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

Supporting Information

Ionization Energies in Solutions with QM:QM approach

Zsuzsanna Tóth, Jakub Kubečka, Eva Muchová, Petr Slavíček*

University of Chemistry and Technology Prague, Department of Physical Chemistry, Technická 5, 16628 Prague 6, Czech Republic

Table S1. The evolution of the calculated mean value of cytosine VIE and FWHM of the distribution with the size of the QM region. The data are presented for a simple electrostatic embedding scheme. SPC/E charges were used for water molecules. In the QM part, the BMK functional with 6-31+g was employed.*

		total size of the system (QM + MM)								
		100		200		400		600		
# water in QM	# samples	VIE	FWHM	VIE	FWHM	VIE	FWHM	# samples	VIE	FWHM
0	100	8.750±0.028	0.668±0.048	8.755±0.029	0.680±0.053	8.767±0.029	0.670±0.050	400	8.771±0.014	0.647±0.022
5	100	8.630±0.028	0.663±0.042	8.639±0.029	0.682±0.039	8.656±0.030	0.697±0.048	400	8.660±0.015	0.682±0.023
10	100	8.541±0.029	0.682±0.048	8.558±0.029	0.682±0.043	8.567±0.029	0.689±0.045	400	8.566±0.014	0.672±0.022
20	100	8.420±0.029	0.675±0.047	8.433±0.029	0.676±0.043	8.444±0.029	0.671±0.041	400	8.460±0.014	0.664±0.022
40	50	8.267±0.042	0.695±0.074	8.313±0.044	0.725±0.066	8.326±0.043	0.721±0.054	100	8.341±0.029	0.678±0.049
60	50	8.156±0.046	0.768±0.080	8.262±0.044	0.740±0.049	8.274±0.044	0.733±0.056	50	8.314±0.043	0.716±0.056

Table S2. Calculated mean values of the VIE for clusters of cytosine and water. The system contained altogether 400 water molecules, from 5 to 40 water molecules explicitly calculated at the BMK and PBE/6-31+g levels, the remaining molecules were represented by SPC/E water charges. Data presented in the table were obtained for a cluster cut from a box simulation.*

	BMK			PBE		
# water in QM	*VIE*	Q^0(cyt)	Q^+(cyt)	*VIE*	Q^0(cyt)	Q^+(cyt)
5	8.656±0.030	0.102±0.005	0.996±0.006	8.098±0.027	0.114±0.006	0.733±0.008
10	8.567±0.029	0.155±0.008	0.983±0.009	7.894±0.025	0.175±0.008	0.642±0.009
20	8.444±0.029	0.187±0.010	0.952±0.011	7.635±0.023	0.213±0.011	0.552±0.012
40	8.326±0.043	0.146±0.015	0.914±0.014	7.344±0.034	0.156±0.016	0.423±0.019

Table S3. VIE of cytosine within the QM:QM model as a function of an increasing system size. We consider either 0 (QM0) or 5 (QM5) water molecules together with cytosine in the QM fragment. In the QM:QM scheme, the BMK functional with the 6-31+g basis set was used. The results are presented for clusters obtained either from classical simulations of a given cluster size in vacuo (S1), or for clusters obtained by cutting from a large box simulation (S2). The results were averaged over 400 samples.*

#water	S1, QM0		S1, QM5		S2, QM0	
	VIE	FWHM	VIE	FWHM	VIE	FWHM
0	8.736±0.001	0.033±0.004	-	-	8.732±0.008	0.395±0.031
50	8.588±0.019	0.893±0.037	8.556±0.018	0.865±0.036	8.490±0.016	0.737±0.025
100	8.529±0.025	1.188±0.047	8.495±0.025	1.162±0.046	8.399±0.014	0.671±0.023
200	8.459±0.019	0.899±0.041	8.427±0.019	0.879±0.040	8.344±0.014	0.677±0.023
400	8.367±0.015	0.724±0.023	8.336±0.015	0.698±0.026	8.290±0.015	0.688±0.024
600	8.368±0.015	0.713±0.023	8.344±0.015	0.697±0.022	8.274±0.014	0.680±0.022

Table S4. Statistical convergence of VIE with the number of samples. Simulation for clusters in vacuo, QM:QM scheme, BMK functional with 6-31+g basis set.*

#water	0	50	100	200	400	600
#sample						
100	8.737±0.002	8.564±0.030	8.525±0.048	8.441±0.035	8.373±0.029	8.377±0.028
200	8.736±0.001	8.574±0.024	8.504±0.0344	8.476±0.027	8.372±0.021	8.393±0.021
300	8.736±0.001	8.576±0.021	8.537±0.029	8.470±0.022	8.370±0.018	8.372±0.018
400	8.735±0.001	8.588±0.019	8.529±0.025	8.459±0.019	8.367±0.015	8.368±0.015
500	8.736±0.001	8.580±0.017	8.535±0.023	8.459±0.017	8.372±0.014	8.378±0.014

Table S5. Statistical convergence of the FWHM with the number of samples. Simulation for clusters in vacuo, QM:QM scheme, BMK functional with 6-31+g basis set.*

#water	0	50	100	200	400	600
#sample						
100	0.034±0.007	0.707±0.052	1.119±0.084	0.830±0.060	0.689±0.046	0.660±0.043
200	0.029±0.005	0.816±0.047	1.147±0.060	0.894±0.047	0.691±0.031	0.687±0.029
300	0.028±0.003	0.867±0.043	1.168±0.049	0.894±0.044	0.713±0.031	0.715±0.025
400	0.034±0.004	0.893±0.037	1.188±0.047	0.899±0.041	0.710±0.026	0.713±0.023
500	0.035±0.004	0.912±0.033	1.183±0.043	0.917±0.037	0.724±0.023	0.718±0.021