Solvation energies of the proton in methanol revisited and generalized

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SUPPORTING INFORMATION:

KEYWORDS: Methanol clusters, Interaction energies, Solvation enthalpies, Solvation free energies, temperature effects.

1 Infrared Spectra of some isomers of methanol tetramer and pentamer

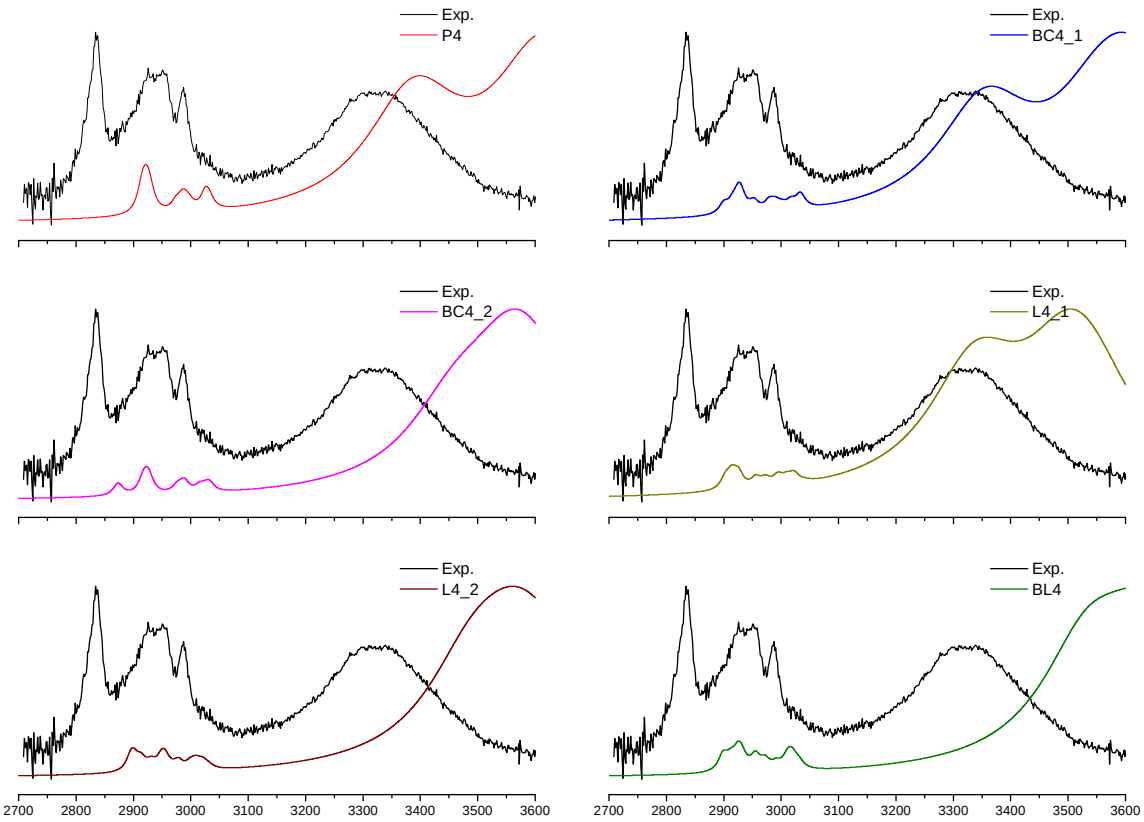

Fig. S 1 Infrared spectra of isomers of the methanol tetramer which are not participating in the population of the cluster based on our relative population analysis.

2 Temperature dependence dielectric constant of methanol

3 Supplementary structures of the protonated methanol clusters

4 Complete references of g09 and g16

Here are the complete references of g09[7] and g16[8].

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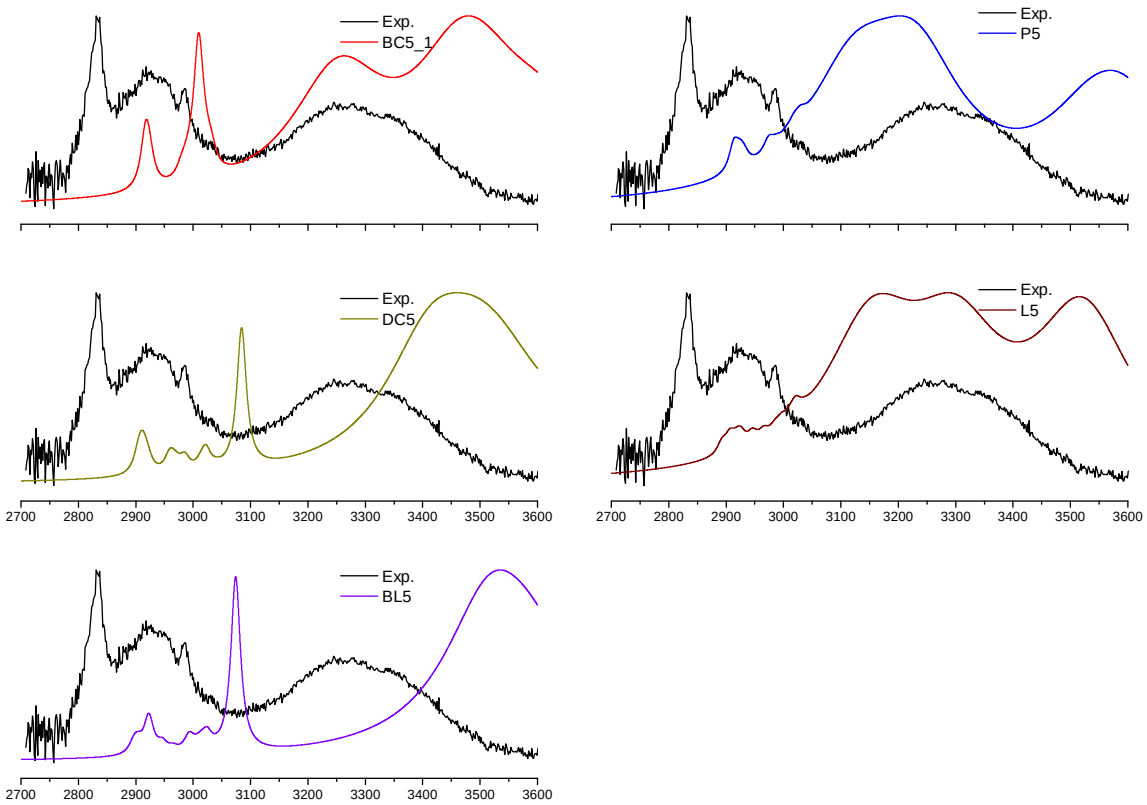

Fig. S 2 Infrared spectra of isomers of the methanol pentamer which are not participating in the population of the cluster based on our relative population analysis.

Table 1 Difference (in kJ mol^{-1}) between the solvation energies calculated at a fixed dielectric constant of $\varepsilon = 32.613$ and those calculated by changing the dielectric constant depending on the temperature.

T(K)	$\Delta\Delta H(H^+,T)$	$\Delta\Delta G(H^+,T)$
20	0.5	-0.5
40	1.7	-1.8
60	2.8	-3.7
80	3.8	-5.8
100	6.6	-4.0
120	7.0	-6.0
140	-2.3	-1.0
160	-2.1	-1.2
180	-1.9	-0.9
200	-1.6	-0.2
220	-1.4	-0.5
240	-1.1	-0.5
260	-0.7	-0.4
280	-0.3	-0.2
300	0.1	0.0
320	0.4	-0.1
340	0.5	1.7
360	0.7	2.1
380	0.7	2.2
400	0.5	2.1

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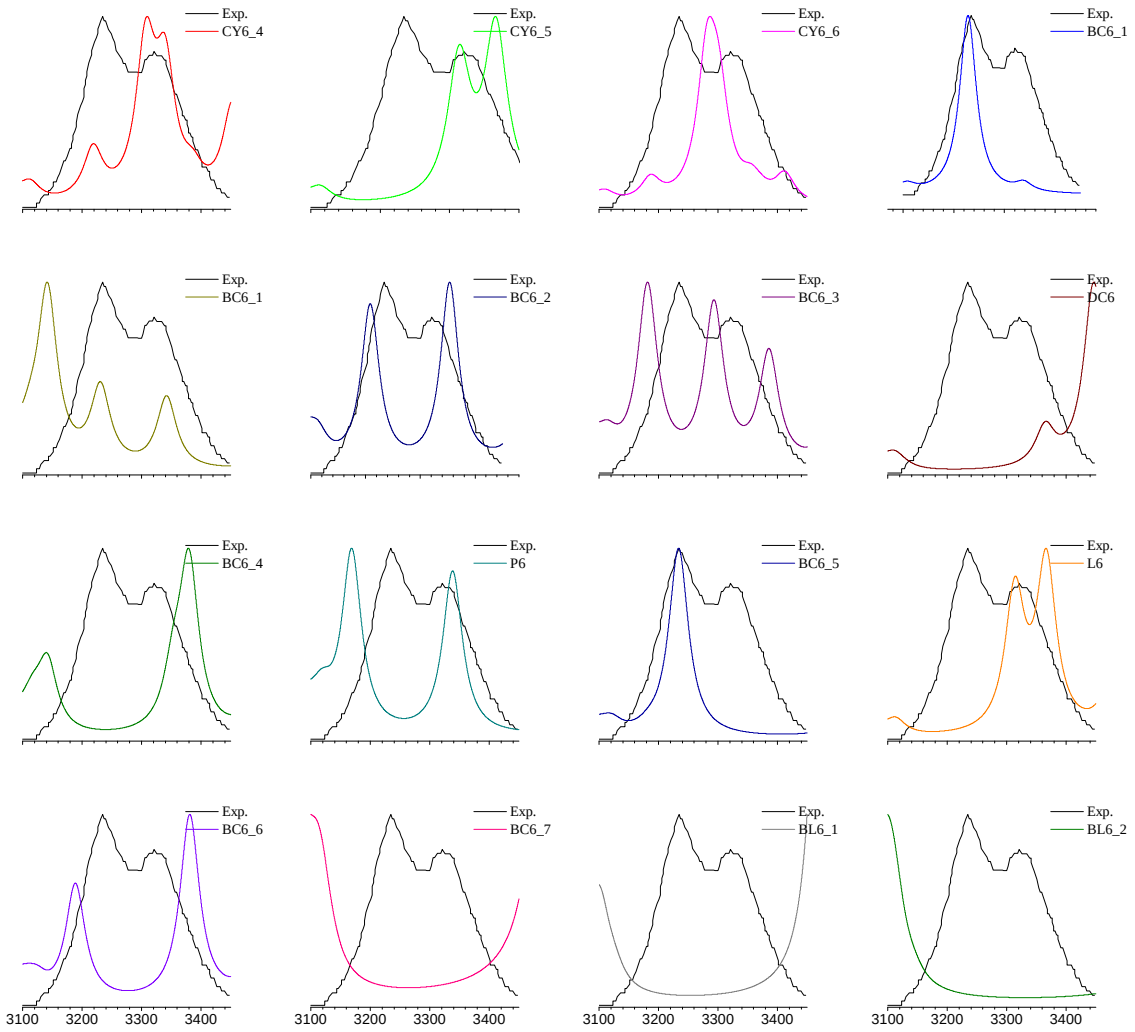

Fig. S 3 Infrared spectra of isomers of the methanol hexamer which are not participating in the population of the cluster based on our relative population analysis.

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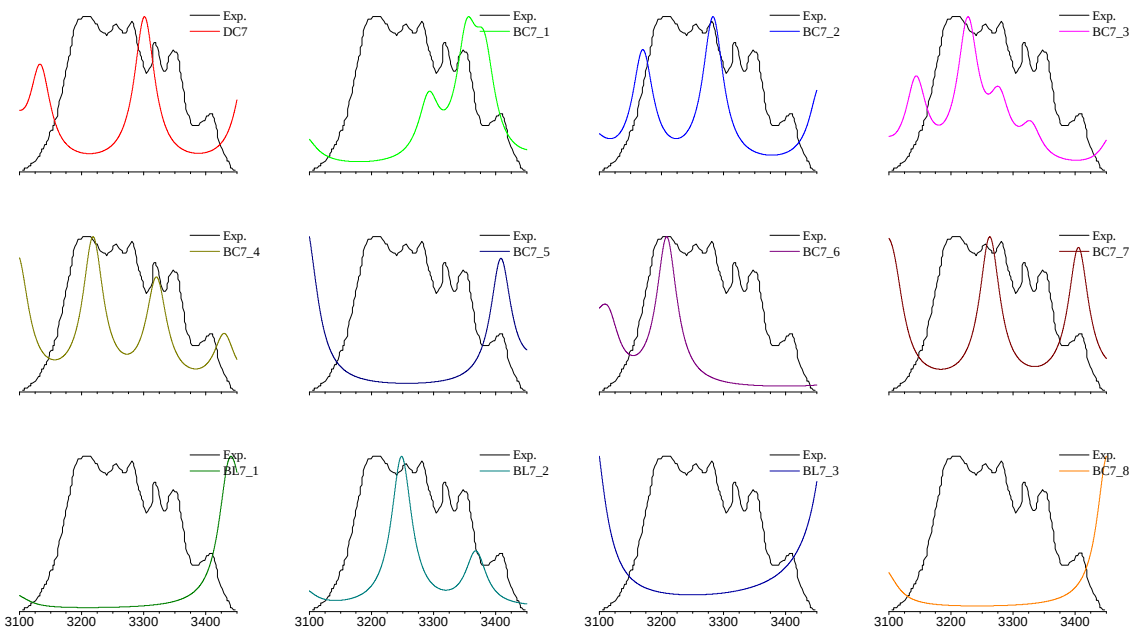

Fig. S 4 Infrared spectra of isomers of the methanol heptamer which are not participating in the population of the cluster based on our relative population analysis.

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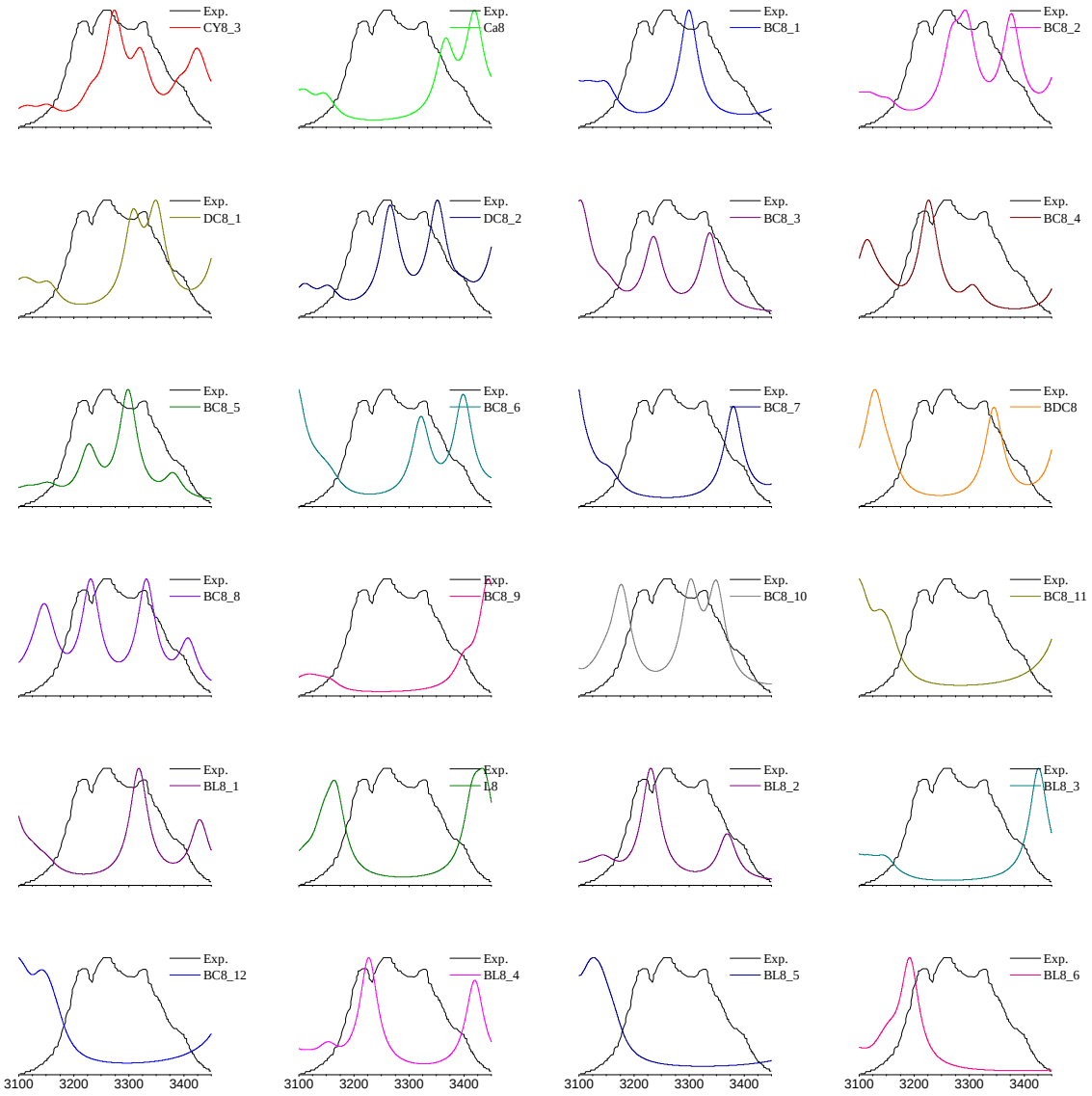

Fig. S 5 Infrared spectra of isomers of the methanol octamer which are not participating in the population of the cluster based on our relative population analysis.

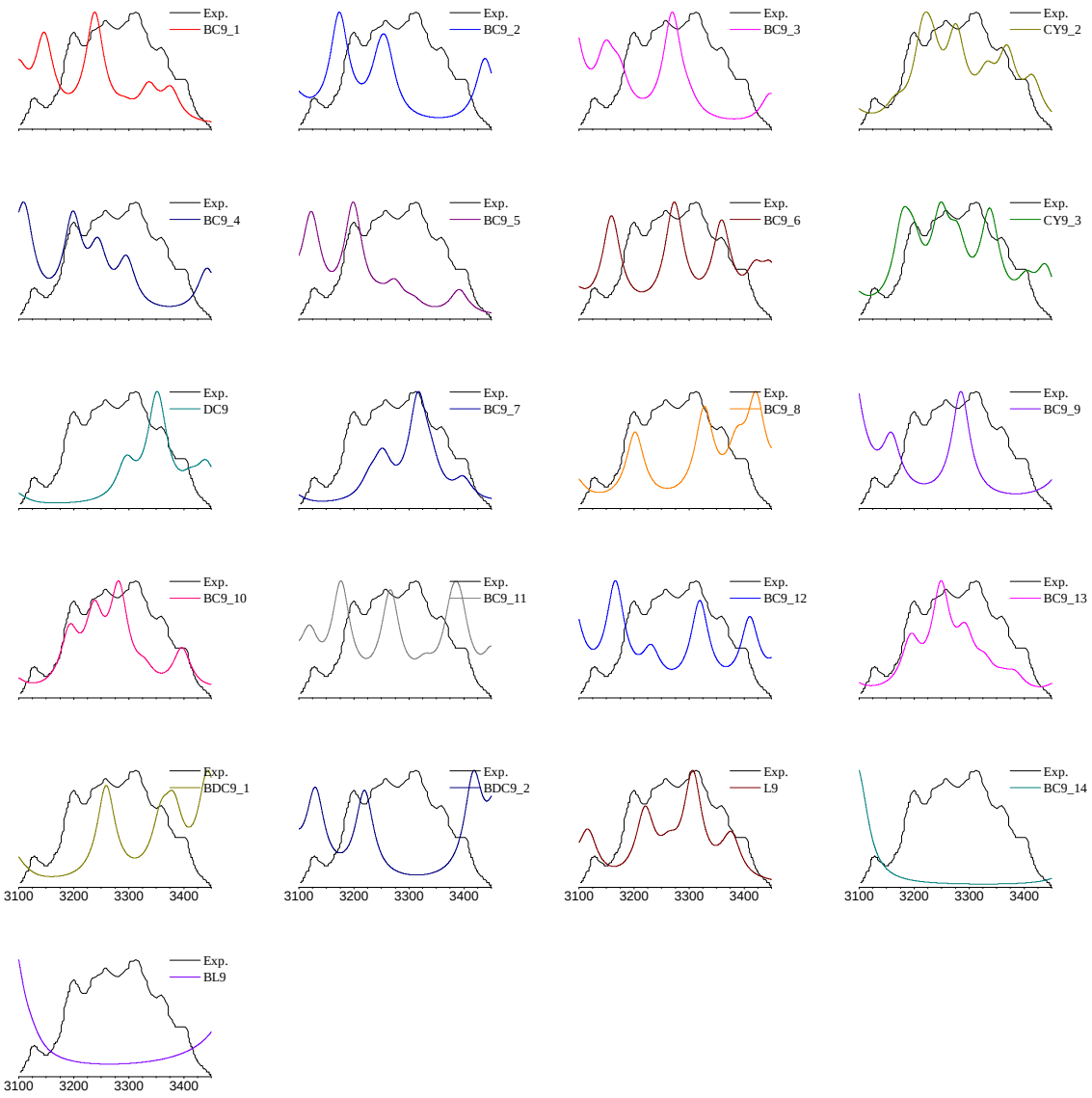

Fig. S 6 Infrared spectra of isomers of the methanol nonamer which are not participating in the population of the cluster based on our relative population analysis.

Table 2 Dielectric constant of methanol at different temperatures. Experimental data have been fitted to the following function $aT^2 + bT + c$, where the parameters (a, b, c) are optimized to $(0.001212, 0.905492, 194.715243)$. The root mean square error and the correlation between the fitted and the experimental data are 0.62 and 0.9979, respectively.

T(K)	Exp.	References	Fit of Exp.
176.60	73.08	[1]	72.60
180.70	70.91	[1]	70.66
182.00	70.52	[1]	70.06
190.90	65.64	[1]	66.02
193.50	65.10	[1]	64.88
204.60	59.85	[1]	60.18
212.30	56.51	[1]	57.10
223.10	52.50	[1]	53.02
232.70	49.19	[1]	49.63
250.60	43.52	[1]	43.91
260.00	40.85	[1]	41.21
262.00	40.48	[1]	40.67
274.20	37.68	[1]	37.55
279.50	36.45	[1]	36.30
283.15	35.65	[2]	35.49
288.00	34.00	[3]	34.45
288.15	34.00	[4]	34.42
288.15	35.53	[5]	34.42
293.15	33.45	[6]	33.42
293.15	33.71	[2]	33.42
293.15	33.95	[5]	33.42
294.20	33.42	[1]	33.21
298.00	33.10	[3]	32.50
298.15	33.05	[5]	32.47
298.15	33.10	[4]	32.47
303.15	31.62	[5]	31.59
303.15	31.71	[2]	31.59
308.00	32.12	[3]	30.79
308.15	30.08	[5]	30.77
308.15	32.12	[4]	30.77
313.15	28.20	[6]	30.00
313.15	29.98	[2]	30.00
318.00	28.44	[3]	29.32
318.15	28.44	[4]	29.30
318.15	29.54	[5]	29.30
323.15	28.24	[2]	28.66
323.15	28.53	[5]	28.66

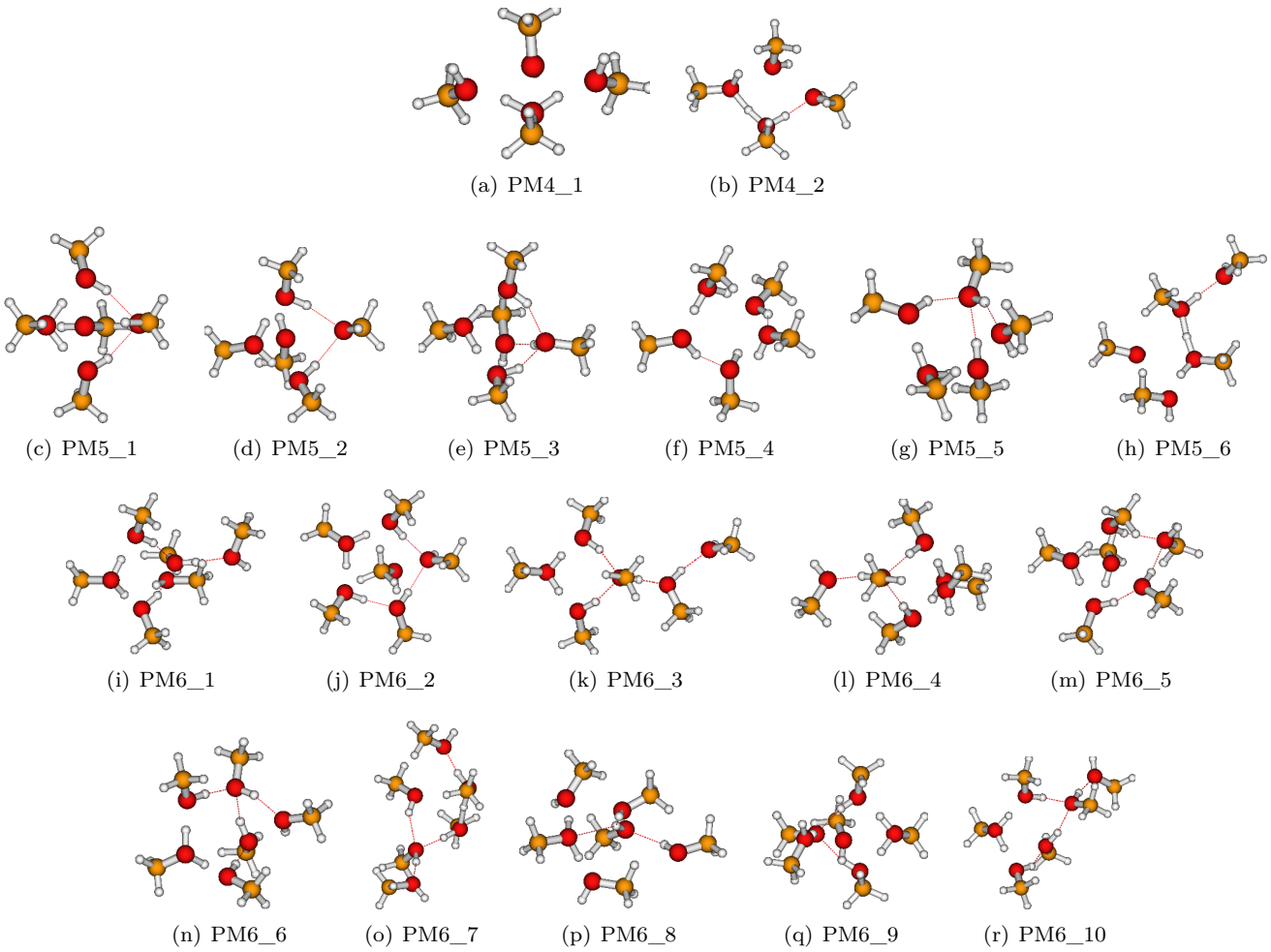

Fig. S 7 Optimized structures of some isomers of the protonated methanol tetramer, pentamer and hexamer.