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

Supplementary information to: Formation of the prebiotic molecule NH_2CHO on astronomical amorphous solid water surfaces: accurate tunneling rate calculations

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Cartesian coordinates of stationary points:

HNCO

N	−0.8975531	−0.1593249	0.0000000
C	0.2988332	−0.2178045	0.0000000
O	1.4340317	−0.4021137	0.0000000
H	−1.4556322	0.6654845	0.0000000

TS of $H + HNCO \longrightarrow NH_2CO$

N	−2.3102196	−0.3766682	−0.0000004
C	−1.0930308	−0.4013962	0.0000008
O	0.0149439	−0.7212172	−0.0000004
H	−2.8822644	0.4379437	0.0000088
H	−3.2446203	−1.6032927	−0.0000053

TS of $NH_2 + H_2CO \longrightarrow NH_2CH_2O$

N	0.465815	0.077152	0.623183
H	0.537642	1.087717	0.471744
H	−0.450786	−0.170730	0.239061
C	0.112568	−0.001936	2.600317
O	−0.821334	0.794605	2.582987
H	1.127538	0.311995	2.881437
H	−0.062542	−1.087154	2.607181

Table 1 Benchmark calculations for the reaction of H+HNCO $\rightarrow$ NH_2CO. (unit of energy: kJ/mol)

Theory	Basis-set	Activation Energy	Deviation
CCSD(T)-F12	VTZ-F12	32.7	
B3LYP	def2-SVPD	11.8	-20.9
	def2-TZVP	15.0	-17.8
BHLYP	def2-SVPD	26.7	-6.0
	def2-TZVP	29.0	-3.7
TPSS	def2-SVPD	-6.2	-38.9
	def2-TZVP	-3.3	-36.0
TPSSH	def2-SVPD	-1.5	-34.2
	def2-TZVP	1.2	-31.5
PBE0	def2-SVPD	19.1	-13.6
	def2-TZVP	22.0	-10.7

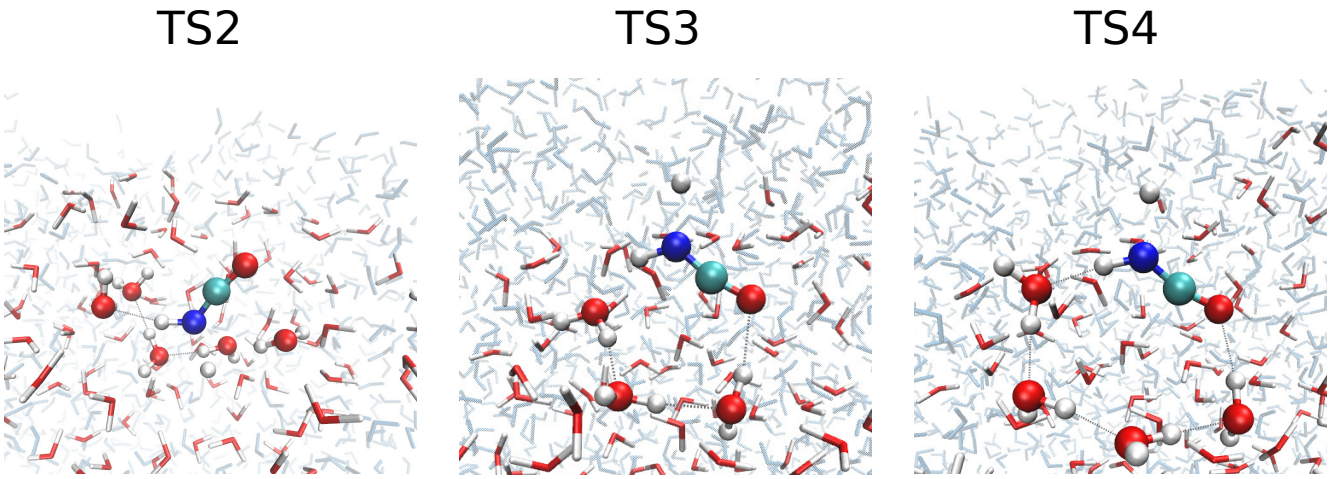

Fig. 1 Optimized structures of three transition states labeled as TS2, TS3 and TS4 at BHLPY/def2-TZVP theory level with D3 dispersion correction. For geometry optimization, the ball-and-stick molecules were in the QM region. The grey and red sticks stand for the active MM water molecules while the blue sticks represent the frozen MM water molecules. For Hessian analysis, the ball-and-stick molecules are still in the QM region, but all other water molecules are in the frozen MM region.

Table 2 Classical rate constants Log(k) (k in cm^3s^{-1}) for the reactions of $H + HNCO \longrightarrow NH_2CO$ and $D + HNCO \longrightarrow NHDCO$ in gas and on the amorphous solid water surface.

T(K)	H gas	H ASW	T(K)	D gas	D ASW
378.95	−15.55	−15.23	350.00	−16.03	−15.77
360.00	−15.82	−15.48	331.58	−16.33	−16.03
342.86	−16.09	−15.72	315.00	−16.63	−16.30
327.27	−16.36	−15.96	300.00	−16.93	−16.56
313.04	−16.63	−16.19	286.36	−17.22	−16.83
300.00	−16.90	−16.43	273.91	−17.52	−17.09
288.00	−17.16	−16.67	262.50	−17.81	−17.35
276.92	−17.43	−16.91	252.00	−18.11	−17.62
266.67	−17.69	−17.14	242.31	−18.4	−17.88
257.14	−17.96	−17.38	233.33	−18.69	−18.14
248.28	−18.22	−17.62	225.00	−18.99	−18.40
240.00	−18.49	−17.85	217.24	−19.28	−18.66
232.26	−18.75	−18.09	210.00	−19.57	−18.91
225.00	−19.01	−18.32	203.23	−19.86	−19.17
218.18	−19.28	−18.56	196.88	−20.15	−19.43
211.76	−19.54	−18.79	190.91	−20.45	−19.69
205.71	−19.80	−19.02	185.29	−20.74	−19.95
200.00	−20.07	−19.26	180.00	−21.03	−20.20
194.59	−20.33	−19.49	175.00	−21.32	−20.46
189.47	−20.59	−19.72	170.27	−21.61	−20.72
184.62	−20.85	−19.96	165.79	−21.90	−20.97
180.00	−21.12	−20.19	161.54	−22.18	−21.23
175.61	−21.38	−20.42	157.50	−22.47	−21.48
171.43	−21.64	−20.66	153.66	−22.76	−21.74
167.44	−21.90	−20.89	150.00	−23.05	−22.00
163.64	−22.16	−21.12	145.00	−23.47	−22.37
160.00	−22.42	−21.35	137.00	−24.20	−23.01
156.52	−22.69	−21.58	130.00	−24.92	−23.64
153.19	−22.95	−21.82	123.00	−25.71	−24.34
150.00	−23.21	−22.05	118.00	−26.33	−24.89
148.00	−23.38	−22.20	112.00	−27.16	−25.62
141.00	−24.01	−22.76	107.00	−27.91	−26.29
135.00	−24.60	−23.28	103.00	−28.57	−26.87
129.00	−25.25	−23.86	99.00	−29.28	−27.49
124.00	−25.84	−24.38	95.00	−30.05	−28.17
119.00	−26.47	−24.94	91.00	−30.89	−28.91
115.00	−27.02	−25.43	88.00	−31.57	−29.51
110.00	−27.76	−26.09	85.00	−32.29	−30.14
107.00	−28.24	−26.51	82.00	−33.07	−30.83
103.00	−28.92	−27.11	80.00	−33.63	−31.32
100.00	−29.47	−27.60	78.00	−34.21	−31.83
95.00	−30.46	−28.47			

Table 3 Instanton rate constants Log(k) (k in cm^3s^{-1}) for the reactions of H + HNCO ⟶ NH_2CO and D + HNCO ⟶ NHDCO in gas and on the amorphous solid water surface.

T(K)	H gas	H ASW	T(K)	D gas	D ASW
289.00	−15.94		225.00	−17.77	
264.00	−16.40	−16.19	210.00		−18.17
243.00	−16.77	−16.82	206.00	−18.34	−18.37
225.00	−17.08	−17.18	190.00	−18.82	−18.83
210.00	−17.33	−17.58	176.00	−19.23	−19.32
196.00	−17.56	−17.85	165.00	−19.54	−19.67
184.00	−17.74	−17.97	154.00	−19.85	−19.98
174.00	−17.88	−18.13	145.00	−20.08	−20.21
164.00	−18.02	−18.33	137.00	−20.28	−20.33
156.00	−18.12	−18.45	130.00	−20.45	−20.52
148.00	−18.21	−18.56	123.00	−20.60	−20.76
141.00	−18.29	−18.67	118.00	−20.71	−20.90
135.00	−18.34	−18.75	112.00	−20.82	−21.04
129.00	−18.42	−18.82	107.00	−20.91	−21.17
124.00	−18.46	−18.88	103.00	−20.97	−21.27
119.00	−18.50	−18.93	99.00	−21.03	−21.32
115.00	−18.53	−18.99	95.00	−21.08	−21.40
110.00	−18.57	−19.04	91.00	−21.12	−21.50
107.00	−18.58	−19.08	88.00	−21.14	−21.55
103.00	−18.61	−19.11	85.00	−21.16	−21.64
100.00	−18.62		82.00	−21.17	−21.67
95.00	−18.65		80.00	−21.17	−21.72
			78.00	−21.17	−21.74

Table 4 Unimolecular rate constants Log(k) (k in s^{-1}) for the reaction of H + HNCO ⟶ NH_2CO on the amorphous solid water surface.

T(K)	Log(k)	T(K)	Log(k)	T(K)	Log(k)
275.00	6.02	156.00	3.68	107.00	2.80
264.00	5.79	148.00	3.54	103.00	2.73
243.00	5.34	141.00	3.41	100.00	2.67
225.00	4.98	135.00	3.30	95.00	2.59
210.00	4.70	129.00	3.18	85.00	2.41
196.00	4.43	124.00	3.09	80.00	2.32
184.00	4.20	119.00	3.01	78.00	2.28
174.00	4.01	115.00	2.94	75.00	2.23
164.00	3.83	110.00	2.85		