basis set 6-311+G(2d) for the C and F atoms and the basis set 6-311G(d) for I atoms.

b. Thermochemical results

Reaction	ΔH_0°	$\Delta H_0^\#$
C ₂ F ₅ I → C ₂ F ₅ + I	234.2*	-
C ₂ F ₅ I → C ₂ F ₄ + IF	268.8	388.7
C ₂ F ₅ I → CF ₃ + CF ₂ I	376.9	-
C ₂ F ₅ I → C ₂ F ₄ I + F	498.4	-

Table S1 Reaction (and transition state) enthalpies at 0 K (in kJ mol⁻¹; *: the fit of the experimental $k_1(T)$ of the present work led to $\Delta H_0^\circ = 240 (\pm 6)$ kJ mol⁻¹).

c. Properties of the PES for C_2F_5I dissociation along the minimum energy path (MEP)

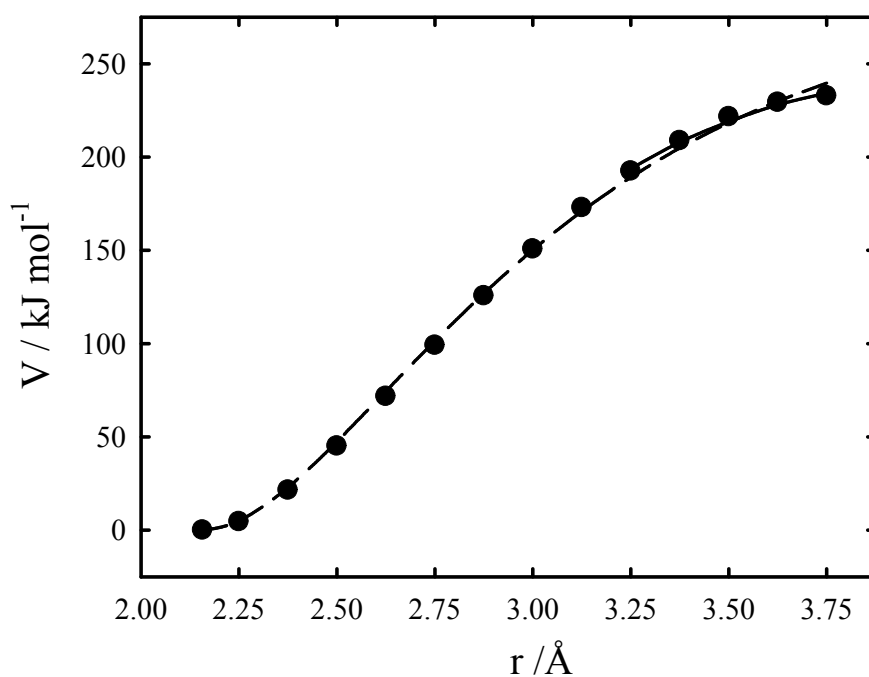


Fig. S1 Electronic potential $V(r)$ for the dissociation process $C_2F_5I \rightarrow C_2F_5 + I$ ($r = \text{C} - \text{I}$ bond length; $V(r)$ calculated at the CCSD(T)//M06-2X level with the basis sets given in ESI-I-a; dashed line: fit with a Morse potential with parameter $\beta = 1.51 \text{ Å}^{-1}$; solid line: fit with $\beta = 1.76 \text{ Å}^{-1}$ for $r > 3.25 \text{ Å}$).

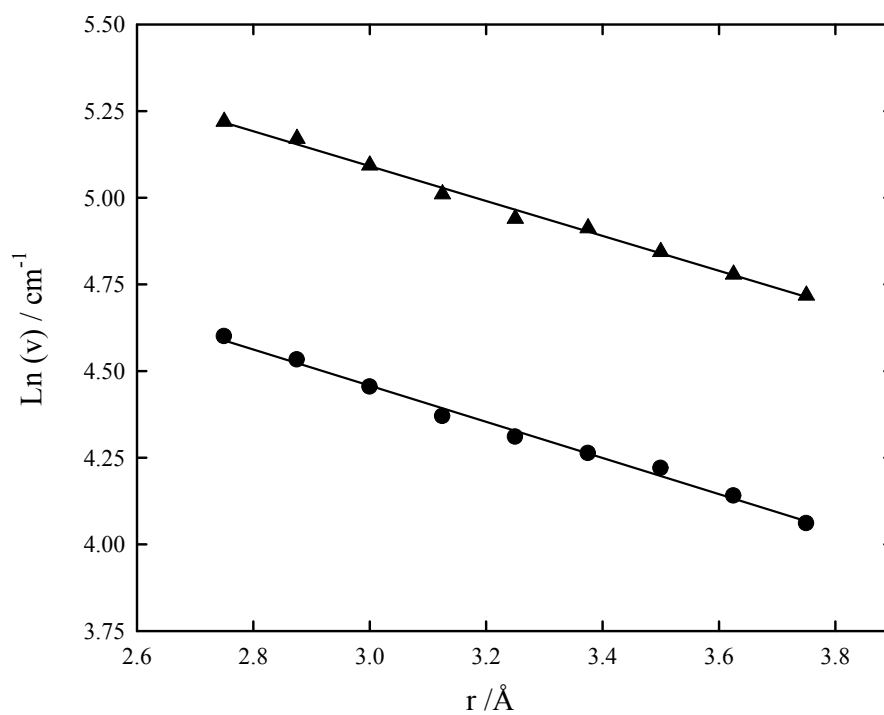


Fig. S2 Frequencies $\nu(r)$ of two transitional modes along the MEP of C_2F_5I dissociation which are transformed into free rotations; exponential representation with decay parameters $\alpha = 0.54 \text{ \AA}^{-1}$ (filled circles) and 0.52 \AA^{-1} (filled triangles).

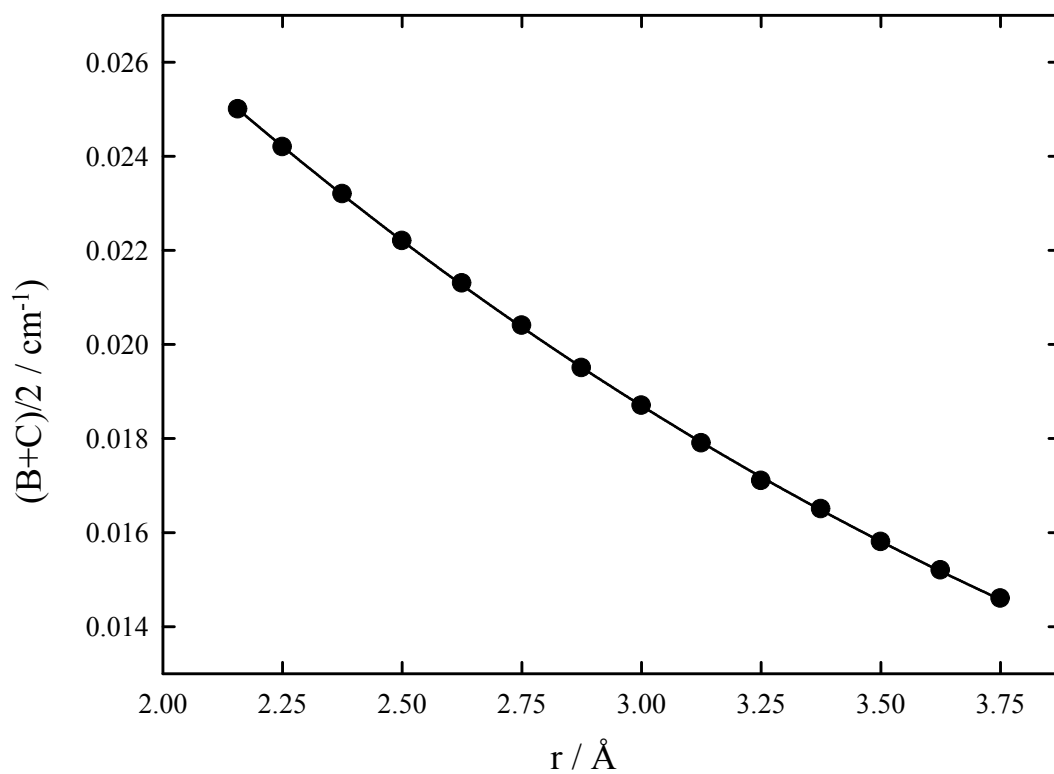


Fig. S3 Effective rotational constants of C_2F_5I dissociation along the MEP (calculated at the M06-2X level with the basis sets from ESI-I-a; fit with $(B + C)/2 = 0.025 \text{ cm}^{-1} [1 + 0.345(r - 2.157) + 0.0656(r - 2.157)^2]$, r in Å).

d. Molecular parameters

Bond dissociation enthalpy for $\text{C}_2\text{F}_5\text{I} \rightarrow \text{C}_2\text{F}_5 + \text{I}$ at 0 K: 234.2 kJ mol⁻¹ (from CCSD(T)//M06-2X calculations, see ESI-I-a).

Torsional $\text{CF}_3\text{-CF}_2\text{I}$ barrier: 24.9 kJ mol⁻¹ (from CCSD(T)//M06-2X calculations, see ESI-I-a).

$\text{C}_2\text{F}_5\text{I}$ vibrational frequencies (in cm⁻¹): 81, 136, 226, 274, 276, 307, 374, 444, 554, 605, 643, 769, 957, 1167, 1240, 1283, 1302, 1371 (from M06-2X calculations, see ESI-I-a).

$\text{C}_2\text{F}_5\text{I}$ rotational constants (in cm⁻¹): 0.0733, 0.0260, 0.0240 (from M06-2X calculations, see ESI-I-a).

C_2F_5 vibrational frequencies (in cm⁻¹): 64, 211, 227, 366, 419, 514, 604, 694, 703, 956, 1117, 1184, 1227, 1273, 1398 (the torsional frequency of 64 cm⁻¹ was calculated at the M06-2X/6-311+G(3df) level; the other frequencies are from the NIST Webbook, <https://webbook.nist.gov/chemistry/>)

C_2F_5 rotational constants (in cm⁻¹): 0.127, 0.0812, 0.0667 (calculated at the M06-2X/6-311+G(3df) level, see ESI-I-a).

ESI-II Modelling of the Unimolecular Dissociation of C₂F₂ and the Reverse Dimerization

Reaction CF + CF → C₂F₂

a. Computational details

Optimized structures and harmonic vibrational frequencies were derived from B3LYP/6-311+G(3df) calculations. The total electronic energy was determined from G4//B3LYP/6-311+G(3df) calculations.

b. Thermochemical results

Reaction	ΔH_0°
C₂F₂ → CF + CF	474.0
CF + CF → C₂F + F	37.7

Table S2 Reaction enthalpies at 0 K (in kJ mol⁻¹).

c. Properties of the PES along the MEP

Fit of the electronic potential with a Morse potential and the parameters $\beta = 2.61 \text{ \AA}^{-1}$ and $D_e = 486.6 \text{ kJ mol}^{-1}$. Fit of the two transitional modes with exponential decay parameters of $\alpha = 0.80 \text{ \AA}^{-1}$ and 0.41 \AA^{-1} . Fit of the effective rotational constants by $(B + C)/2 = 0.135 \text{ cm} / [1 + 0.6836(r - 2.0) + 0.0335(r - 2.0)^2]$, for more details, see Section ESI-I-a.

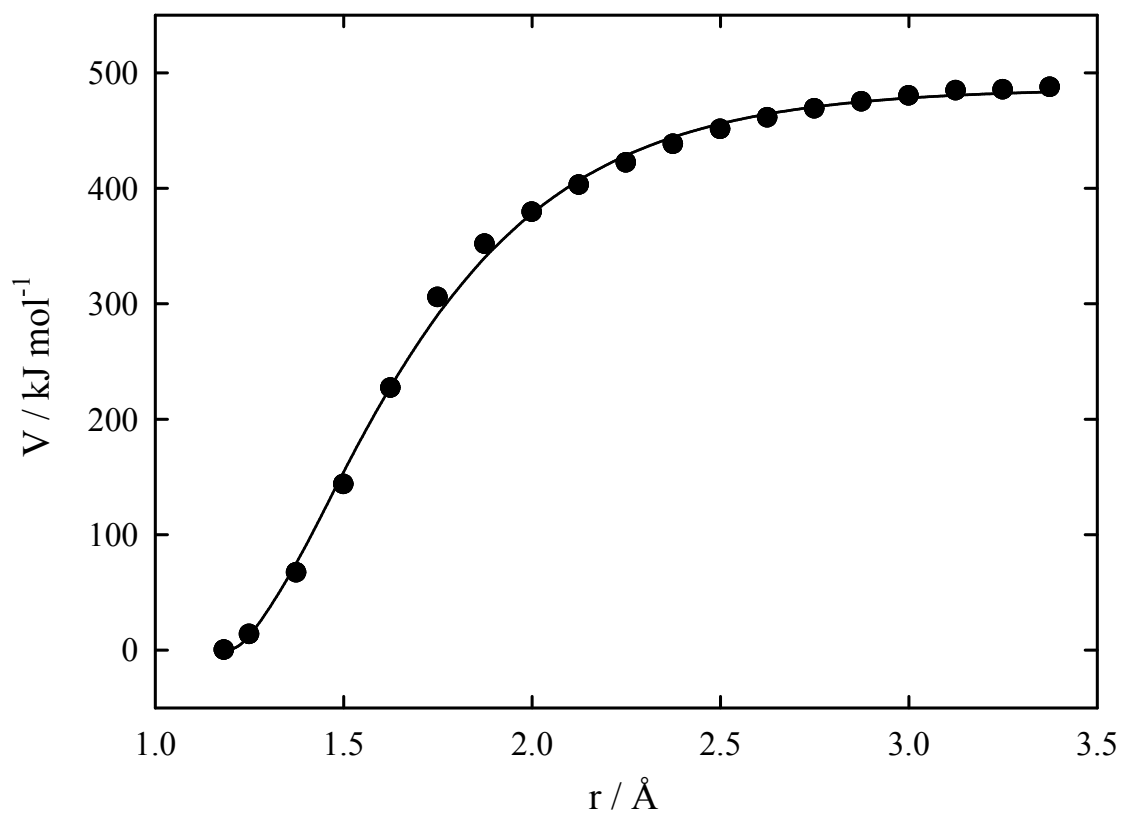


Fig. S4 Electronic potential for $\text{C}_2\text{F}_2 \rightarrow \text{CF} + \text{CF}$ dissociation ($r = \text{C} - \text{C}$ bond length; $V(r)$ calculated at the G4//B3LYP/6-311+G(3df) level. Fit with a Morse potential with the parameters $\beta = 2.61 \text{ \AA}^{-1}$ and $D_e = 486.6 \text{ kJ mol}^{-1}$.

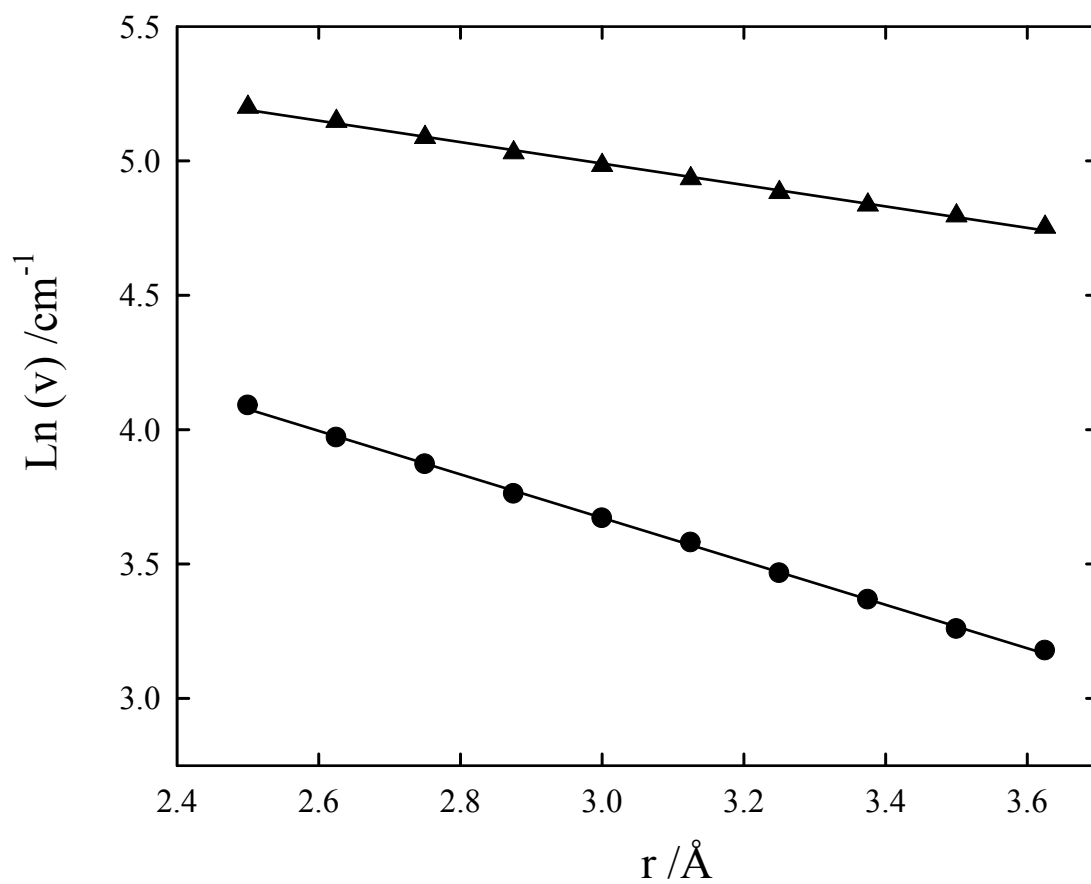


Fig. S5 Frequencies $\nu(r)$ of the two transitional modes along the MEP of C_2F_2 dissociation (calculated at the B3LYP/6-311+G(3df)) which are transformed into free rotations; exponential representation with decay parameters $\alpha = 0.80 \text{ \AA}^{-1}$ (filled circles) and 0.41 \AA^{-1} (filled triangles).

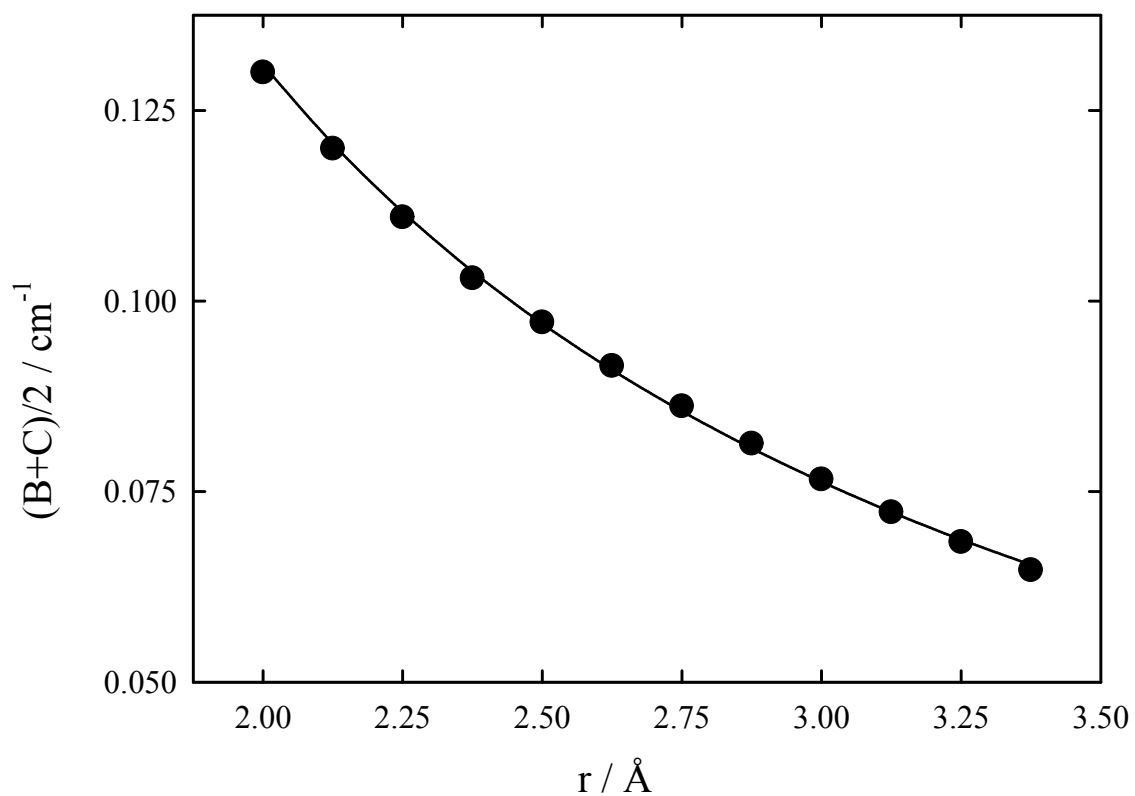


Fig. S6 Effective rotational constants of C_2F_2 dissociation along the MEP (calculated at the B3LYP/6-311+G(3df) level with the basis sets from ESI-I-a; fit with $(B + C)/2 = 0.135 \text{ cm}^{-1} [1 + 0.684(r - 2.0) + 0.0335(r - 2.0)^2]$, r in Å).

d. Molecular parameters

Dissociation enthalpy for $\text{C}_2\text{F}_2 \rightarrow \text{CF} + \text{CF}$ at 0 K (in kJ mol⁻¹): 474.0 (from G4//B3LYP/6-311+G(3df) calculations).

C_2F_2 vibrational frequencies (in cm⁻¹): 287 (2), 358 (2), 800, 1369, 2550 (from B3LYP/6-311+G(3df) calculations).

C_2F_2 rotational constant (cm⁻¹): 0.119 (from B3LYP/6-311+G(3df) calculations).

CF vibrational frequency (cm⁻¹): 1298 (from B3LYP/6-311+G(3df) calculations).

CF rotational constant (cm⁻¹): 1.416 (from B3LYP/6-311+G(3df) calculations).

e. Modelled rate constants for the recombination $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F}_2$

T / K	$k_{\text{rec},0}/ [\text{Ar}]$	$k_{\text{rec},\infty}$	F_{cent}
750	1.78×10^{18}	2.84×10^{12}	0.26
1000	5.50×10^{17}	4.31×10^{12}	0.21
1500	9.67×10^{16}	7.77×10^{12}	0.16
2000	2.57×10^{16}	1.17×10^{13}	0.13

Table S3. Modelled rate constants for the reaction $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F}_2$ (in cm³ mol⁻¹ s⁻¹). (Centrifugal barrier parameters $C_v = 1.29 \cdot 10^{-2}$ cm⁻¹ and $\nu = 1.12$; $-\langle \Delta E \rangle / hc = 100$ cm⁻¹ assumed).

ESI-III Modelling of the Reaction $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F} + \text{F}$

a. Computational details

Optimized structures and harmonic vibrational frequencies were obtained from B3LYP/6-311+G(3df) calculations. The total electronic energy was derived from G4//M06-2X/6-311+G(3df) calculations. The reaction channel $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F} + \text{F}$ is endothermic by 37.7 kJ mol⁻¹ but, at sufficiently high temperatures, can contribute to the consumption of CF and thus compete with the dimerization $\text{CF} + \text{CF} = \text{C}_2\text{F}_2$.

b. Thermochemical results

Reaction	ΔH_0°
$\text{C}_2\text{F}_2 \rightarrow \text{C}_2\text{F} + \text{F}$	511.7
$\text{C}_2\text{F}_2 \rightarrow \text{CF} + \text{CF}$	474.0
$\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F} + \text{F}$	37.7

Table S4. Reaction enthalpies at 0 K (in kJ mol⁻¹).

c. Properties of the PES along the MEP

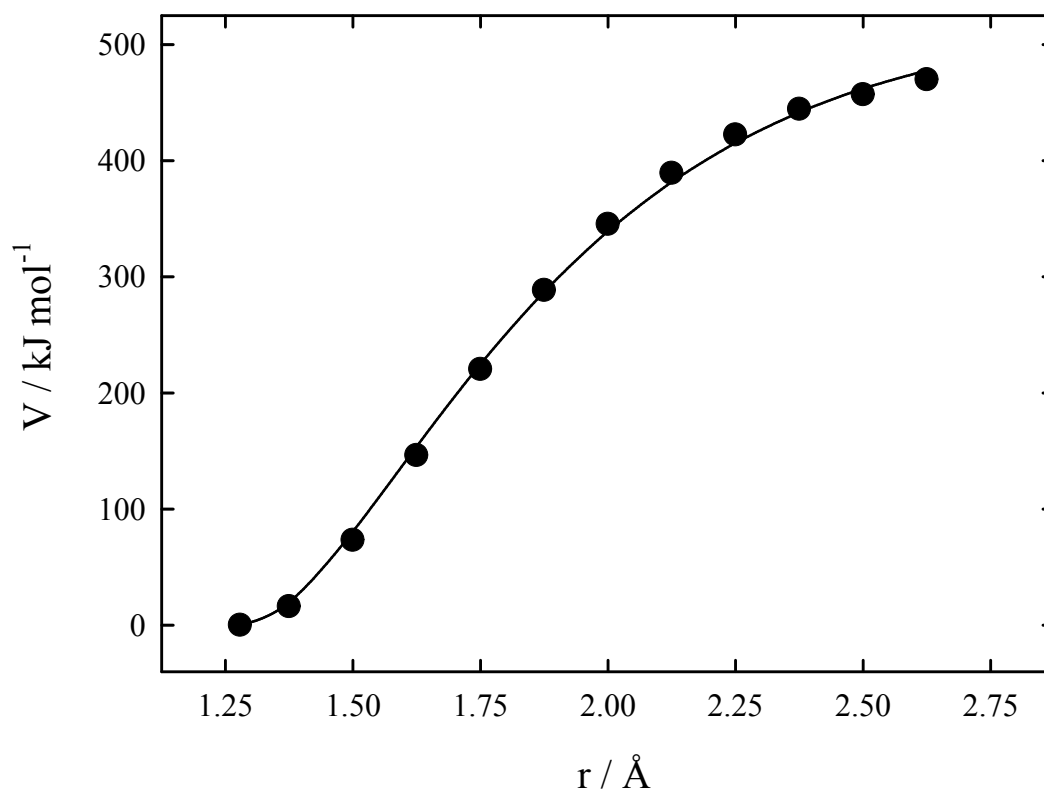


Fig. S7 Electronic potential for $\text{C}_2\text{F}_2 \rightarrow \text{C}_2\text{F} + \text{F}$ dissociation ($r = \text{C} - \text{F}$ bond length; $V(r)$ calculated at the G4//M06-2X/6-311+G(3df) level. Fit with a Morse potential and the parameter $\beta = 2.24 \text{ Å}^{-1}$ and $D_e = 528.0 \text{ kJ mol}^{-1}$.

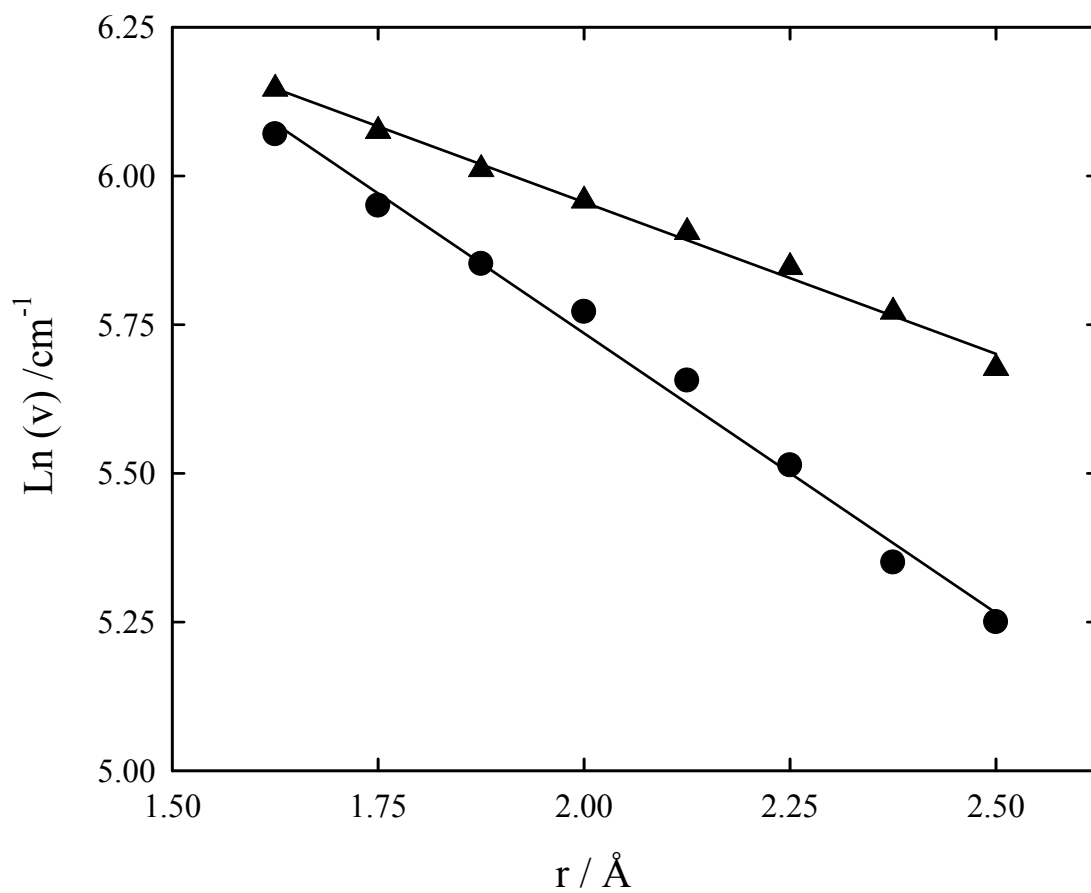


Fig. S8 Frequencies $\nu(r)$ of the two transitional modes along the MEP of $\text{C}_2\text{F}_2 \rightarrow \text{C}_2\text{F} + \text{F}$ dissociation (calculated at the M06-2X/6-311+G(3df)), which are transformed into free rotations; exponential representation with decay parameters $\alpha = 0.95 \text{ \AA}^{-1}$ (filled circles) and 0.51 \AA^{-1} (filled triangles).

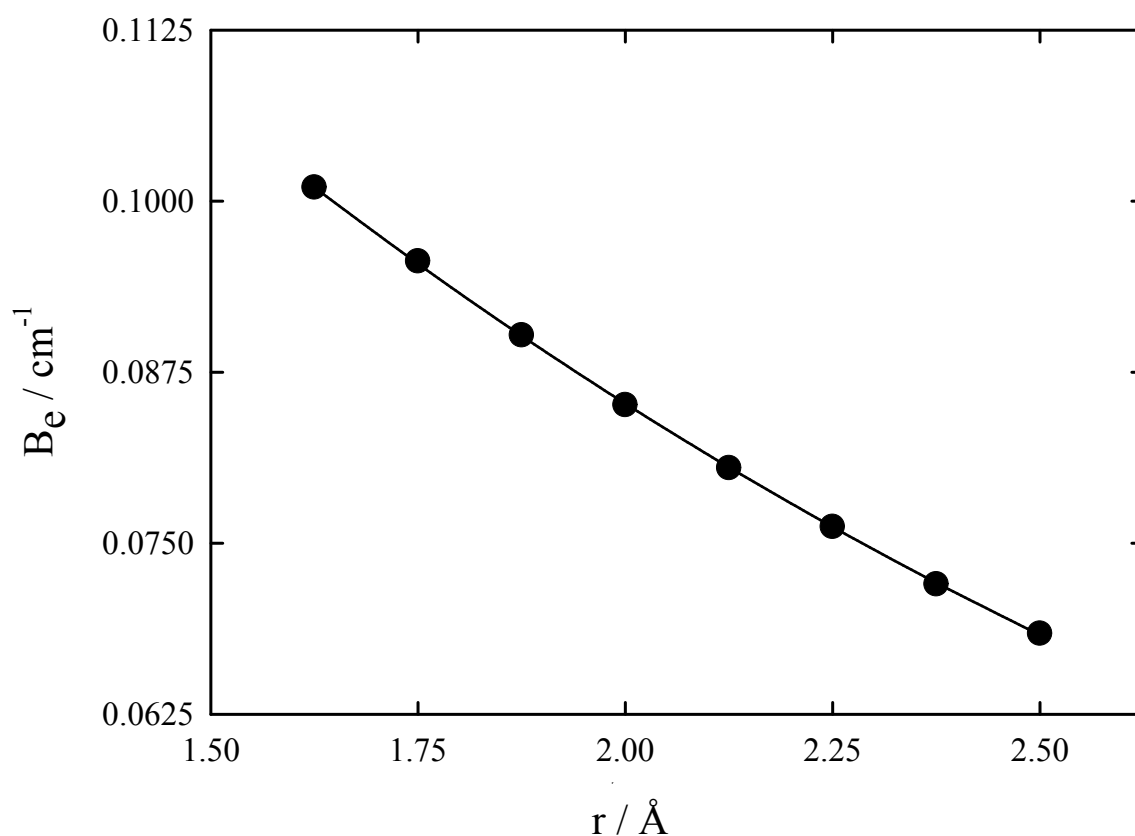


Fig. S9 Effective rotational constants of $C_2F_2 \rightarrow C_2F + F$ dissociation along the MEP (calculated at the M06-2X/6-311+G(3df) level with the basis sets from ESI-I-a; fit with $(B_e = 0.101/[1 + 0.4552(r - 1.625) + 0.1055(r - 1.625)^2])$, r in Å).

d. Molecular parameters

Bond dissociation enthalpy for $C_2F_2 \rightarrow C_2F + F$ in kJ mol^{-1} : 511.7 (from G4//M06-2X/6-311+G(3df) calculations).

C_2F_2 vibrational frequencies (cm^{-1}): 287 (2), 358 (2), 800, 1369, 2550 (from B3LYP/6-311+G(3df) calculations).

C_2F_2 rotational constants (cm^{-1}): 0.119 (from B3LYP/6-311+G(3df) calculations).

C_2F vibrational frequency (cm^{-1}): 371, 1018, 1819 (from B3LYP/6-311+G(3df) calculations).

C_2F rotational constants (cm^{-1}): 49.771, 0.359, 0.359 (from B3LYP/6-311+G(3df) calculations).

e. Rate constant for $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F} + \text{F}$

In the absence of a collisional stabilization of the intermediate C_2F_2 , the rate constant for the reaction $\text{CF} + \text{CF} \rightarrow \text{C}_2\text{F} + \text{F}$ was modelled to be

$$k = 5.14 \times 10^{11} (T/1000 \text{ K})^{1.12} \exp(-4205 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

ESI-IV. Energy Diagrams for $\text{CF}_2 + \text{CF}_2$ and $\text{CF}_3 + \text{CF}_3$

Calculations of MEPs for the C_2F_4 and C_2F_6 systems, like for the C_2F_5 system shown in Fig. 7, were made at the G4MP2 and G4 ab initio composite level. The connectivity between reactants and products was verified by Intrinsic Reaction Coordinate (IRC) calculations. Rate constants calculations were made within the framework of transition state theory.

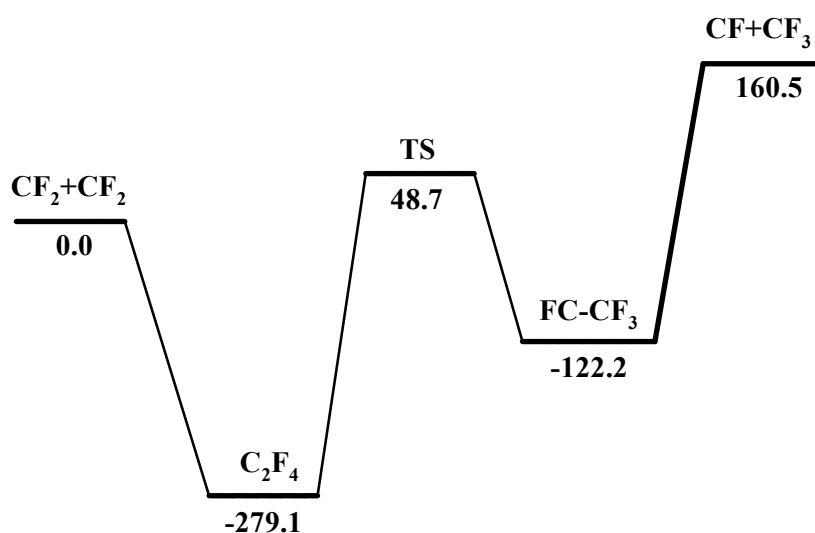


Fig. S13 Schematic MEP energy diagram for the C_2F_4 system (calculations at the G4 ab initio level, energies in kJ mol^{-1}).

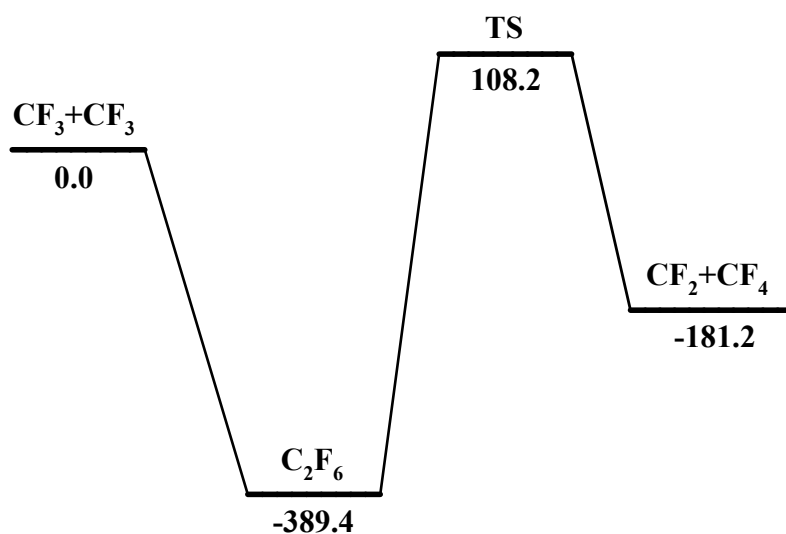


Fig. S14 Schematic MEP energy diagram for the C_2F_6 system (calculations at the G4MP2 ab initio level, energies in kJ mol⁻¹).

T / K	$k / \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
750	1.16×10^2
1000	1.92×10^4
1500	4.64×10^6
2000	9.35×10^7

$$k = 5.99 \times 10^9 (T/1000 \text{ K})^{3.12} \exp(-12650 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Table S6. Rate constants for a reaction $\text{CF}_3 + \text{CF}_3 \rightarrow \text{CF}_2 + \text{CF}_4$.

a. Molecular parameters

Transition state vibrational frequencies (in cm⁻¹): 620i, 50, 86, 177, 291, 331, 396, 396, 529, 589, 625, 66, 718, 928, 1143, 1240, 1263, 1294 (from B3LYP/6-31 G (2 df, p) calculations).

Transition state rotational constants (in cm^{-1}): 0.109, 0.0516, 0.0479 (from B3LYP/6-31 G (2 df, p) calculations).

CF_3 vibrational frequencies (in cm^{-1}): 508.7 (2), 701.4, 1086, 1253.8 (2) [S3].

CF_3 rotational constants (in cm^{-1}): 0.364 (2), 0.189 [S4].

SI-V. Modelled Rate Constants for the Reactions of C_2F_5 with $\text{C}_2\text{F}_5\text{I}$

Optimized structures and vibrational frequencies were derived at the M06-2X/LanL2DZ level. The energies were calculated with the M06-2X functional combined with the 6-311+G(3df) basis set for the C and F atoms and the 6-311G(d) basis set for I (<https://bse.pnl.gov/bse/portal>), see refs. S1 and S2. The connectivity between reagents and products was verified by IRC calculations. Rate constants were calculated within the framework of transition state theory.

Reaction	ΔH_0°	$\Delta H_0^\#$
$\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_3\text{CFI}$	-46.1	164.8
$\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_2\text{CF}_2\text{I}$	0.84	181.1

Table S7. Calculated reaction and TS enthalpies at 0 K (in kJ mol^{-1})

T / K	$k / \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
750	3.55×10^{-2}
1000	6.50×10^1
1500	1.72×10^5
2000	1.15×10^7

$$k = 2.71 \times 10^{10} (T/1000 \text{ K})^{3.12} \exp(-19850 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Table S8. Rate constants for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_3\text{CFI}$.

T / K	$k / \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
750	1.13×10^{-2}
1000	4.02×10^1
1500	2.08×10^5
2000	1.95×10^7

$$k = 1.24 \times 10^{11} (T/1000 \text{ K})^{3.15} \exp(-21850 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Table S9. Rate constants for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_2\text{CF}_2\text{I}$.

a. Molecular parameters

Transition state vibrational frequencies for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_3\text{CFI}$ (in cm^{-1}): 1020i, 19, 28, 38, 53, 68, 112, 152, 177, 206, 221, 247, 274, 281, 312, 332, 347, 402, 418, 466, 496, 543, 556, 575, 600, 673, 713, 820, 917, 1087, 1142, 1166, 1170, 1201, 1206, 1276, 1295, 1376 (from M06-2X/LanL2DZ calculations).

Transition state rotational constants for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_3\text{CFI}$ (in cm^{-1}): 0.0176, 0.00392, 0.00698 (from M06-2X/LanL2DZ calculations).

Transition state vibrational frequencies for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_2\text{CF}_2\text{I}$ (in cm^{-1}): 1006i, 10, 20, 26, 45, 71, 92, 118, 183, 195, 203, 207, 228, 262, 272, 312, 344, 348, 349, 409, 476, 508, 526, 556, 571, 608, 650, 710, 815, 917, 1087, 1100, 1138, 1171, 1210, 1264, 1284, 1324, 1376 (from M06-2X/LanL2DZ calculations).

Transition state rotational constants for $\text{C}_2\text{F}_5 + \text{CF}_3\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_6 + \text{CF}_2\text{CF}_2\text{I}$ (in cm^{-1}): 0.0341, 0.00511, 0.00493 (from M06-2X/LanL2DZ calculations).

ESI References

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