

# How symmetry influences the dissociation of protonated cyclic peptides.

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## Supporting Information.

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Table S1 Details of the simulation.  $\Lambda$  is the total integration time,  $N$  the number of trajectories,  $E_v$ , the initial excess vibrational energy,  $\langle K \rangle^{SP}$  the average kinetic energy of the starting point state and their corresponding standard deviations  $\sigma_{\langle K \rangle}$ .  $T^{SP}$  corresponds to the temperature computed from  $\langle K \rangle^{SP}$ .

	$\Lambda$	$N$	$E_v$	$\langle K \rangle^{SP}$ kcal/mol	$\sigma_{\langle K \rangle}$	$T^{SP}$ K
cycloTyr-ProH <sup>+</sup>	20ps	4992	367	180	18	888
		4963	392	192	19	947
		4905	417	204	21	1007
		4784	442	216	22	1067
		3722	467	229	23	1128
		4275	492	241	24	1187
		3140	517	253	26	1248
cycloPhe-HisH <sup>+</sup>	25ps	4923	467	226	22	1052
		4898	492	238	23	1108
		11891	517	250	25	1164
		4633	542	262	26	1220
		8862	567	274	27	1276
		4051	592	286	28	1333
		3613	617	298	29	1388

Table S2 Microcanonical rate constants and their corresponding uncertainty extracted from chemical dynamics simulations by a simultaneous fit approach using the three-state model.  $\chi^2_{red}$  is the reduced chi-square per degree of freedom evaluating the quality of the fit.

	T <sup>SP</sup> K	k <sub>IS</sub>	ek <sub>IS</sub>	k <sub>SI</sub>	ek <sub>SI</sub>	k <sub>PI</sub>	ek <sub>PI</sub>	k <sub>PS</sub>	ek <sub>PS</sub>	$\chi^2_{red}$
		10 <sup>-5</sup> fs <sup>-1</sup>								
cycloTyr-ProH <sup>+</sup>	888	1.728	0.008	0.699	0.071	2.163	0.057	0.181	0.005	0.39
	947	2.998	0.012	1.556	0.059	2.926	0.053	0.452	0.007	0.61
	1007	4.970	0.016	0.530	0.045	5.016	0.048	0.868	0.011	0.91
	1067	7.786	0.023	0.808	0.041	7.598	0.046	1.480	0.016	0.79
	1128	12.230	0.049	2.192	0.058	10.759	0.067	2.693	0.034	1.52
	1187	14.824	0.075	0.927	0.064	12.845	0.089	5.583	0.059	3.00
	1248	21.755	0.145	1.318	0.092	18.444	0.129	7.190	0.108	3.84
cycloPhe-HisH <sup>+</sup>	1052	2.640	0.028	5.643	0.177	5.446	0.106	0.190	0.012	4.60
	1108	3.574	0.030	4.639	0.134	6.080	0.094	0.412	0.015	4.32
	1164	4.794	0.035	3.859	0.115	8.146	0.093	0.696	0.020	9.23
	1220	6.113	0.051	3.119	0.129	10.286	0.114	1.071	0.031	5.15
	1276	7.990	0.073	3.513	0.146	12.645	0.136	1.867	0.046	11.39
	1333	10.726	0.120	5.167	0.200	15.352	0.180	2.972	0.073	7.14
	1388	12.658	0.177	3.461	0.238	18.858	0.241	4.393	0.112	9.79

Table S3 Effective frequencies factors (in fs<sup>-1</sup>) and energy thresholds (in kcal/mol) extracted from a fit using the RRK model.

	cycloTyr-ProH <sup>+</sup>	cycloPhe-HisH <sup>+</sup>
$\nu^{IS}$	0.085 ± 0.015	0.016 ± 0.002
$E_a^{IS}$	29.660 ± 0.695	13.423 ± 0.340
$\nu^{PI}$	0.031 ± 0.008	0.011 ± 0.002
$E_a^{PI}$	25.627 ± 1.157	11.347 ± 0.467
$\nu^{PS}$	0.427 ± 0.182	0.499 ± 0.117
$E_a^{PS}$	42.404 ± 1.755	25.561 ± 0.580

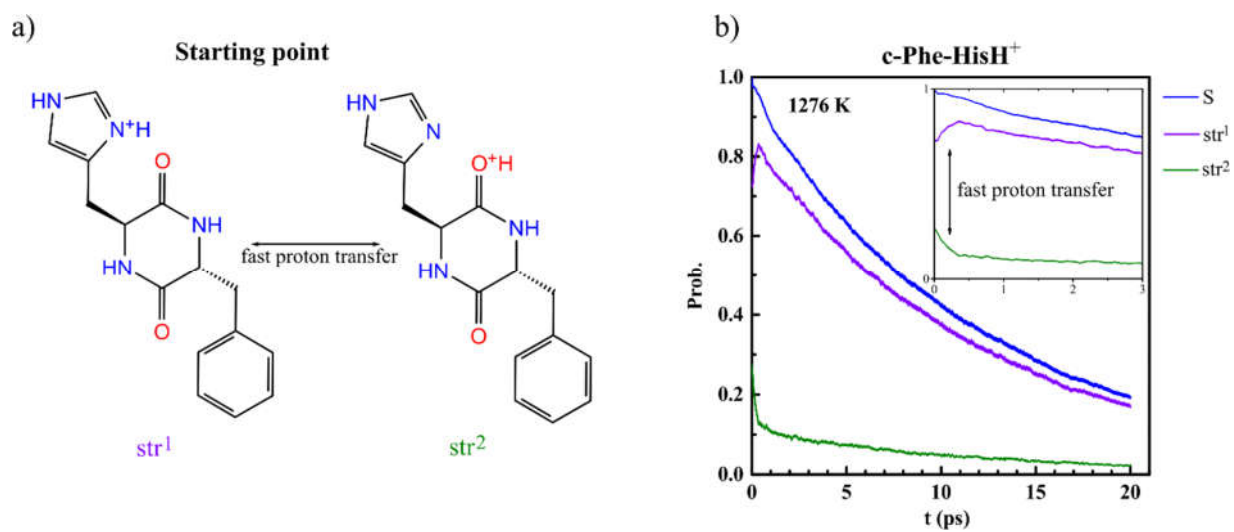


Figure S1 a) Starting point definition ( $S = \text{str}^1 + \text{str}^2$ ) in c-Phe-HisH<sup>+</sup> system due to the fast proton transfer detected during the chemical dynamics simulations. b) Starting point population at 1276 K decomposed into its components. The inset highlights the fast proton transfer that takes place within 1 ps.