**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].

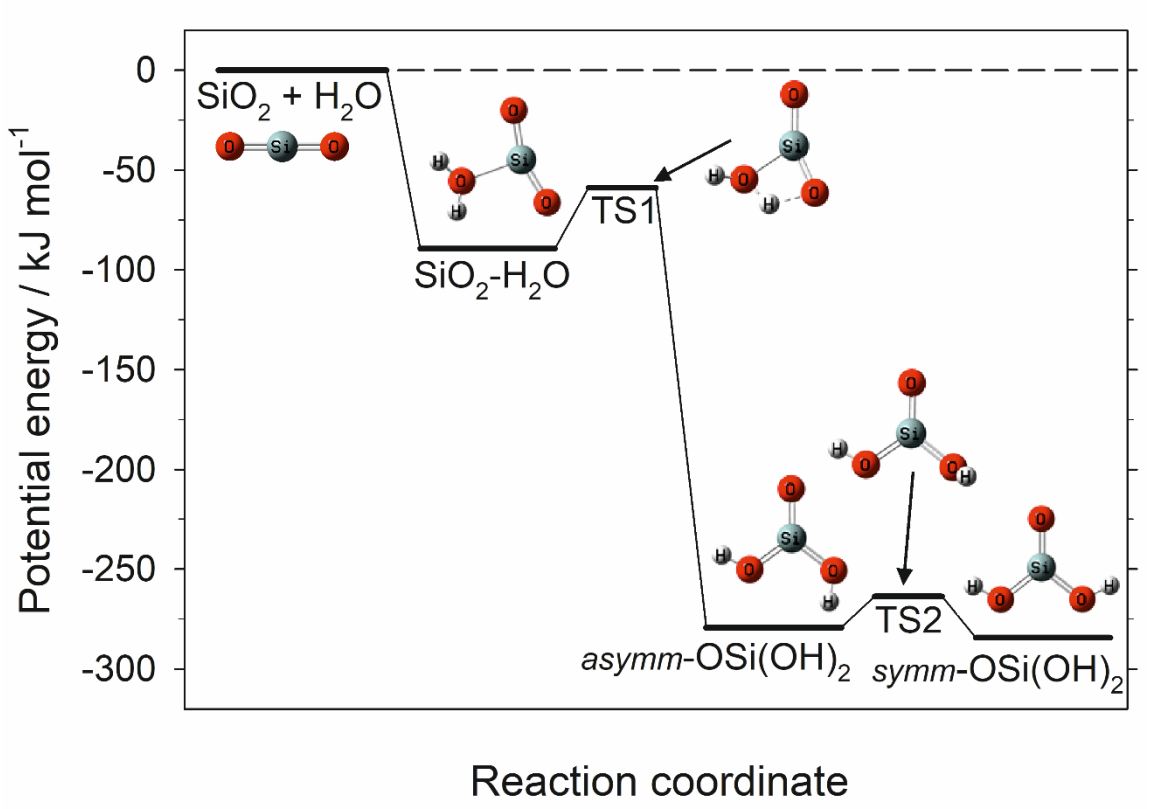

**Table S1.** Molecular properties and heats of formation (at 0 K) of the stationary points on the $SiO_2 + H_2O$ potential energy surface.

| 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.<br>O, 1.192, 0.925, 0.<br>O, -1.811, 0.571, 0. | 6.9129 | 297 (×2), 991, 1437 | -277.8 |
| $H_2O$ | O, 0.001, 0., 0.001<br>H 0, 0.0123, 0., 0.963<br>H, 0.933, 0., -0.237 | 798.21<br>438.23<br>282.91 | 1672, 3802, 3906 | -238.9 |
| $SiO_2$-$H_2O$ | Si, -0.249, 0.279, -0.005<br>O, -1.475, -0.619, 0.067<br>O, 0.559, 1.568, -0.006<br>O, 1.151, -1.028, -0.133<br>H, 2.031, -0.735, 0.149<br>H, 0.933, -1.916, 0.189 | 7.8896<br>6.9337<br>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<br>O, 1.737, 0.255, 0.0153<br>O, -0.865, -1.227, 0.043<br>O, -1.063, 1.052, -0.110<br>H, -1.556, 0.0415, 0.044<br>H, -1.185, 1.761, 0.537 | 10.746<br>5.9435<br>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<br>O, 0.032, 1.352, -0.836<br>H, -0.024, 2.202, -0.385<br>O, 0.134, -1.240, -0.867<br>H, 0.182, -1.062, -1.813<br>O, -0.059, 0.006, 1.635 | 8.4623<br>7.2060<br>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<br>O, 0.556, 1.387, 0.013<br>H, -0.084, 2.098, -0.112<br>O, 1.129, -1.118, 0.370<br>H, 1.674, -1.527, -0.305<br>O, -1.570, -0.422, -0.042 | 8.2175<br>7.3069<br>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<br>O, 0., 1.275, -0.874<br>H, 0., 2.137, -0.444<br>O, 0., -1.275, -0.874<br>H, 0., -2.137, -0.444<br>O, 0., 0., 1.642 | 8.2547<br>7.3870<br>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]<br><br>$\log_{10}(k$ / 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]<br><br>$\log_{10}(k$ / 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).

## References

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