

Supporting Information

Shock Wave and Theoretical Modeling Study of the Dissociation of CH₂F₂

II. Secondary Reactions

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(i) Additional absorption-time profiles

Fig. SI-1 As Fig. 2 of the main article, but for $T = 2221$ K and $[\text{Ar}] = 5.4 \cdot 10^{-5} \text{ mol cm}^{-3}$.

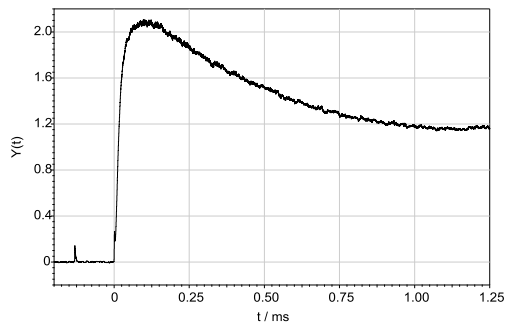


Fig. SI-2 As Fig. 2 of the main article, but for $T = 1782$ K and $[\text{Ar}] = 7.4 \cdot 10^{-5} \text{ mol cm}^{-3}$.

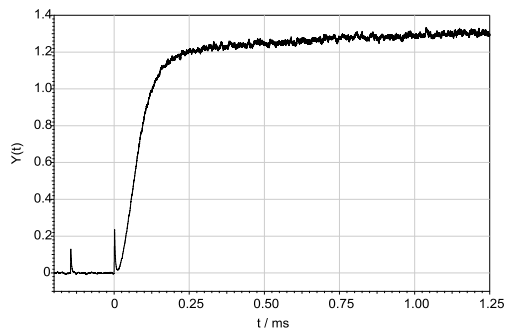


Fig. SI-3 As Fig. 2 of the main article, but for $T = 1656$ K and $[\text{Ar}] = 8.3 \cdot 10^{-5} \text{ mol cm}^{-3}$.

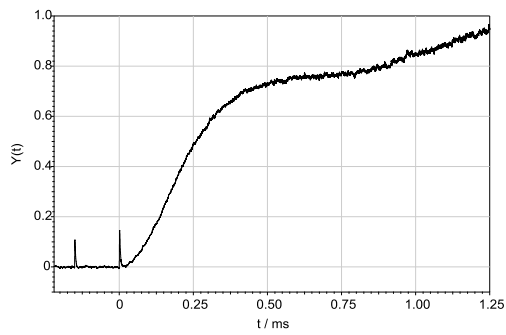


Fig. SI-4 As Fig. 2 of the main article, but for $[\text{CH}_2\text{F}_2]_{t=0} / [\text{Ar}] = 0.11 \cdot 10^{-3}$, $T = 2036$ K and $[\text{Ar}] = 6.4 \cdot 10^{-5} \text{ mol cm}^{-3}$.

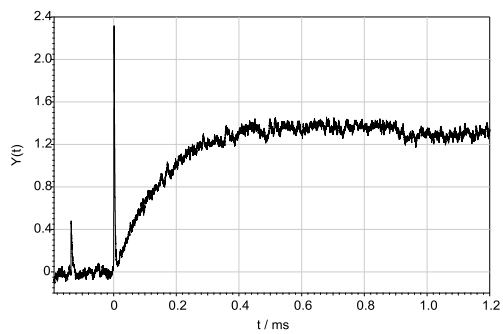
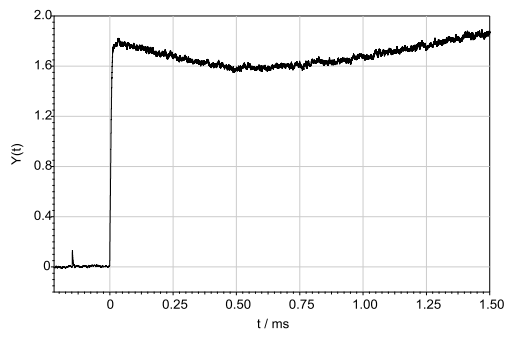


Fig. SI-5 As Fig. 4 of the main article, but for $T = 1730$ K and $[\text{Ar}] = 7.9 \cdot 10^{-5} \text{ mol cm}^{-3}$.



(ii) Reactant, transition state, and product parameters from G4 calculations; for the reactions of Table 3 of the main text

Table SI-1 Molecular parameters for reaction (12): $\text{CHF}_2 \rightarrow \text{CF}_2 + \text{H}$ (frequencies and rotational constants in cm^{-1} , from G4 calculations of the present work; $\Delta H_0^0 = 264 \text{ kJ}\cdot\text{mol}^{-1}$).

Species	Frequencies	Rotational constants
CHF_2	542, 991, 1178, 1195, 1340, 3043	2.267, 0.367, 0.320
CF_2	664, 1134, 1244	2.904, 0.418, 0.366 ($\sigma = 2$)

Table SI-2 As Table SI-1, but for reaction (13): $\text{CHF} \rightarrow \text{CF} + \text{H}$ ($\Delta H_0^0 = 307 \text{ kJ}\cdot\text{mol}^{-1}$).

Species	Frequencies	Rotational constants
CHF	1223, 1462, 2826	15.780, 1.251, 1.159
CF	1325	1.421

Table SI-3 As Table SI-1, but for reaction (14): $\text{CH}_2\text{F} \rightarrow \text{CHF} + \text{H}$ ($\Delta H_0^0 = 391 \text{ kJ}\cdot\text{mol}^{-1}$).

Species	Frequencies	Rotational constants
CH_2F	566, 1164, 1201, 1465, 3077, 3266	8.803, 1.039, 0.938
CHF	as Table SI-2	as Table SI-2

Table SI-4 As Table SI-1, but for reaction (15): $\text{CHF} + \text{CH}_2\text{F}_2 \rightarrow \text{CHF}_2 + \text{CH}_2\text{F}$ ($\Delta H_0^\ddagger = 51.6 \text{ kJ}\cdot\text{mol}^{-1}$).

Species	Frequencies	Rotational constants
CHF	as Table SI-2	as Table SI-2
CH ₂ F ₂	530, 1090, 1116, 1176, 1262, 1435, 1508, 2949, 3013 (a)	1.684, 0.354, 0.308 ($\sigma = 2$) (a)
CHF ₂	as Table SI-1	as Table SI-1
CH ₂ F	as Table SI-3	as Table SI-3
CHF - - - CH ₂ F ₂ (b)	914i, 65, 164, 263, 418, 474, 587, 989, 1082, 1142, 1175, 1182, 1301, 1360, 1451, 2096, 2861, 3039 (c)	0.306, 0.0940, 0.0803

Table SI-5 As Table SI-1, but for reaction (16): $\text{H}_2 + \text{CHF} \rightarrow \text{CH}_2\text{F} + \text{H}$ ($\Delta H_0^\ddagger = 31.8 \text{ kJ}\cdot\text{mol}^{-1}$).

Species	Frequencies	Rotational constants
H ₂	4399	60.624 ($\sigma = 2$)
CHF	as Table SI-2	as Table SI-2
CH ₂ F	as Table SI-3	as Table SI-3
CHF - - - H ₂ (b)	504i, 504, 717, 929, 1174, 1270, 1387, 2771, 3303 (c)	3.100, 0.882, 0.765

Table SI-6 As Table SI-1, but for reaction (18) of the main text: $\text{H} + \text{CF} \rightarrow \text{C} + \text{HF}$
 $(\Delta H_0^\ddagger = 99.2 \text{ kJ}\cdot\text{mol}^{-1})$.

Species	Frequencies	Rotational constants
CF	1298	1.401
HF	4055	20.838
C - - F - - H (b)	1654i, 502, 2119 (d)	31.409, 0.654, 0.641

Table SI-7 As Table SI-1, but for reaction (19) of the main text: $\text{H} + \text{CH}_2\text{F}_2 \rightarrow \text{CHF}_2 + \text{H}_2$
 $(\Delta H_0^\ddagger = 46.0 \text{ kJ}\cdot\text{mol}^{-1})$.

Species	Frequencies	Rotational constants
CH_2F_2	as Table SI-4	as Table SI-4
CHF_2	as Table SI-1	as Table SI-1
H_2	as Table SI-5	as Table SI-5
CH_2F_2 - - - H (b)	1343i, 277, 361, 539, 1079, 1155, 1162, 1227, 1333, 1398, 1421, 3007 (c)	0.981, 0.341, 0.287

Table SI-8 As Table SI-1, but for reaction (20) of the main text: $\text{H} + \text{CF}_2 \rightarrow \text{CF} + \text{HF}$
 $(\Delta H_0^\ddagger = 36.0 \text{ kJ}\cdot\text{mol}^{-1})$, reaction forming CHF_2 intermediate)

Species	Frequencies	Rotational constants
CF_2	as Table SI-1	as Table SI-3
CF	as Table SI-2	as Table SI-2
HF	as Table SI-6	as Table SI-6
CF - - - HF (b)	1281i, 310, 681, 930, 1318, 2134 (c)	1.986, 0.280, 0.249

Notes

- a: from M. W. Chase Jr, NIST-JANAF Thermochemical Tables (4th edn., *J. Phys. Chem. Ref. Data* **1998**, 9, 1 – 1951.
- b: Transition state.
- c: G4 calculations, scaled by 0.9854.
- d: CBS-APNO calculations, scaled by 0.9251.