Supporting Information

Experimental and Modelling Study of the Multichannel Thermal Dissociations of CH_3F and CH_2F

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SI-1 Modelling of single-channel rate constants for the dissociation of CH_3F

CH_3F (+Ar)→ $^3CH_2$ + HF (+Ar) **(1)**

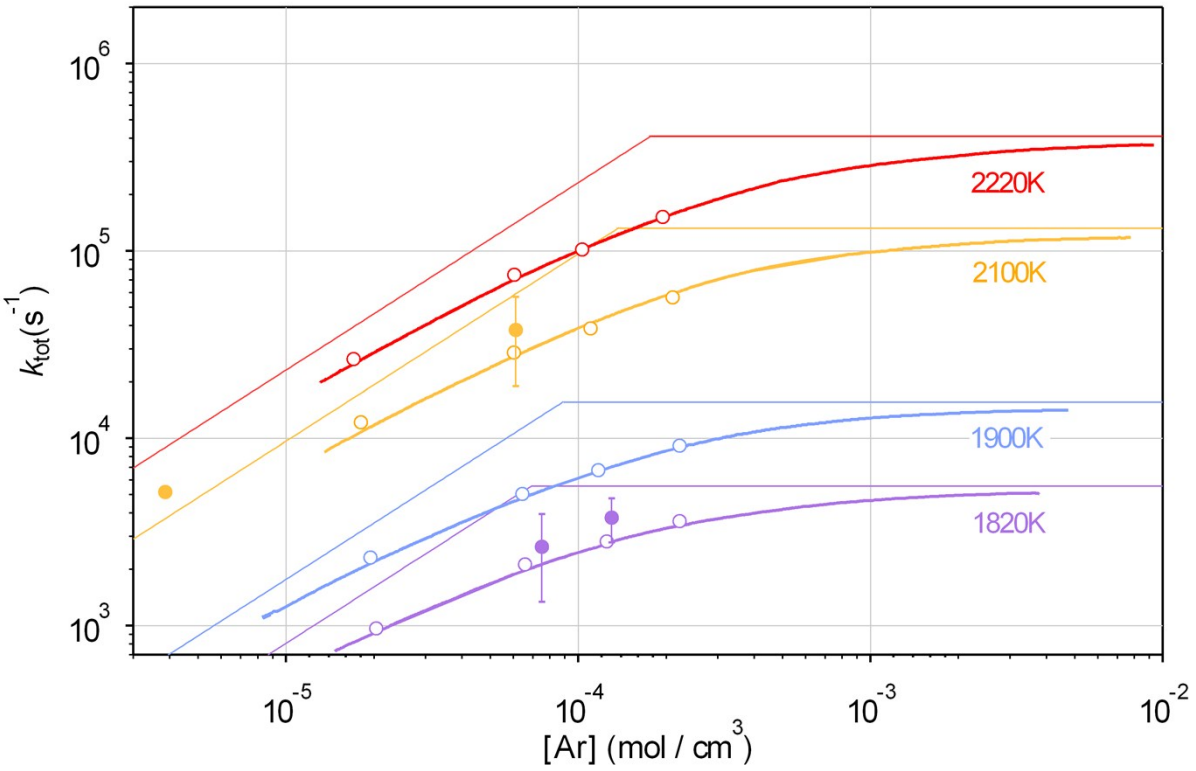

Fig. SI-1 Experimental falloff curves of the dissociation of CH_3F (open circles from ref.3 and closed circles from the present work) and modelled single-channel falloff curves and limiting low- and high-pressure rate constants from ref. 3.

CH_3F (+Ar)→ ^1CHF + H_2 (+Ar) **(2)** $\Delta H^{\neq}_0 = 404\ kJ\ mol^{-1}$

$\Delta H^{\neq}_0$ and molecular parameters from G4 calculations (B3LYP/6-31G(2df) scaled by 0.9854) of the present work, see text.

Molecular parameters for reactions (2) – (9):

Species	Frequencies(cm^{-1})	Rotational constants(cm^{-1})	σ

CH_3F	1084, 1191(2), 1473(2), 1489, 2970, 3043(2)	5.240, 0.864, 0.864	3
CH_2F	566, 1164, 1201, 1465, 3077, 3226	8.803, 1.039, 0.938 15.78, 1.251, 1.159	1 1
CHF	1223, 1462, 2826		
CF	1298	1.401	1
H_2	4399	60.624	2
CH	2773	14.184	1
HF	4139	20.956	1
$CHF \cdots H_2$	504(i), 503, 717, 929, 1174, 1270, 1387, 2771, 3303	3.100, 0.882, 0.765	1
CH2 ··· HF	1464(i),621,786,982,1062,1313, 2090,2997,3184	5.558, 0.668, 0651	1

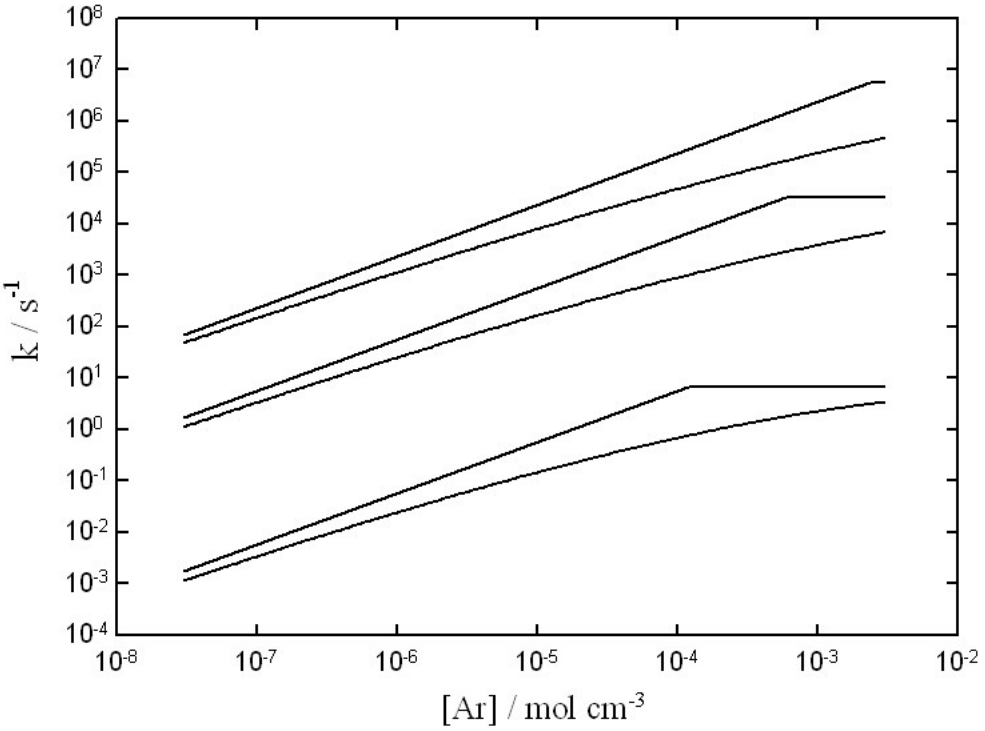

Fig. SI-2 Modelled single-channel falloff curves and limiting low- and high-pressure rate constants for the reaction CH_3F (+Ar)→ $^1CHF + H_2$ (+Ar) (2) from the present work at T= 1500, 2000, and 2500 K (from bottom to top; values according to Table 3).

CH_3F (+ Ar)→ $^1CH_2$ + HF (+Ar) **(3)** $\Delta H^{\neq}_0 = 477.8\ kJ\ mol^{-1}$

For molecular parameters, see CH_3F (+Ar)→ $^1CHF + H_2$ (+Ar)

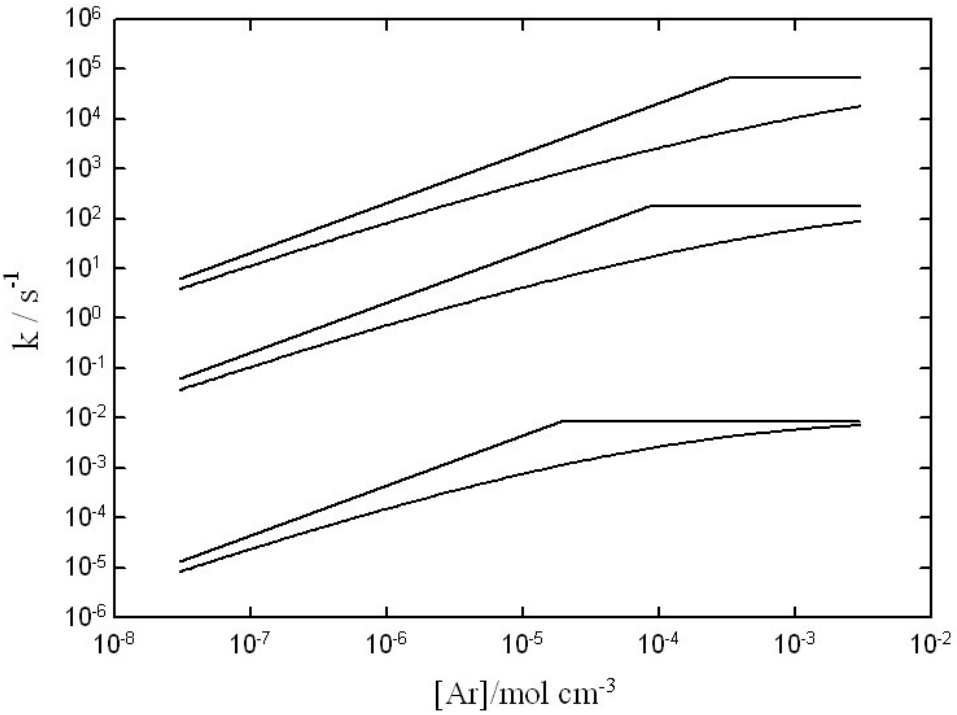

Fig. SI-3 Modelled single-channel falloff curves and limiting low- and high-pressure rate constants for the reaction CH_3F (+Ar)→ $^1CH_2$ + HF (+Ar) (3) from the present work at T= 1500, 2000, and 2500 K (from bottom to top; values according to Table 3).

CH_3F (+ Ar)→ CH_2F + H (+Ar) (4)

For molecular parameters, see CH_3F (+Ar)→ $^1CHF + H_2$ (+Ar)

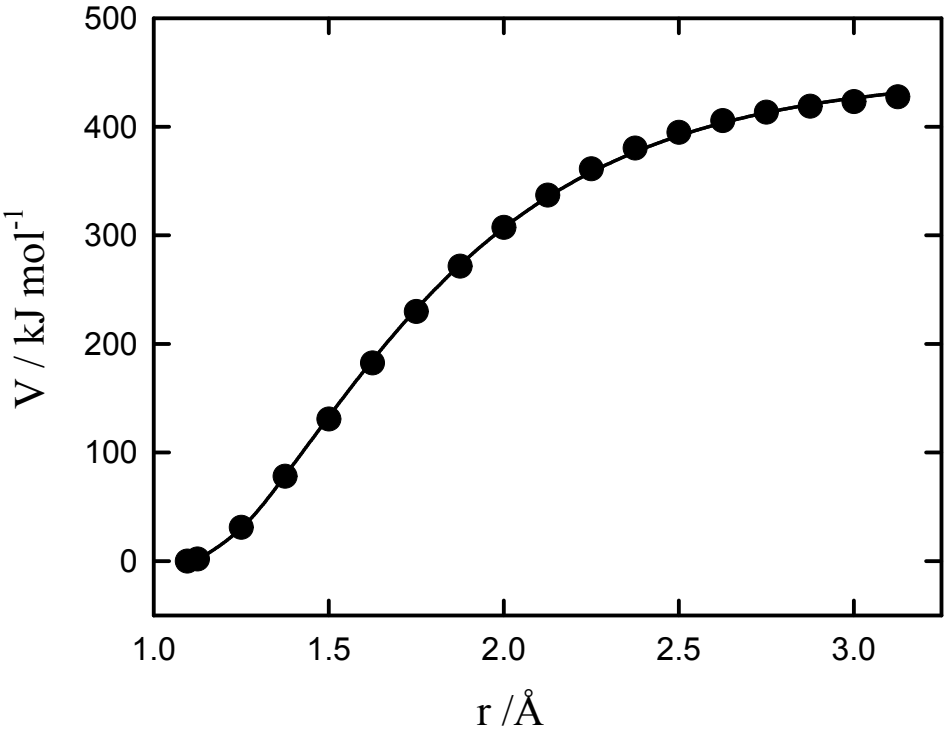

Fig. SI-4 Potential energy for the breaking bond in the reaction $CH_3F \rightarrow CH_2F + H$ (fit with a Morse function with the parameters $\beta =$ 1.94 Å^{-1} , r_e = 1.1 Å , and D_e = 452.7, the latter corresponding to $^{\Delta H_0^0}$ = 415.5 kJ mol^{-1}).

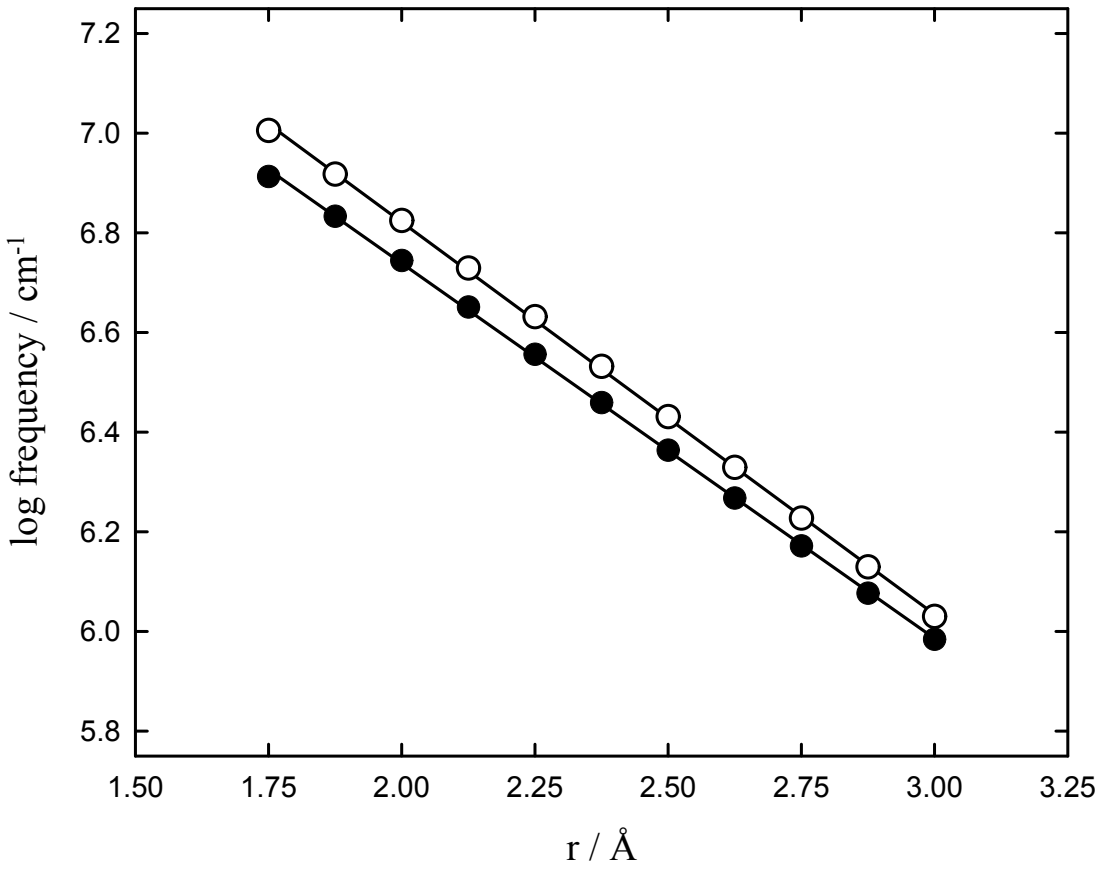

Fig. SI-5 Frequencies of the two transitional modes in the reaction $CH_3F \rightarrow CH_2F + H$ (fit with exponential curves with decay parameters $\alpha = 0.79$ and 0.75 Å^{-1}).

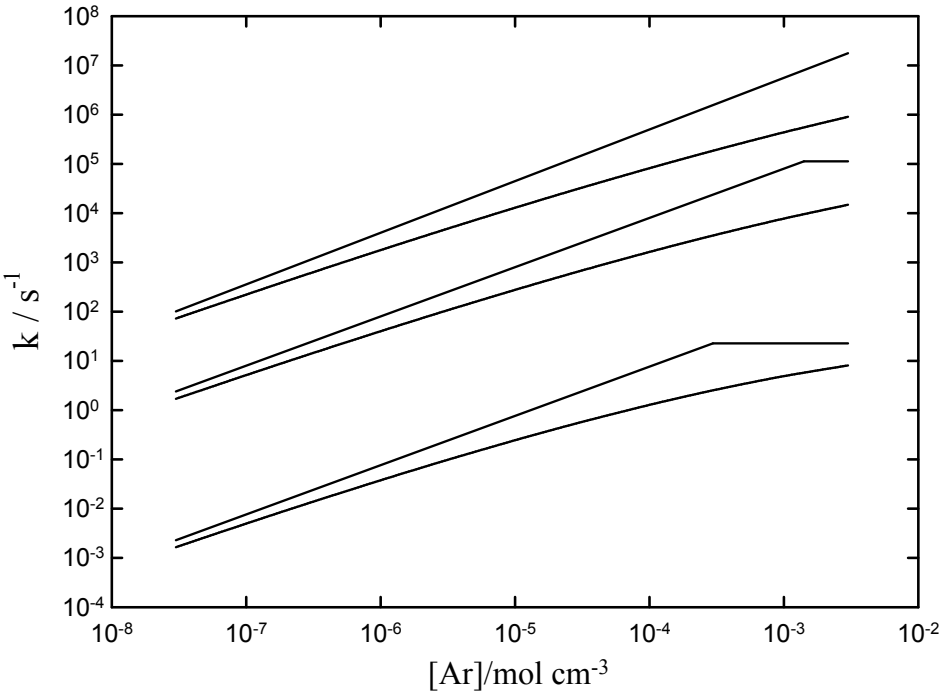

Fig. SI-6 Modelled single-channel falloff curves and limiting low- and high-pressure rate constants for the reaction CH_3F (+Ar)→ CH_2F + H (+Ar) (4) from the present work at *T*= 1500, 2000, and 2500 K (from bottom to top; values according to Table 3).

SI-2 Modelling of single-channel rate constants for the dissociation of CH_2F

CH_2F (+Ar) → CHF + H (+Ar) $\Delta H_0^0 = 393\ kJ\ mol^{-1}$ (7)

CH_2F (+Ar)→ CF + H_2 (+Ar) $\Delta H_0^0 = 272\ kJ\ mol^{-1}$ (8)

CH_2F (+Ar) → CH + HF (+Ar) $\Delta H_0^0 = 348\ kJ\ mol^{-1}$ (9)

with $\Delta H_0^{\neq} = 347.7, 354.8, 390.8\ kJ\ mol^{-1}$ for reactions (8), (9), and (7), respectively. For molecular parameters, see CH_3F (+Ar)→ ^{1}CHF + H_2 (+Ar). G4 calculations from the present work.

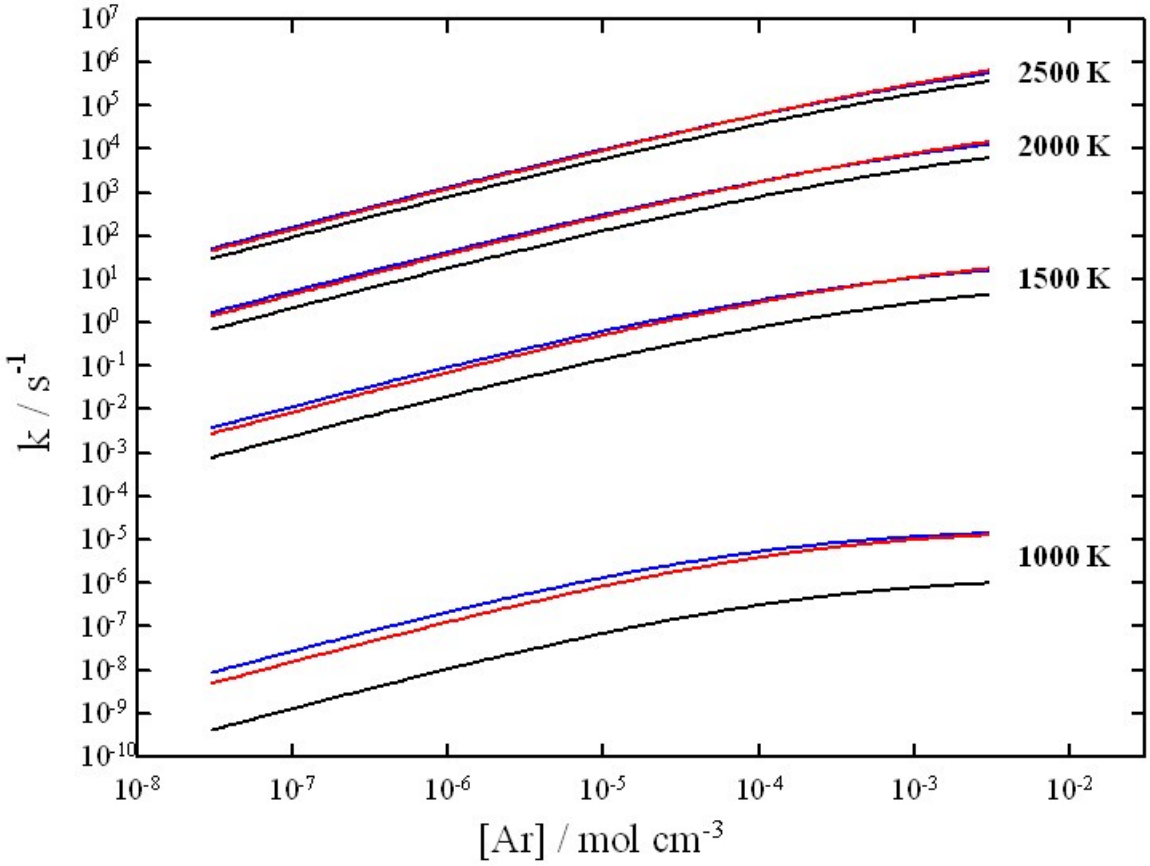

Fig. SI-7 Modelled single-channel falloff curves and limiting low- and high-pressure rate constants for the reactions CH_2F (+Ar)→ CHF + H (+Ar) (7) (black curves), CH_2F (+Ar)→ CH + HF (+Ar) (9) (red curves), and CH_2F (+Ar)→ CF + H_2 (+Ar) (8) (blue curves) from ref. 6 at *T*= 1000, 1500, 2000, and 2500 K (from bottom to top; values according to Table 3).