Supporting Information

Master Equation Modelling of Non-equilibrium Chemistry in Stellar Outflows

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Figure S1. Potential energy surface for the reaction between SiO_2 and H_2O. Energies are calculated at the cbs-qb3 level of theory [*Montgomery et al.*, 1999].

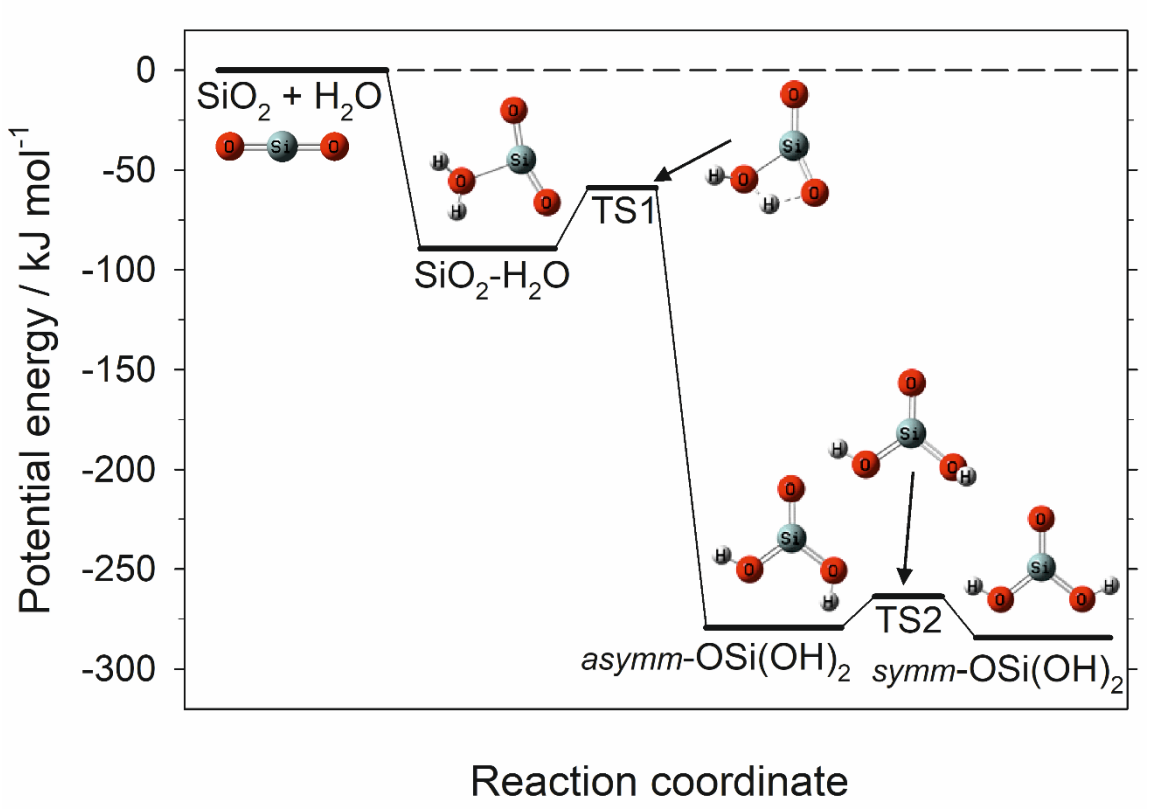

Table S1. Molecular properties and heats of formation (at 0 K) of the stationary points on the $SiO_2 + H_2O$ potential energy surface.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) [a]	Rotational constants (GHz) [a]	Vibrational frequencies (cm^{-1}) [a]	$\Delta_f H^o$(0 K) (kJ mol^{-1}) [b]
SiO_2	Si, -0.310, 0.748, 0. O, 1.192, 0.925, 0. O, -1.811, 0.571, 0.	6.9129	297 (×2), 991, 1437	-277.8
H_2O	O, 0.001, 0., 0.001 H 0, 0.0123, 0., 0.963 H, 0.933, 0., -0.237	798.21 438.23 282.91	1672, 3802, 3906	-238.9
SiO_2-H_2O	Si, -0.249, 0.279, -0.005 O, -1.475, -0.619, 0.067 O, 0.559, 1.568, -0.006 O, 1.151, -1.028, -0.133 H, 2.031, -0.735, 0.149 H, 0.933, -1.916, 0.189	7.8896 6.9337 3.7010	176, 304, 328, 376, 394, 441, 736, 991, 1395, 1569, 3719, 3835	-606.1
TS from SiO_2-H_2O to *asymm*-$OSi(OH)_2$ (TS1)	Si, 0.285, -0.170, -0.011 O, 1.737, 0.255, 0.0153 O, -0.865, -1.227, 0.043 O, -1.063, 1.052, -0.110 H, -1.556, 0.0415, 0.044 H, -1.185, 1.761, 0.537	10.746 5.9435 3.8530	1227*i*, 293, 314, 487, 510, 747, 800, 966, 1276, 1361, 2123, 3791	-575.6
asymm-$OSi(OH)_2$	Si, 0.028, 0.035, 0.123 O, 0.032, 1.352, -0.836 H, -0.024, 2.202, -0.385 O, 0.134, -1.240, -0.867 H, 0.182, -1.062, -1.813 O, -0.059, 0.006, 1.635	8.4623 7.2060 3.8919	314, 324, 357, 411, 476, 805, 866, 882, 989, 1295, 3849, 3853	-796.0
TS from *asymm*-$OSi(OH)_2$ to *symm*-$OSi(OH)_2$ (TS2)	Si, -0.092, -0.103, 0.077 O, 0.556, 1.387, 0.013 H, -0.084, 2.098, -0.112 O, 1.129, -1.118, 0.370 H, 1.674, -1.527, -0.305 O, -1.570, -0.422, -0.042	8.2175 7.3069 3.9011	444*i*, 322, 342, 348, 513, 679, 827, 892, 1002, 1279, 3841, 3918	-780.4
symm-$OSi(OH)_2$	Si, 0., 0., 0.124 O, 0., 1.275, -0.874 H, 0., 2.137, -0.444 O, 0., -1.275, -0.874 H, 0., -2.137, -0.444 O, 0., 0., 1.642	8.2547 7.3870 3.8984	313, 321, 361, 424, 492, 821, 837, 907, 1019, 1278, 3859, 3861	-801.0

[a] Calculated at the b3lyp/6-311+g(2d,p) level of theory [*Frisch et al.*, 2016].

[b] Calculated at the cbs-qb3 level of theory [*Montgomery et al.*, 1999], using reference values $\Delta_f H^o(SiO_2)$ = -277.8 kJ mol^{-1} and $\Delta_f H^o(H_2O)$ = -238.9 kJ mol^{-1} from the *Active Thermochemical Tables* [*Ruscic and Bross*, 2021].

Table S2. Reaction scheme for forming gas-phase Ca, Fe and Mg silicate molecules in the stellar outflow

No.	Reaction	Rate coefficient [a]	$\Delta H_{0\,K}$ [b] kJ mol^{-1}
3	$SiO + OH \rightarrow SiO_2 + H$	$9.6 \times 10^{-13}\ 10^{(5.94e\text{-}4\ T)}$ [c]	-4.1
-3	$SiO_2 + H \rightarrow SiO + OH$	$1.2 \times 10^{-10}\ 10^{(4.57e\text{-}4\ T)}$ [c]	+4.1
1	$SiO_2 + H_2O + M \rightarrow OSi(OH)_2 + M$	$\log_{10}(k$ / cm^6 molecule^{-2} s$^{-1}) = -0.0153r^4 + 0.2753r^3 - 1.9485r^2 + 7.2568r - 36.054$ [d] $\log_{10}(k$ / cm^6 molecule^{-2} s$^{-1}) = -0.0077r^4 + 0.1359r^3 - 0.9445r^2 + 3.4265r - 33.278$ [e]	-277
-1	$OSi(OH)_2 + M \rightarrow SiO_2 + H_2O + M$	$\log_{10}(k$ / cm^3 molecule^{-1} s$^{-1}) = -0.1425r^5 + 2.6562r^4 - 19.356r^3 + 68.941r^2 - 121.28r + 61.044$ [d] $\log_{10}(k$ / cm^3 molecule^{-1} s$^{-1}) = -1.592r - 10.340$ [e]	+277
2	$Ca + OSi(OH)_2 \rightarrow CaSiO_3 + H_2$	$2.8 \times 10^{-10}\ (1000/T)^{0.28}$ [c]	-234
-2	$CaSiO_3 + H_2 \rightarrow Ca + OSi(OH)_2$	$3.5 \times 10^{-10} \exp(-26590/T)$ [c]	+234
	$Fe + OSi(OH)_2 \rightarrow FeSiO_3 + H_2$	$7.0 \times 10^{-11} \exp(-5550/T)$ [c]	-81
	$FeSiO_3 + H_2 \rightarrow Fe + OSi(OH)_2$	$4.8 \times 10^{-11} \exp(-15870/T)$ [c]	+81
	$Mg + OSi(OH)_2 \rightarrow MgSiO_3 + H_2$	$5.4 \times 10^{-12} \exp(-7560/T)$ [c]	-45
	$MgSiO_3 + H_2 \rightarrow Mg + OSi(OH)_2$	$1.3 \times 10^{-11} \exp(-12040/T)$ [c]	+45

[a] Units: bimolecular, cm^3 molecule^{-1} s^{-1}; termolecular, cm^6 molecule^{-2} s^{-1} ; [b] Calculated at the CBS-QB3 level of theory [*Montgomery et al.*, 1999; *Frisch et al.*, 2016]; [c] *Plane* [2013]. [d] Master Equation calculation including optical transitions, for a distance *r* from the star R Dor (see main text). [e] Master Equation calculation *not* including optical transitions, for a distance *r* from the star R Dor (see main text).

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