Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Shock wave and modelling study of the unimolecular dissociation of $Si(CH_3)_2F_2$: an access to spectroscopic and kinetic properties of SiF_2

C. J. Cobos[1], L. Sölter[2, 3], E. Tellbach[2, 3],
and J. Troe[2, 3, *]

Electronic Supplementary Information

[1] INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET, Argentina

[2] Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

[3] Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg 11, D-37077 Göttingen, Germany

* Email: juergen.troe@mpibpc.mpg.de

ESI – 1 Modelling of oscillator strengths for UV absorptions of SiF_x (x = 1 – 3)

Table S1 Experimental absorption cross sections of SiF_2 (σ, base e, in cm^2) at temperatures near 1600 and 3000 K (see main text).

λ / nm	σ (1600 K)/ $10^{-18}cm^2$	σ (3000 K)/$10^{-18}cm^2$
200	1.0	-
210	4.5	-
215	19.0	19.0
222	24.5	20.5
230	15.5	16.0
235	8.4	11.0
240	3.0	-
245	1.0	-
250	0.5	-
255	0.5	-

Table S2 Wavelengths of UV- absorption maxima λ (in nm) and oscillator strengths f (determined by time-dependent density functional theory, TD-DFT, on the ωB97X-D level and with 6-311+G(3df) basis set; the calculations in **ESI – 1** and **ESI – 2** employed the Gaussian 09 software. revision – A.02-SMP, of ref. S1).

DFT model	λ (SiF_3)	f (SiF_3)	λ (SiF_2)	f (SiF_2)	λ (SiF)	f (SiF)
ωB97X-D	186	0.1259	225	0.1902	278	0.1104
	185	0.1259			218	0.0226
					195	0.0436

ESI – 2 Rate Constants of the unimolecular decomposition of $Si(CH_3)_2F_2$

a. Reaction enthalpies

All calculations were performed at the CBS-QB3 and G4 ab initio composite levels with geometries and harmonic vibrational frequencies derived at the B3LYP/6-311++G(3df,3pd) DFT level.

Table S3 Dissociation enthalpies of $Si(CH_3)_2F_2$ and $Si(CH_3)F_2$ (from CBS-Q//B3LYP/6-311++G(3df,3pd) and G4//B3LYP/6-311++G(3df,3pd) calculations, enthalpies at 0 K and in kJ mol^{-1}).

Reaction	CBS-Q//B3LYP/6-311++G(3df,3pd)	G4//B3LYP/6-311++G(3df,3pd)
$Si(CH_3)_2F_2 \rightarrow Si(CH_3)F_2 + CH_3$	410.0	401.7
$Si(CH_3)F_2 \rightarrow SiF_2 + CH_3$	173.2	169.9

b. Properties of the potential energy surface along the minimum-energy path(MEP) for the reaction $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$

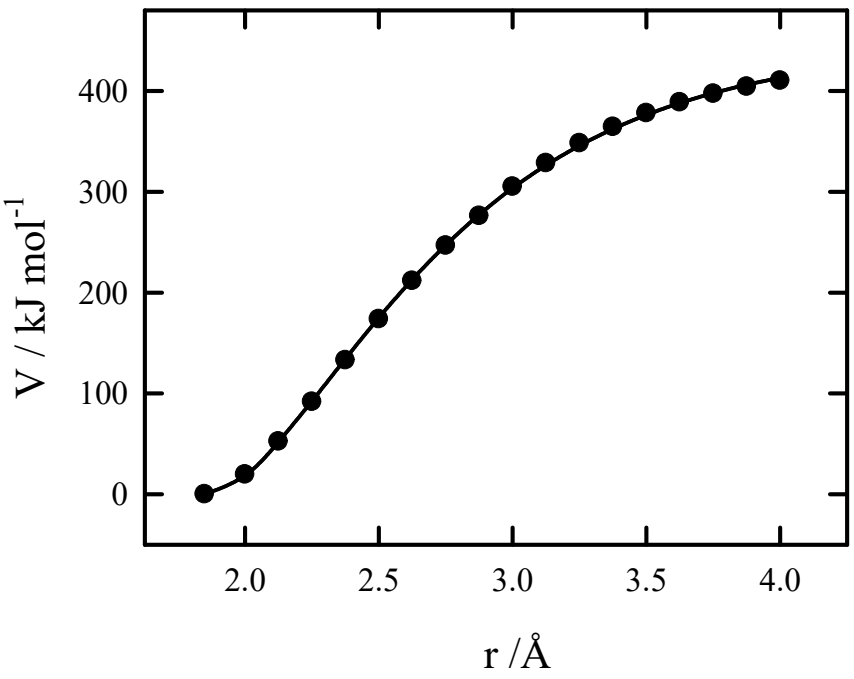

Fig. S1 Electronic potential for the reaction $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$ along the MEP. G4//B3LYP/6-311++G(3df,3pd) calculations fitted with a Morse function with D_e = 447.3 kJ mol^{-1} and β =1.51 $Å^{-1}$

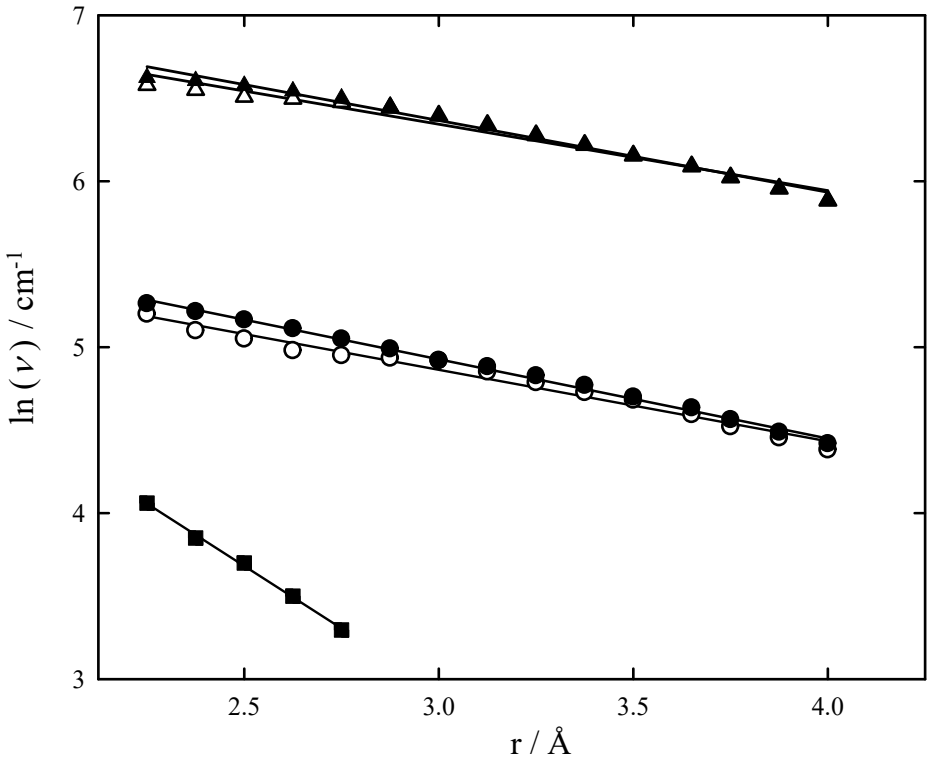

Fig. S2 Transitional modes ν of the reaction $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$ along the MEP, calculated at the B3LYP/6-311++G(3df,3pd) level. Exponential decay functions with decay parameters α = 1.50 (■), 0.43 (o), 0.48 (•), 0.40 (Δ) and 0.43 $Å^{-1}$ (▲).

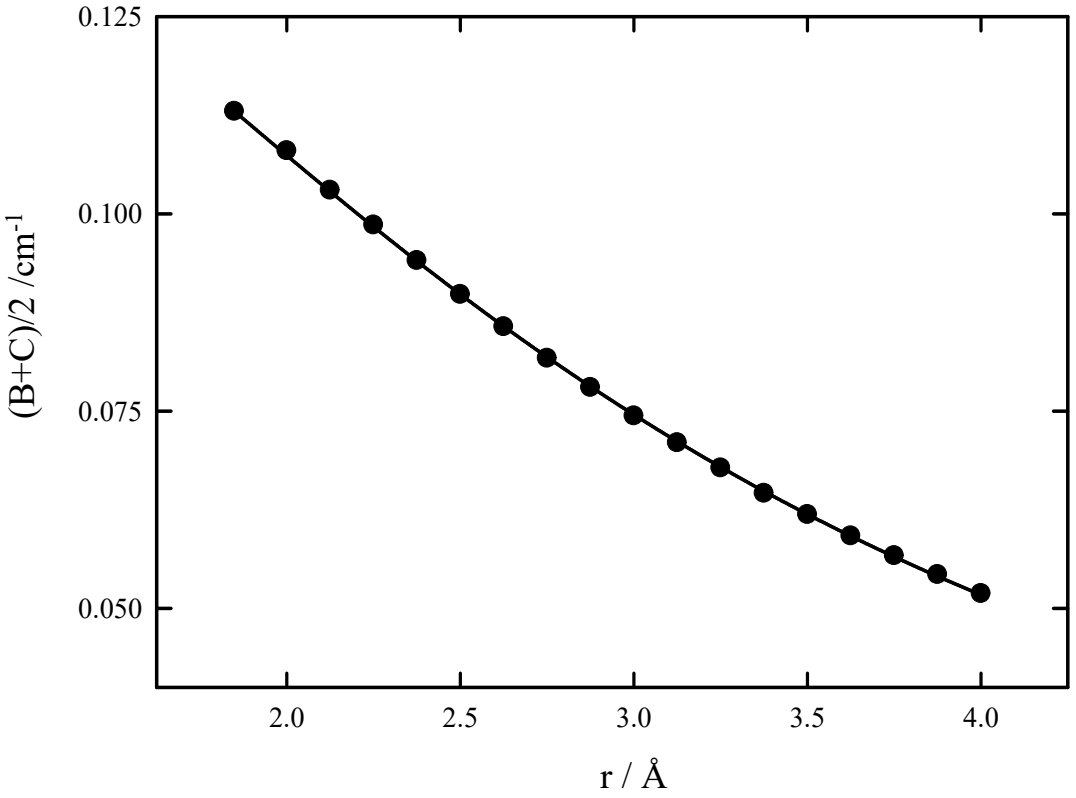

Fig. S3 Rotational constants of $Si(CH_3)_2F_2$ calculated along the MEP for the reaction $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$, calculated at the B3LYP/6-311++G(3df,3pd) level (fit with a function $(B+C)/2 = 0.113\ cm^{-1} /[1 + 0.330\ (r - 1.849) + 0.103\ (r - 1.849)^2]$.

c. Modelling of limiting high pressure rate constants

Table S4 Modelled limiting rate high pressure constants for the recombination reaction $CH_3 + (CH_3)SiF_2 \rightarrow (CH_3)_2SiF_2$ ($k_{rec,\infty}$, in $cm^3\ mol^{-1}\ s^{-1}$) and the reverse dissociation reaction $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$ (k_∞, in s^{-1}) (calculations with the simplified statistical adiabatic channel/classical trajectory model, SACM/CT, of ref. S2 and S3, employing the parameters of Figs. S1 - S3, PST = phase space theory, rigidity factors $f_{rigid} = k_{rec,\infty} / k_{rec,\infty}^{PST}$, equilibrium constants $K_c = k_\infty / k_{rec,\infty}$, in mol cm^{-3}).

T/K	$k_{rec,\infty}^{PST}$	f_{rigid}	$k_{rec,\infty}$	K_c	k_∞
1500	3.65×10^{14}	5.05×10^{-2}	1.84×10^{13}	5.62×10^{-11}	1.03×10^{3}
1750	3.84×10^{14}	5.13×10^{-2}	1.97×10^{13}	4.91×10^{-9}	9.66×10^{4}
2000	3.98×10^{14}	5.20×10^{-2}	2.07×10^{13}	1.25×10^{-7}	2.58×10^{6}
2500	4.21×10^{14}	5.30×10^{-2}	2.23×10^{13}	9.04×10^{-6}	2.02×10^{8}

k_∞ = 1.24 x 10^{19} (T/2000 K)$^{-6.63}$ exp(-58400 K/T) s^{-1}

d. Modelling of limiting low pressure rate constants

Table S5 Modelled limiting low pressure rate coefficients (k_0, in cm^3 mol^{-1} s^{-1}) for the reaction $Si(CH_3)_2F_2$ (+ Ar) → CH_3 + $Si(CH_3)F_2$ (+ Ar) (strong collision rate coefficients k_0^{SC}, calculated following ref. S4 and employing the parameters of Figs. S1 – S3; weak collision efficiencies β_c = k_0 / k_0^{SC}, as following from the master-equation treatment of ref. S5, were determined with assumed standard values of average energies transferred per collision of <ΔE> = - 100/hc cm^{-1}).

T/K	k_0^{SC}	β_c	k_0
1500	1.18x10^{12}	0.038	4.49x10^{10}
1750	1.24x10^{13}	0.028	3.46x10^{11}
2000	4.88x10^{13}	0.021	1.02x10^{12}
2500	1.71x10^{14}	0.011	1.89x10^{12}

k_0 = [Ar] 2.94 x 10^{25} (T/2000 K)$^{-25.04}$ exp(-61980 K/T) cm^3 mol^{-1} s^{-1}

e. Modelling of falloff curves

Falloff curves for the reaction $Si(CH_3)_2F_2$ (+ Ar) → CH_3 + $Si(CH_3)F_2$ (+ Ar) were represented in the representation proposed in ref. S6 – S8 (see main text), employing center broadening factors F_{cent} estimated according to ref. S8 and leading to values of F_{cent} = 0.039 (1500 K), 0.045 (1750 K), 0.051 (2000 K) and 0.073 (2500 K).

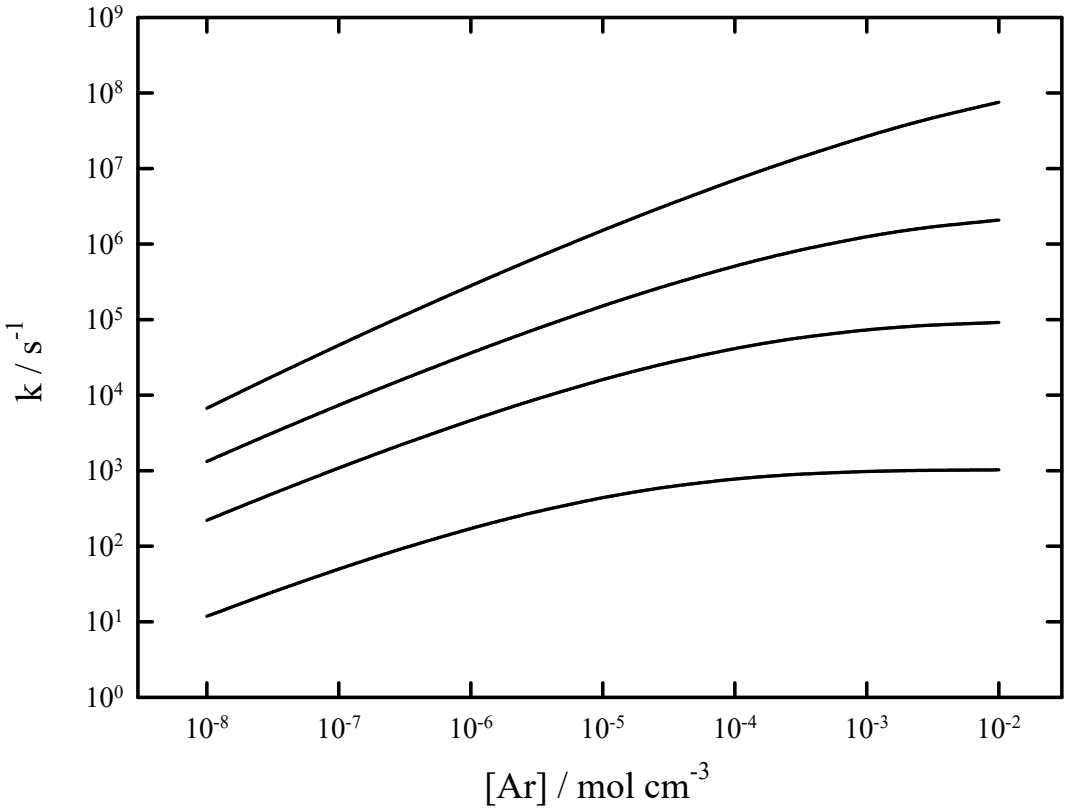

Fig. S4 Modelled falloff curves for $Si(CH_3)_2F_2$ (+ Ar) → CH_3 + $Si(CH_3)F_2$ (+ Ar). Calculations for 1500, 1750, 2000 and 2500 K (from bottom to top).

f. Molecular parameters

Bond dissociation enthalpy for $Si(CH_3)_2F_2 \rightarrow CH_3 + Si(CH_3)F_2$ at 0 K: ΔH_0^0 = 401.7 kJ mol^{-1} (from G4//B3LYP/6-11++G(3df,3pd) calculations).

$Si(CH_3)_2F_2$ vibrational frequencies: 141, 153, 193, 210, 250, 320, 322, 635, 707, 758, 789, 801, 828, 905, 930, 1307, 1309, 1453, 1455, 1462, 1465, 3034, 3036, 3106, 3109, 3111, 3111 cm^{-1} (from B3LYP/6-311++G(3df,3pd) calculations).

$Si(CH_3)_2F_2$ rotational constants: A = 0.126, B = 0.114, C = 0.112 cm^{-1} (σ = 2) (from B3LYP/6-311++G(3df,3pd) calculations).

$Si(CH_3)F_2$ vibrational frequencies: 130, 213, 271, 324, 635, 774, 778, 846, 897, 1270, 1441, 1454, 3029, 3112, 3131 cm^{-1} (from B3LYP/6-311++G(3df,3pd) calculations).

$Si(CH_3)F_2$ rotational constants: A = 0.231, B = 208, C = 0.123 cm^{-1} (σ = 1) (from B3LYP/6-311++G(3df,3pd) calculations).

CH_3 vibrational frequencies: 541, 1407, 1407, 3111, 3289, 3289 cm^{-1} (from B3LYP/6-311++G(3df,3pd) calculations).

CH_3 rotational constants: A = 9.601, B = 9.601, C = 4.800 cm^{-1} (σ = 3) (from B3LYP/6-311++G(3df,3pd) calculations).

Lennard-Jones parameters: $\sigma(Si(CH_3)_2F_2) \approx \sigma(SiF_4)$ = 4.88 Å and $\varepsilon/k(Si(CH_3)_2F_2) \approx \varepsilon/k(SiF_4)$ = 171.9 K (from ref. S9); σ(Ar) = 3.47 Å, ε/k(Ar) = 114 K (from ref. S10).

g. References

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