Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI)

for

Dynamics of Structural Diffusion in Phosphoric Acid Hydrogen-Bond Clusters

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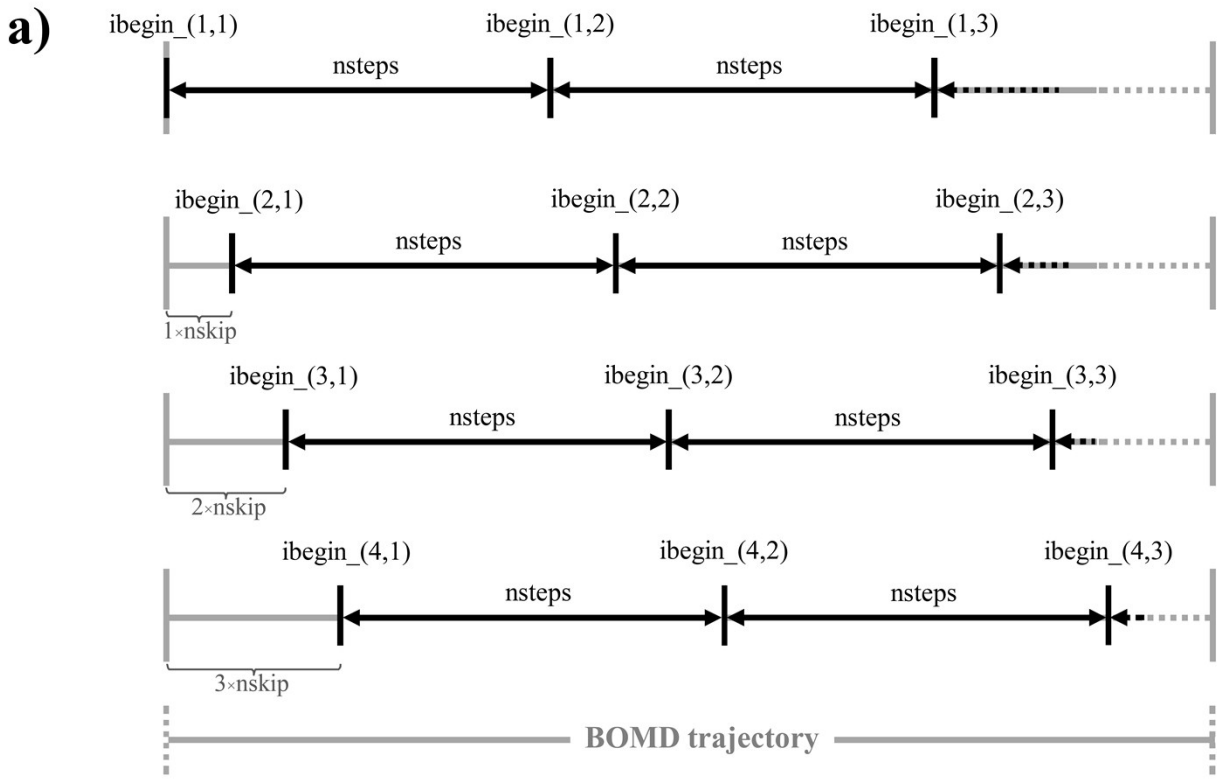


Figure S1 a) Overlap data collection method used in the analyses of time-dependent properties, in which measurements at any instant contribute several sets of samples.[40]

nskip = equally spaced time origin; ibegin_(m,n) = time origin; nsteps = constant overlapped interval.

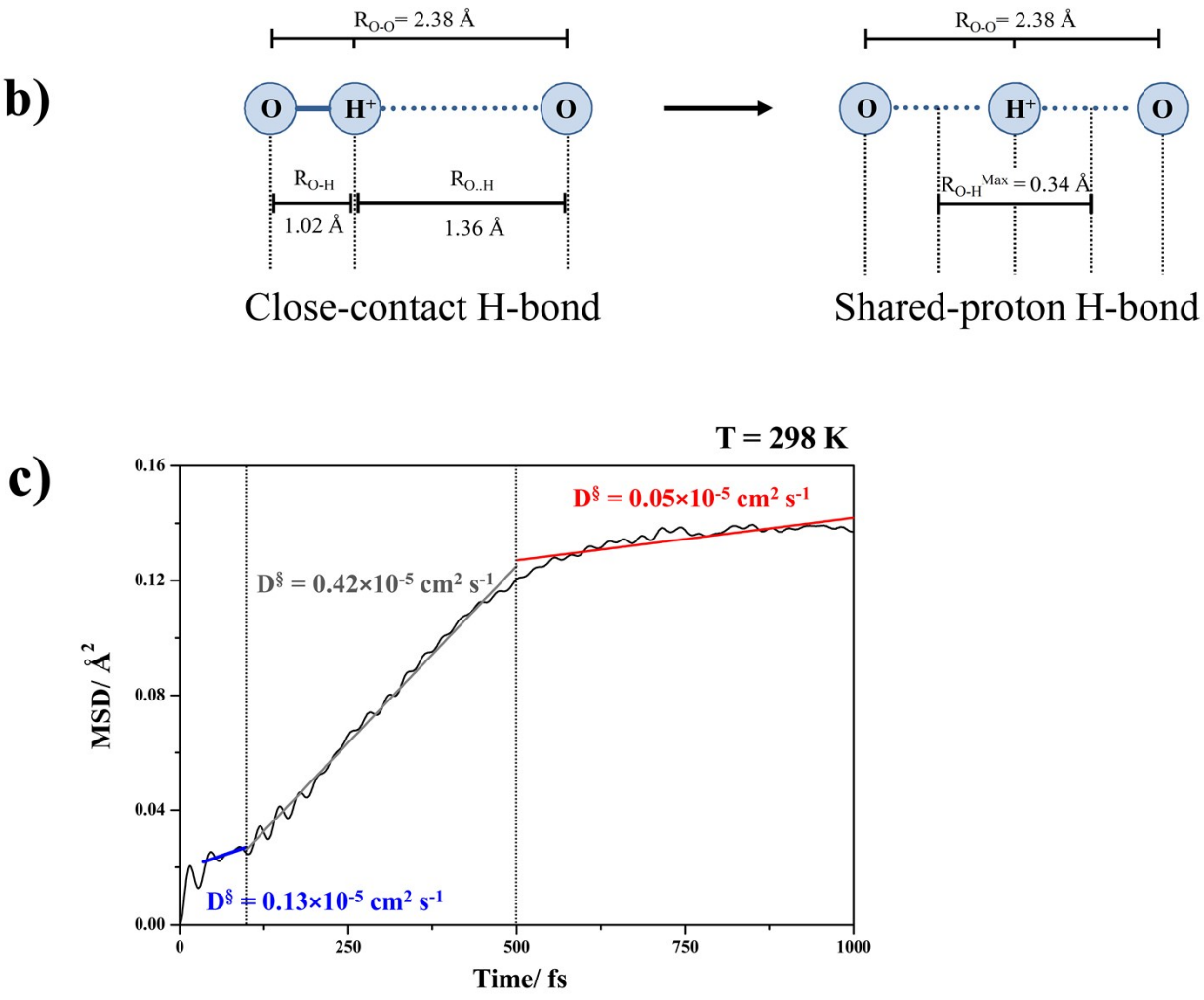


Figure S1 (cont.) b) Maximum possible shuttling distance ($R_{O\text{-}H}^{Max}$) of a proton confined in $O\text{-}H^{+}..O$ H-bond.

c) Example of MSD plot for an exchanging proton in protonated H_3PO_4 H-bond obtained from NVT-BOMD simulation at 298 K.

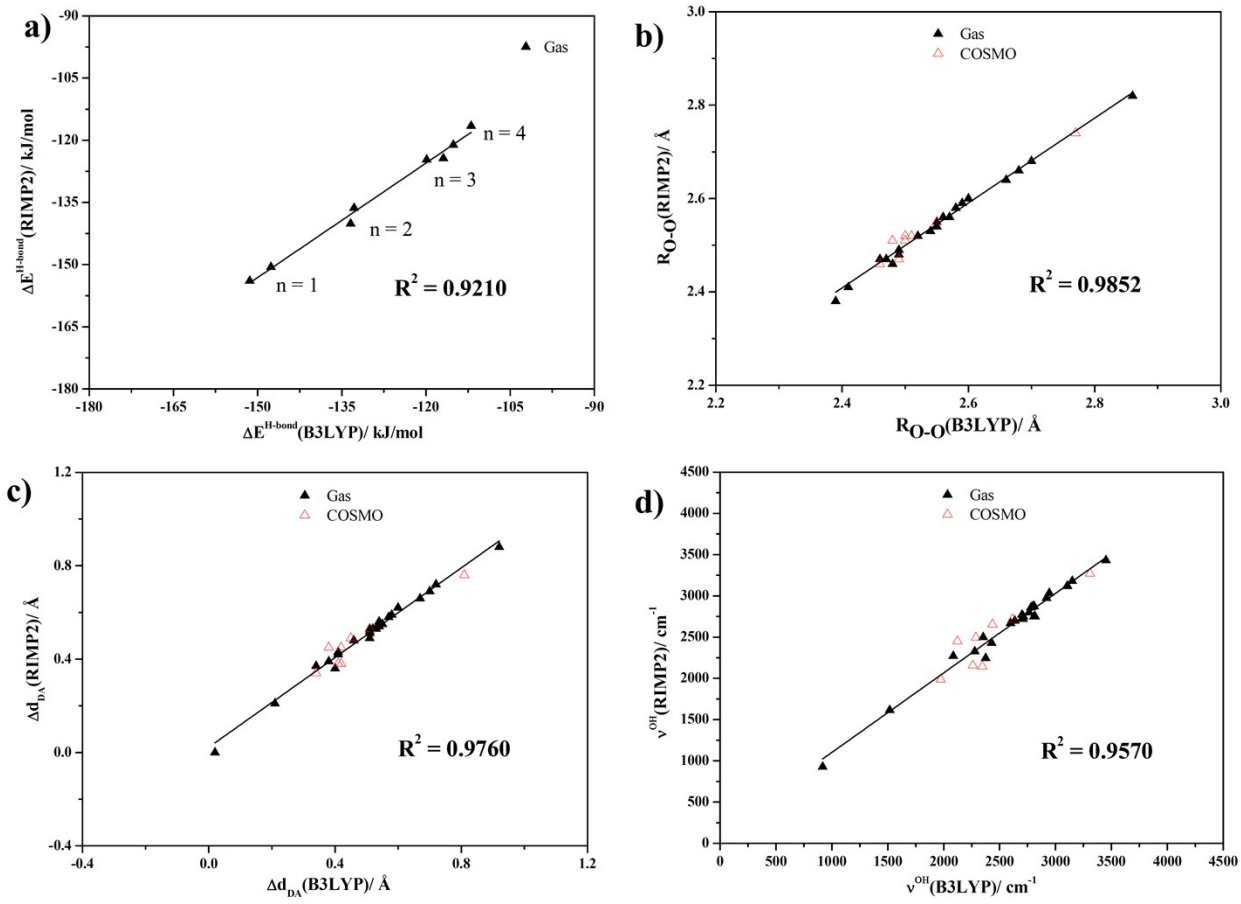


Figure S2 Correlations (R^2) of the static results of $H^+(H_3PO_4)_n$ (n = 2–5) obtained from RIMP2/TZVP and B3LYP/TZVP calculations in the gas phase (ε = 1) and in continuum solvent (ε = 61).

a) Interaction energy per H-bond ($\Delta E^{H\text{-}bond}$).

b) $R_{O\text{-}O}$ distance.

c) Asymmetric stretching coordinate (Δd_{DA}).

d) Asymmetric O-H stretching frequency (ν^{OH}).

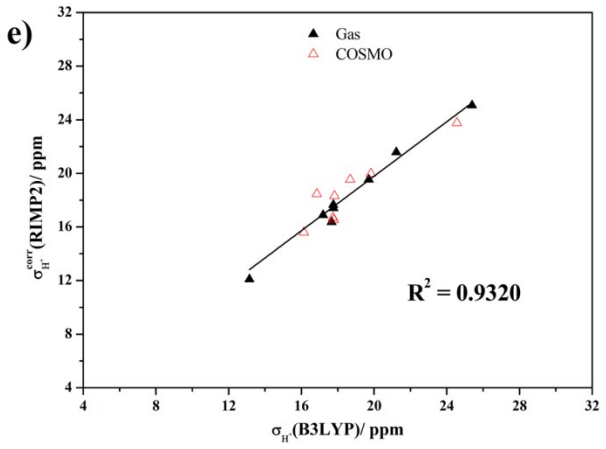


Figure S2 (cont.) e) Isotropic shielding constant (σ_{H^+}).

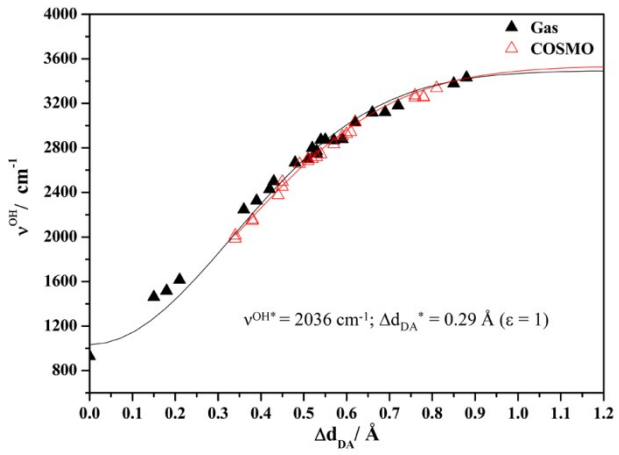


Figure S3 Plots of asymmetric O-H stretching frequencies (ν^{OH}) and asymmetric stretching coordinates (Δd_{DA}) of protonated H-bonds in $H^+(H_3PO_4)_n$ (n = 2–5) obtained from RIMP2/TZVP calculations. ν^{OH*} = threshold asymmetric O-H stretching frequency; $\Delta d_{DA}{}^{*}$ = threshold asymmetric stretching coordinate.

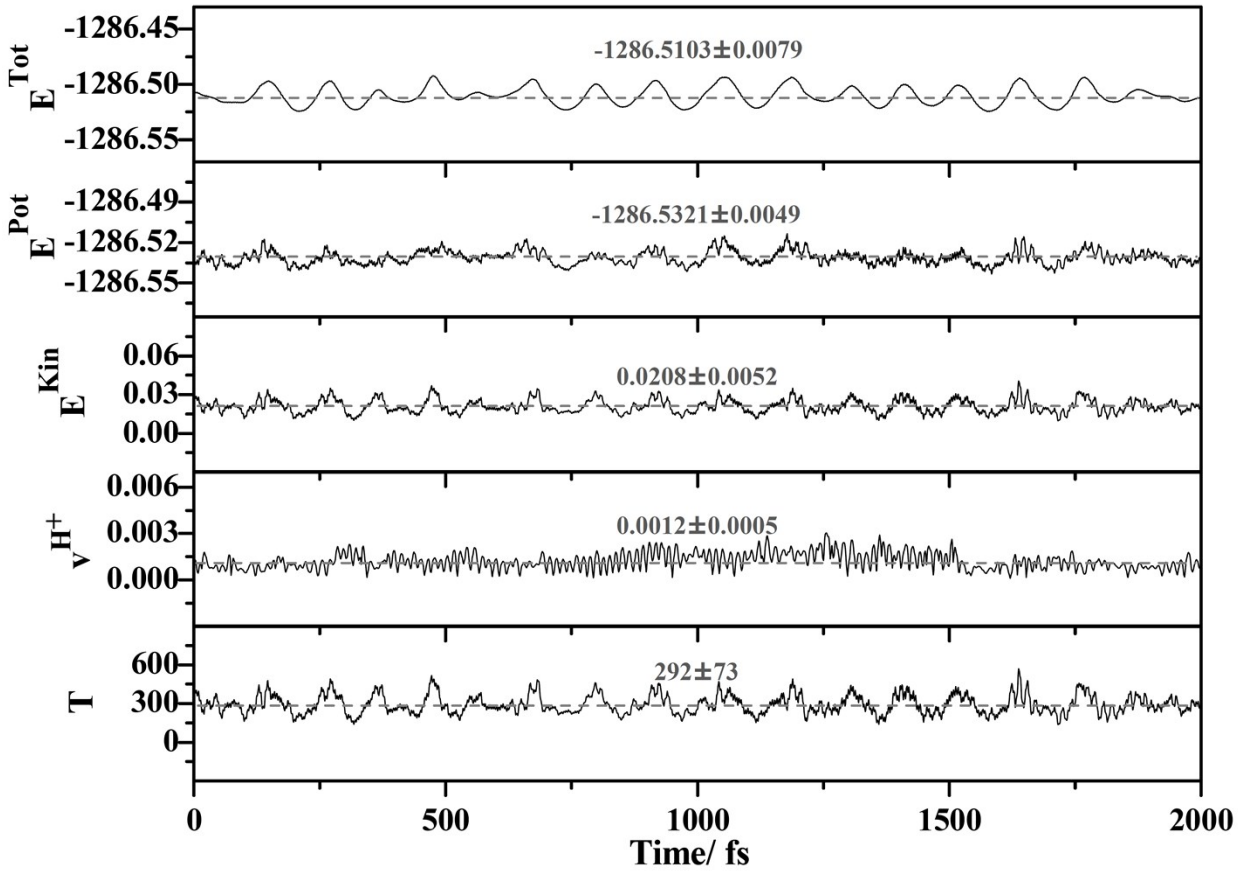


Figure S4 Energy conservation and velocity plots obtained from NVT-BOMD simulations on $H^+(H_3PO_4)_2$ at 298 K. Energies and velocity are in au. E^{Tot}, E^{Pot} and E^{Kin} = total, potential and kinetic energies, respectively; v^{H+} = velocity of the exchanging proton; T = temperature.

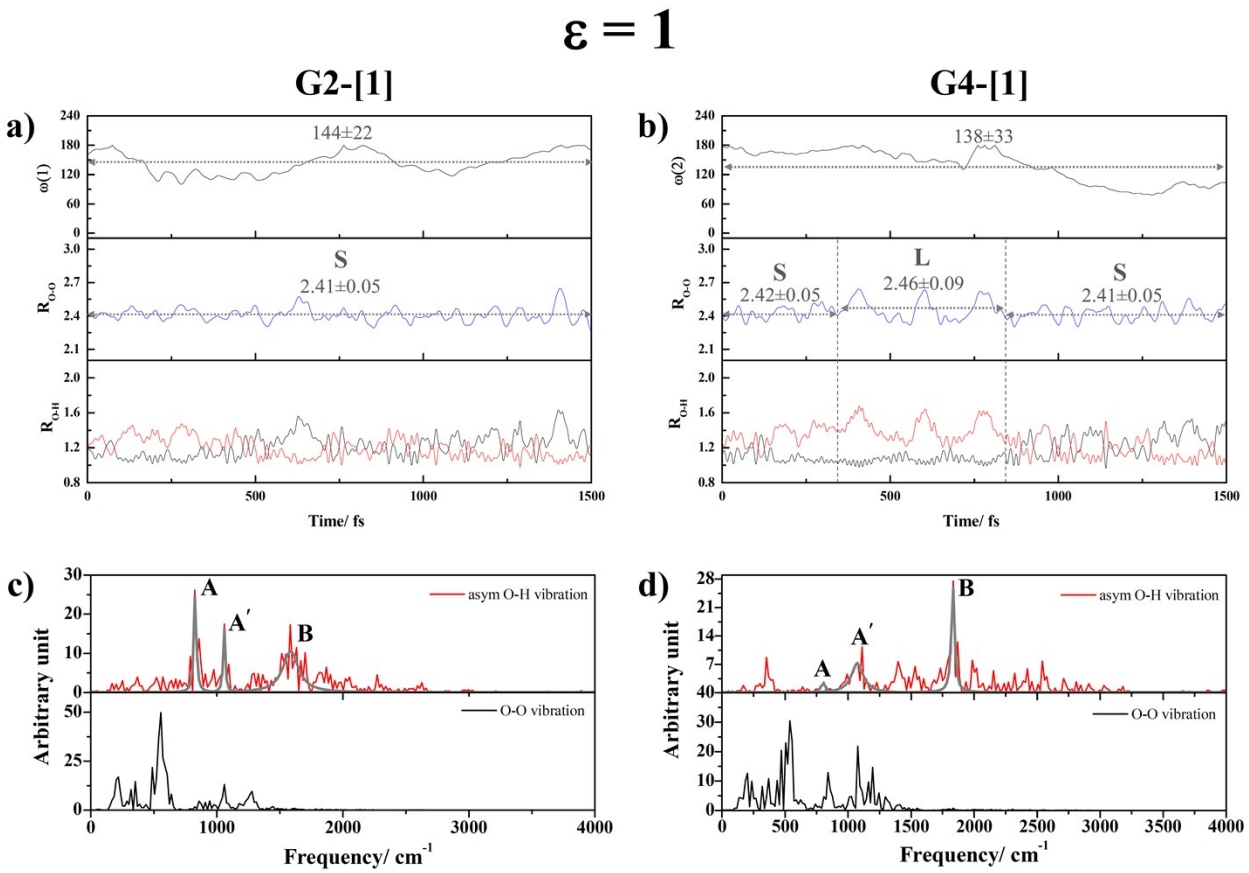


Figure S5 a) – b) Proton transfer profiles and time evolutions of the dihedral angles of H-bonds **(1)** and **(2)** in $H^+(H_3PO_4)_2$ and $H^+(H_3PO_4)_4$ obtained from NVT-BOMD simulations in low local-dielectric environment at 298 K, respectively.

c) – d) Vibrational spectra of H-bonds **(1)** and **(2)** in $H^+(H_3PO_4)_2$ and $H^+(H_3PO_4)_4$ obtained from NVT-BOMD simulations in low local-dielectric environment at 298 K, respectively. $R_{O\text{-}O}$ and $R_{O\text{-}H}$ are in Å and ω(1) and ω(2) are in degrees; **L** and **S** = large-amplitude and small-amplitude O-O vibrations, respectively; **A** and **A′** = oscillatory shuttling peaks; **B** = structural diffusion peak.

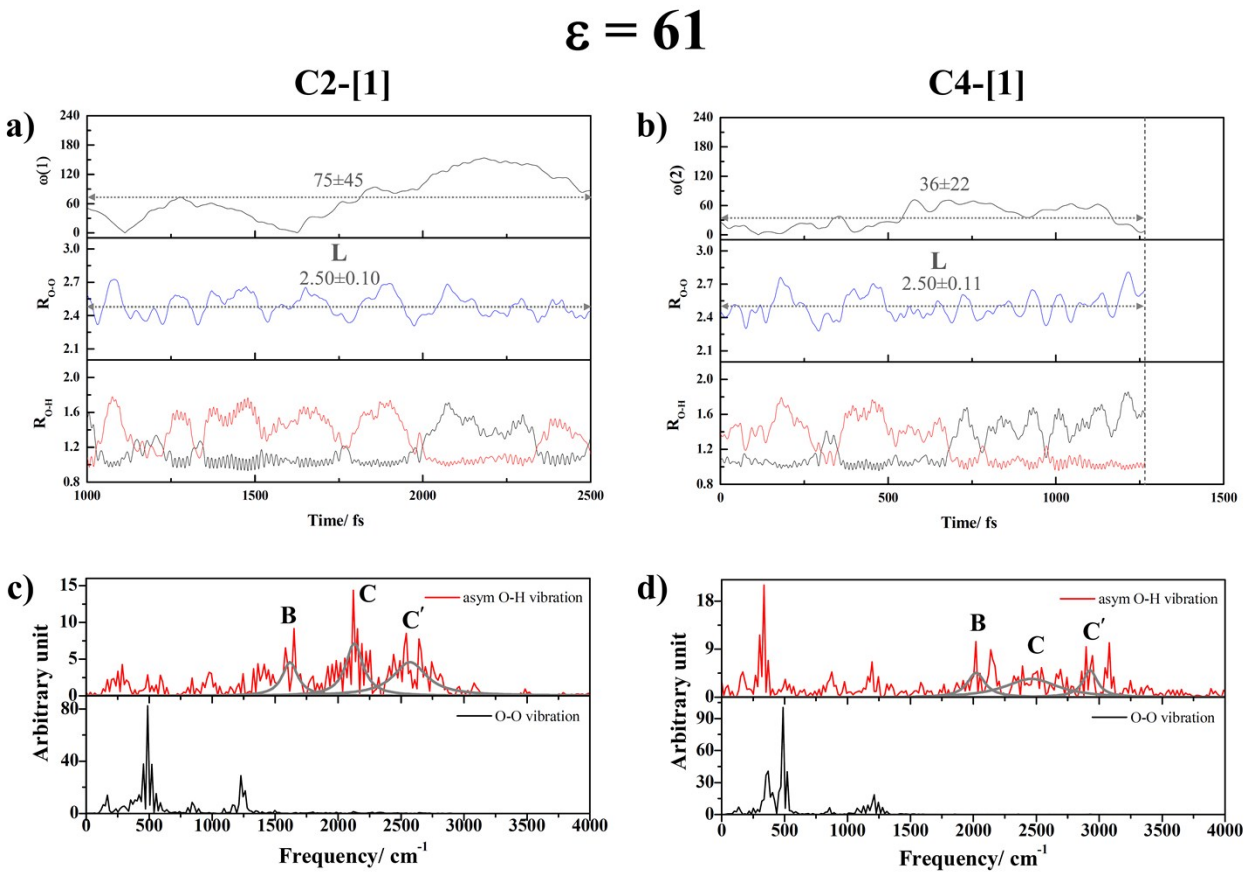


Figure S6 a) – b) Proton transfer profiles and time evolutions of the dihedral angles of H-bonds **(1)** and **(2)** in $H^+(H_3PO_4)_2$ and $H^+(H_3PO_4)_4$ obtained from NVT-BOMD simulations in high local-dielectric environment at 298 K, respectively.

c) – d) Vibrational spectra of H-bonds **(1)** and **(2)** in $H^+(H_3PO_4)_2$ and $H^+(H_3PO_4)_4$ obtained from NVT-BOMD simulations in high local-dielectric environment at 298 K, respectively. $R_{O\text{-}O}$ and $R_{O\text{-}H}$ are in Å and ω(1) and ω(2) in degrees; **L** and **S** = large-amplitude and small-amplitude O-O vibrations, respectively; **B** = structural diffusion peak; **C** and **C′** = characteristic peaks of proton in double-well potential.

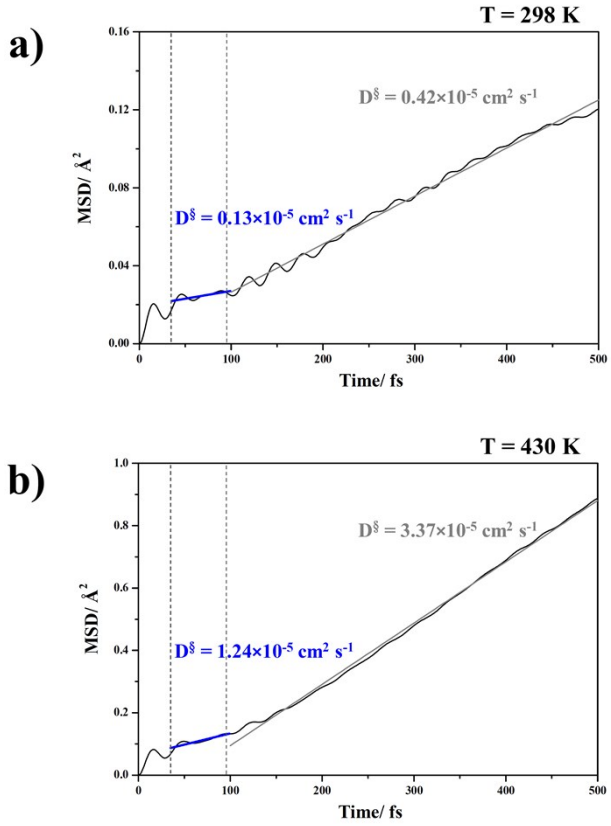


Figure S7 a) – b) Examples of the MSD plots of the exchanging proton obtained from NVT-BOMD simulations on $H^+(H_3PO_4)_2$.

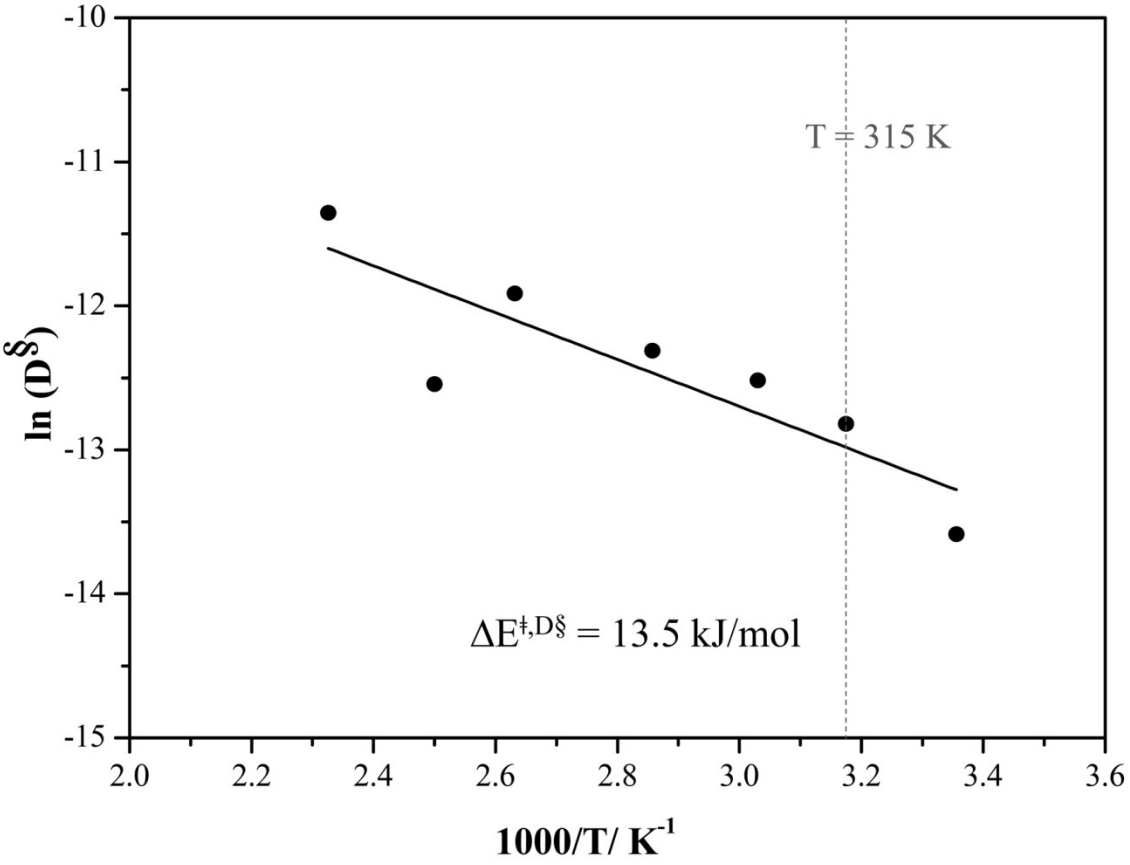
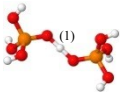
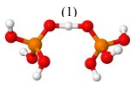
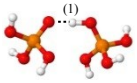
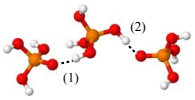
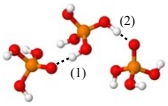
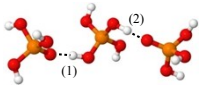
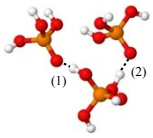
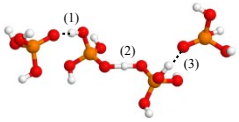
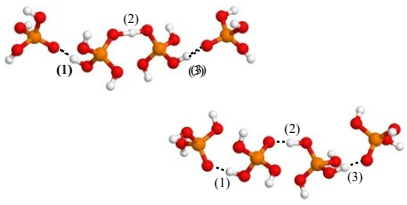


Figure S8 Plots of the natural log of the self-diffusion coefficients ($D^{§}$) as a function of 1000/T. $\Delta E^{‡,D§}$ = activation energy obtained from the simple Arrhenius equation (Eqn (2)).

Table S1 Static Results of $H^+(H_3PO_4)_n$ (n = 2–5) Obtained from RIMP2/TZVP Calculations.[a]

Gas	COSMO	ΔE^{Tot}	ΔE^{sol}	H-bond	R_{O-O}	Δd_{DA}	ν^{OH}	$\sigma_{H^+}^{corr}$	$\delta_{H^+}^{corr}$	ω
G2-[1]	C									
		-153.9	-	(1)*	2.38	0.00	928	12.10	19.86	161
		-								
G2-[2]	C2-[2]									
		-150.6	-284.0	(1)*	2.39	0.18	1516	13.20	18.76	20
		-50. 5		(1)*	2.46	0.34	1986	15.60	16.36	35
G3-[1]	C3-[1]									
		-280.3	-288.0	(1)	2.60	0.62	3033	21.58	10.38	2
				(2)	2.46	0.36	2246	16.36	15.60	170
		-101.4		(1)	2.55	0.53	2718	19.99	11.97	4
				(2)	2.47	0.38	2156	16.69	15.27	37
G3-[2]	C3-[2]									
		-272.7	-294.4	(1)	2.48	0.42	2428	17.41	14.55	56
				(2)	2.49	0.43	2500	17.65	14.31	67
		-100.2		(1)	2.48	0.38	2146	18.32	13.64	157
				(2)	2.50	0.45	2495	16.53	15.43	78
G4-[1]	C4-[1]									
		-373.1	-	(1)	2.55	0.53	2854	-	-	47
				(2)*	2.39	0.15	1460	-	-	178
				(3)	2.52	0.54	2712	-	-	52
		-								
G4-[2]	C4-[2]									
		-374.0	-311.5	(1)	2.56	0.54	2871	-	-	49
				(2)*	2.41	0.21	1615	-	-	11
				(3)	2.52	0.48	2668	-	-	59
		-135.6		(1)	2.56	0.54	2871	-	-	18
				(2)	2.45	0.38	2156	-	-	26
				(3)	2.50	0.44	2376	-	-	27

[a] Energies, distances, vibrational frequencies and torsional angles are in kJ/mol, Å, cm^{-1} and degrees, respectively. Isotropic shielding constants and ^1H NMR chemical shifts are in ppm. ΔE^{Tot} = total interaction energy; ΔE^{sol} = solvation energy; R_{O-O} = H-bond distance; Δd_{DA} = asymmetric stretching coordinate; ν^{OH} = asymmetric O-H stretching frequency; $\sigma_{H^+}^{corr}$ = isotopic shielding constant; $\delta_{H^+}^{corr}$ = ^1H NMR chemical shift; ω = torsional angle of H-bond; COSMO = continuum aqueous solution; * = H-bond susceptible to proton exchange.

Table S1 (cont.)

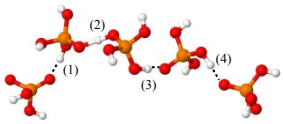
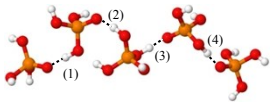
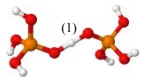
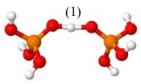
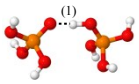
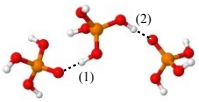
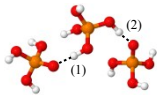
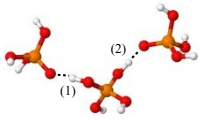
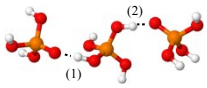
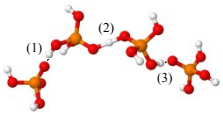
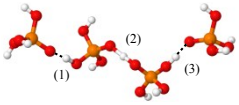
Gas	COSMO	ΔE^{Tot}	ΔE^{sol}	H-bond	R_{O-O}	Δd_{DA}	ν^{OH}	$\sigma^{corr}_{H^+}$	$\delta^{corr}_{H^+}$	ω
G5-[1]		-466.1	-	(1)	2.52	0.49	2930	-	-	50
				(2)*	2.39	0.15	1920	-	-	176
				(3)	2.55	0.53	2231	-	-	35
				(4)	2.48	0.58	2913	-	-	158
		-								
G5-[2]		-484.5	-	(1)	2.58	0.58	2974	-	-	54
				(2)	2.53	0.49	2721	-	-	13
				(3)	2.56	0.56	2860	-	-	40
				(4)	2.47	0.37	2270	-	-	20
		-								

Table S2 Static Results of $H^+(H_3PO_4)_n$ (n = 2–5) Obtained from B3LYP/TZVP Calculations.[a]

Gas	COSMO	ΔE^{Tot}	ΔE^{sol}	H-bond	R_{O-O}	Δd_{DA}	ν^{OH}	σ_{H^+}	δ_{H^+}	ω
G2-[1]		-151.4	-	(1)	2.39	0.02	919	13.14	18.78	161
		-								
G2-[2]	C2-[2]	-147.6	-280.0	(1)	2.39	0.12	1396	13.59	18.33	7
		-46. 2		(1)	2.46	0.34	1937	16.14	15.78	45
G3-[1]	C3-[1]	-266.8	-287.4	(1)	2.60	0.60	2944	21.22	14.26	1
				(2)	2.48	0.40	2376	17.66	10.70	52
		-86.9		(1)	2.55	0.51	2616	19.83	12.09	14
				(2)	2.49	0.41	2261	17.74	14.18	24
G3-[2]	C3-[2]	-265.6	-278.1	(1)	2.49	0.41	2429	17.76	14.16	84
				(2)	2.49	0.41	2353	17.77	14.15	95
		-76.0		(1)	2.50	0.42	2346	17.82	14.10	22
				(2)	2.50	0.42	2289	17.79	14.13	3
G4-[1]		-350.7	-	(1)	2.69	0.75	3139	27.84	4.08	144
				(2)	2.41	0.07	1358	16.31	15.61	161
				(3)	2.52	0.44	2415	20.35	11.57	145
		-								
G4-[2]	C4-[2]	-359.6	-	(1)	2.52	0.46	2598	20.18	11.74	87
				(2)	2.41	0.21	1518	14.26	17.66	64
				(3)	2.56	0.54	2797	18.93	12.99	80
		-								

[a] Energies, distances, vibrational frequencies and torsional angles are in kJ/mol, Å, cm^{-1} and degrees, respectively. Isotropic shielding constants and ^1H NMR chemical shifts are in ppm. ΔE^{Tot} = total interaction energy; ΔE^{sol} = solvation energy; R_{O-O} = H-bond distance; Δd_{DA} = asymmetric stretching coordinate; ν^{OH} = asymmetric O-H stretching frequency; σ_{H+} = isotopic shielding constant; δ_{H+} = ^1H NMR chemical shift; ω = torsional angle of H-bond; COSMO = continuum aqueous solution; * = H-bond susceptible to proton exchange.

Table S2 (cont.)

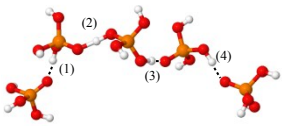
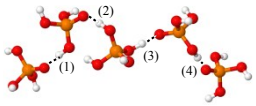
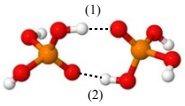
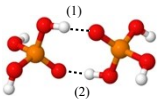
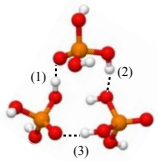
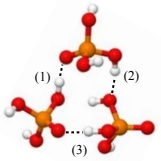
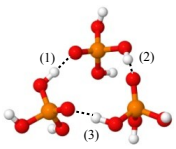
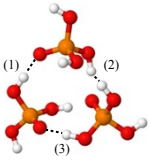
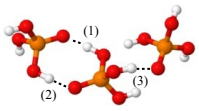
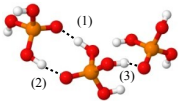
Gas	COSMO	ΔE^{Tot}	ΔE^{sol}	H-bond	R_{O-O}	Δd_{DA}	ν^{OH}	$\sigma^{corr}_{H^+}$	$\delta^{corr}_{H^+}$	ω
G5-[1]		-447.8	-	(1)	2.58	0.56	2870	-	-	70
				(2)	2.43	0.27	1792	-	-	165
				(3)	2.46	0.34	2117	-	-	55
				(4)	2.58	0.56	2894	-	-	173
		-								
G5-[2]		-460.5	-	(1)	2.54	0.51	2710	-	-	20
				(2)	2.57	0.54	2782	-	-	40
				(3)	2.46	0.34	2087	-	-	14
				(4)	2.58	0.57	2920	-	-	55
		-								

Table S3 Example of Static Results of $(H_3PO_4)_n$ (n = 2–3) Obtained from RIMP2/TZVP Calculations.[a]

Gas	COSMO	ΔE^{Tot}	ΔE^{sol}	H-bond	$R_{O\text{-}O}$	Δd_{DA}	ν^{OH}	σ_H^{corr}	δ_H^{corr}	ω
G2-[3]	C2-[3]									
		-137.4	-99.3	(1)	2.58	0.57	2867	20.74	11.22	11
				(2)	2.58	0.57	2867	20.88	11.08	11
		-66. 1		(1)	2.59	0.57	2832	20.74	11.22	21
				(2)	2.58	0.57	2832	20.71	11.25	38
G3-[3]	C3-[3]	-198.3	-142.4	(1)	2.54	0.53	2771	20.00	11.96	82
				(2)	2.68	0.72	3181	22.83	9.13	107
				(3)	2.64	0.66	3118	22.39	9.57	27
		-84. 8		(1)	2.54	0.51	2700	11.98	12.12	80
				(2)	2.74	0.78	3257	23.62	8.34	102
				(3)	2.60	0.60	2925	21.65	10.31	20
G3-[4]	C3-[4]	-225.5	-162.9	(1)	2.55	0.53	2750	19.79	12.17	72
				(2)	2.55	0.53	2750	19.85	12.11	67
				(3)	2.55	0.53	2750	19.92	12.04	69
		-132.6		(1)	2.62	0.62	3029	22.56	9.40	1
				(2)	2.60	0.61	2943	21.67	10.29	73
				(3)	2.55	0.52	2700	19.66	12.30	39
G3-[5]	C3-[5]	-242.8	-121.6	(1)	2.54	0.51	2699	19.37	12.59	5
				(2)	2.56	0.55	2873	20.28	11.68	18
				(3)	2.74	0.88	3399	25.60	6.36	80
		-108. 5		(1)	2.55	0.51	2682	19.49	12.47	4
				(2)	2.59	0.59	2904	20.65	11.31	13
				(3)	2.74	0.89	3342	25.66	6.30	80

[a] Energies, distances, vibrational frequencies and torsional angles are in kJ/mol, Å, cm^{-1} and degrees, respectively. Isotropic shielding constants and ^1H NMR chemical shifts are in ppm. ΔE^{Tot} = total interaction energy; ΔE^{sol} = solvation energy; $R_{O\text{-}O}$ = H-bond distance; Δd_{DA} = asymmetric stretching coordinate; ν^{OH} = asymmetric O-H stretching frequency; $\sigma_{H^+}^{corr}$ = isotopic shielding constant; $\delta_{H^+}^{corr}$ = ^1H NMR chemical shift; ω = torsional angle of H-bond; COSMO = continuum aqueous solution.

Table S4 Drifts in Energies and Velocity of the Exchanging Proton Obtained from NVT-BOMD Simulations on $H^+(H_3PO_4)_2$ at 298 K.[a]

A	δ_A	<A>	σ_A
E^{Tot}	0.0260	-1286.5103	0.0079
E^{Pot}	0.0698	-1286.5312	0.0049
E^{Kin}	0.0406	0.0208	0.0052
v^{H+}	0.1246	0.0012	0.0005
T	0.0407	292.4317	73.0601

[a] Energies and velocity are in atomic unit (au) and temperature in K. δ_A = drift of property A; <A> = average of property A; σ_A = SD of property A; E^{Tot} = total energy; E^{Pot} = potential energy; E^{Kin} = kinetic energy; v^{H+} = velocity of proton; T = temperature.

Table S5 Self-Diffusion Coefficients (D) of the Exchanging Proton Obtained from NVT-BOMD Simulations on $H^+(H_3PO_4)_2$ over the Temperature (T) Range of 298–430 K.[a]

T	D MSD§ ($\times 10^{-5}$)	T	D ^{1}H PFG-NMR* ($\times 10^{-5}$)
298	0.12	298	0.04
315	0.27	310	0.07
330	0.36	330	0.14
350	0.45	350	0.23
380	0.67	380	0.46
400	0.66	400	0.66
430	1.16	420	0.90

[a] D and T are in $cm^2\ s^{-1}$ and K, respectively. * = values taken from Ref. [11]; § = values obtained from the MSD plots.

Table S6 ^{1}H NMR Chemical Shifts, Line Widths and the Areas under the Lorentzian Peak Functions **A**, **A′** and **B** obtained from NVT-BOMD Simulations on $H^{+}(H_3PO_4)_2$ over the Temperature Range of 298–430 K.[a]

T	Peaks	$\delta^{corr,MD}_{H^+}$	$\Delta\delta^{corr,MD}_{H^+}$	I	ln (T_2^*)
298	**A**	19.78	0.36	16	13.68
	A′	19.19	0.58	8	13.19
	B	18.41	0.48	5	13.39
315	**A**	19.76	0.32	14	13.79
	A′	19.23	0.62	9	13.14
	B	17.96	1.32	7	13.28
330	**A**	19.91	0.15	6	14.54
	A′	19.46	0.63	13	13.12
	B	18.45	0.54	5	13.28
380	**A**	19.83	0.12	4	14.72
	A′	19.42	0.28	5	13.93
	B	18.85	1.37	15	12.35
400	**A**	19.66	0.20	5	14.24
	A′	19.42	0.07	2	15.31
	B	19.02	1.02	13	12.65
430	**A**	19.74	0.03	2	16.02
	A′	19.58	0.62	16	13.14
	B	18.65	1.13	7	13.47

[a] ^{1}H NMR chemical shift and line width are in ppm. The temperature and area are in K and arbitrary unit, respectively. $\delta^{corr,MD}_{H^+}$ = ^{1}H NMR chemical shift; $\Delta\delta^{corr,MD}_{H^+}$ = ^{1}H NMR line width; **A** and **A′** = oscillatory shuttling peaks; **B** = structural diffusion peak; T = temperature; I = area under the Lorentzian peak function.