Electronic Supplementary Information

Ab Initio Molecular Dynamics Study of Solvated Electrons in Methanol Clusters

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Table S1. VDE values of $(CH_3OH)_n^-$ methanol cluster anions at $t = 0$ of the dynamics. These clusters were carved out from $n = 128$ interior state cluster configurations of our previous QCMD simulations.[1] VDEs are computed at the BHandHLYP/GPW+aug-MOLOPT-TZVP level of theory. The values in parenthesis are MP2/6-31(1+3+)G(d) values of our previous study.[2]

Configuration	*VDE* / meV		
	$n = 8$	$n = 16$	$n = 32$
1	697 (662)	1215	1100
2	524 (470)	1200	989
3	511 (455)	1330	1231
4	668 (636)	1065	1348
5	691 (658)	1328	1462
6	630 (585)	1290	1667
7	428 (378)	1295	1490
8	534 (487)	1424	1743
9	988 (963)	1778	1909
10	994 (963)	1927	1918

Table S2. VDE values of $(CH_3OH)_8^-$ surface state clusters taken from the present AIMD trajectories. The configurations were selected to have VDE values greater than ~150 meV. BHandHLYP/GPW+aug-MOLOPT-TZVP values were calculated with the dual basis representation (see the Methods section), while BHandHLYP/6-31(1+3+)G(d) and MP2/6-31(1+3+)G(d) were calculated using atom centered basis sets.

Configuration	*VDE* / meV		
	BHandHLYP/ GPW+aug-MOLOPT-TZVP	BHandHLYP / 6-31(1+3+)G(d)	MP2/ 6-31(1+3+)G(d)
1	249	384	209
2	180	317	172
3	225	326	139
4	446	505	232
5	410	479	238
6	304	387	177
7	270	351	124
8	354	447	234
9	327	412	207
10	200	305	131

Figure S1. A correlation diagram for the VDE values of 100 selected configurations of interior state $(CH_3OH)_8^-$ clusters. The diagram compares VDE values computed with the MP2/6-31(1+3+)G(d) and the BHandHLYP/GPW+aug-MOLOPT-TZVP models. The strong correlation is evident.

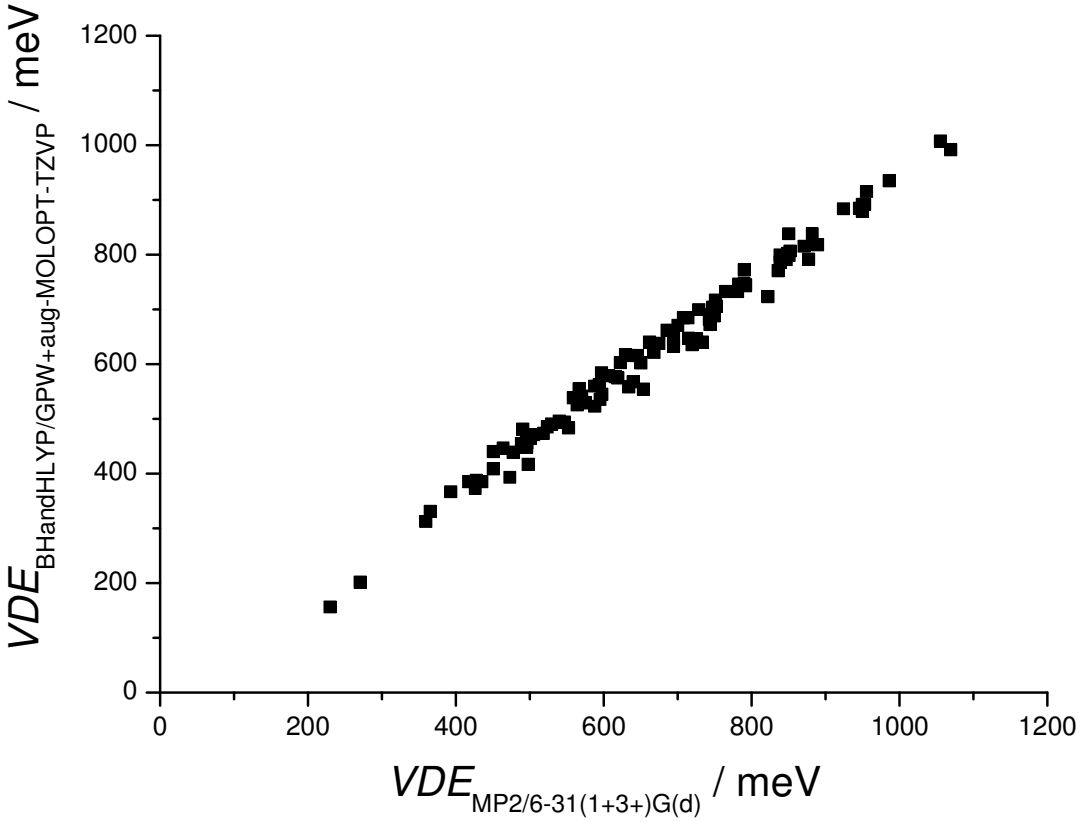


Figure S2. Four snapshots of a typical trajectory of methanol cluster anions with n = 8 molecules at t = 0 ps, 1 ps, 1.8 ps and 5 ps. The excess electron starts the dynamics from a preformed cavity state and ends up in a surface state. The cluster structure breaks to smaller clusters. The shrinking spin density volumes surrounded by the same isosurface values indicate more diffuse electron distribution from the top to the bottom.

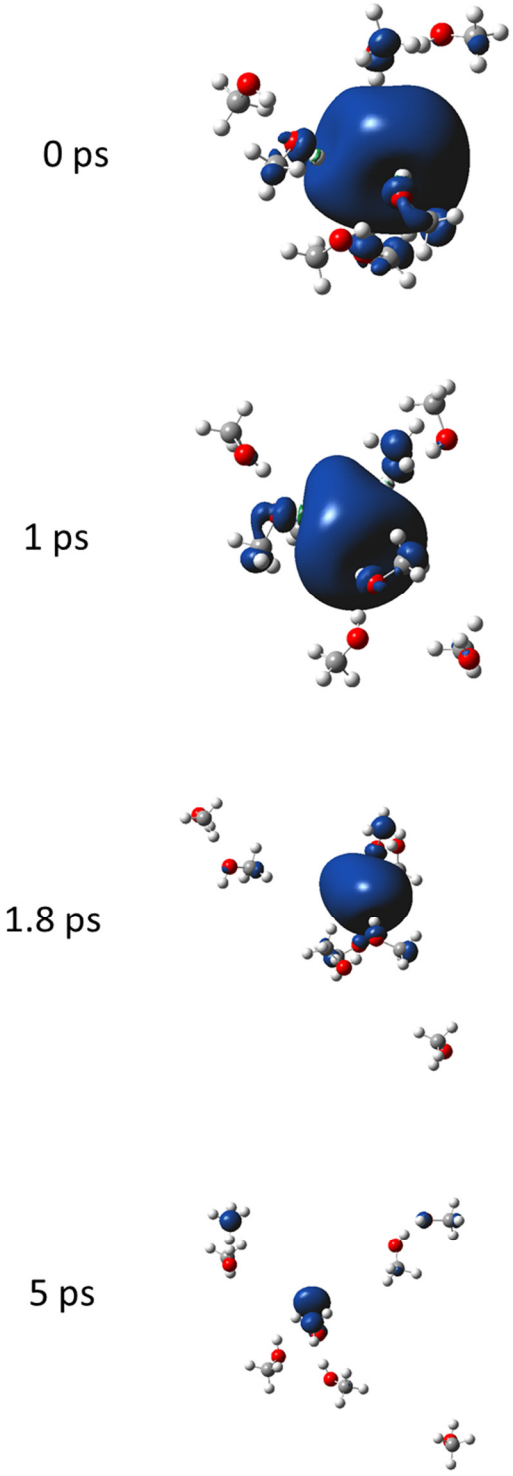


Figure S3. The time evolution of the VDE of methanol cluster anions with n = 8 molecules. The excess electron starts the dynamics from a preformed cavity state and ends up in a surface state.

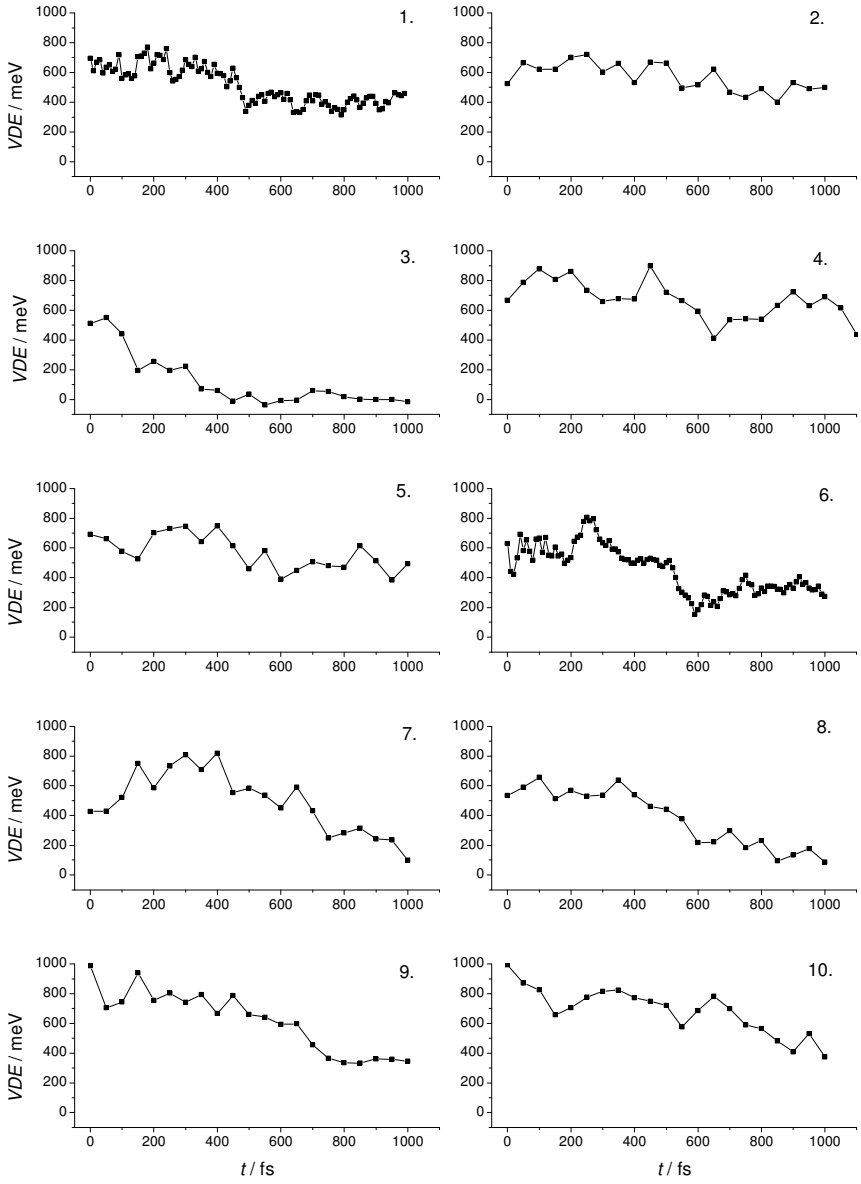


Figure S4. The time evolution of the VDE of methanol cluster anions with n = 16 molecules. The excess electron starts the dynamics from a preformed cavity state.

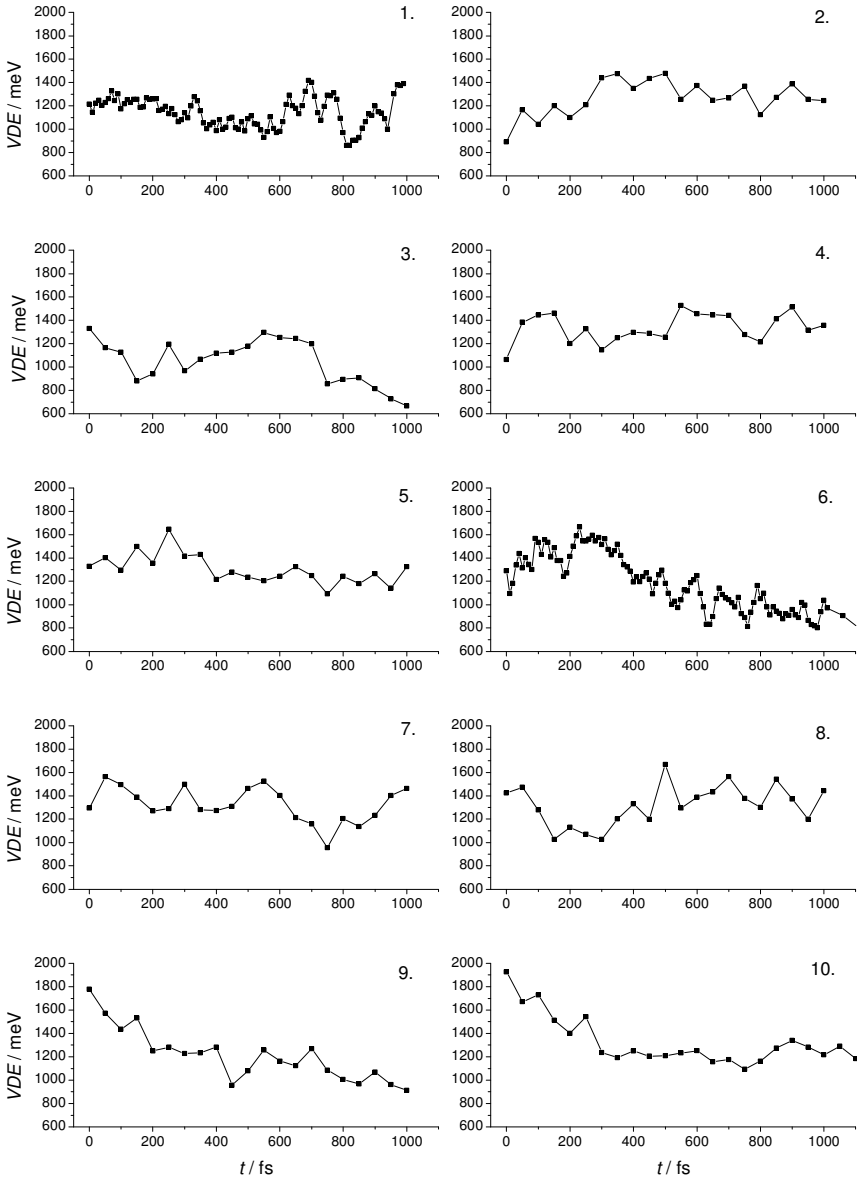


Figure S5. The time evolution of the VDE of a methanol cluster anion with n = 16 molecules for a 10 ps long trajectory (see Trajectory #10 in Figure S4). The excess electron starts the dynamics from a preformed interior state and ends up in a surface state, although still partly embedded in the interior. The initial and the final structures of the dynamics are also shown.

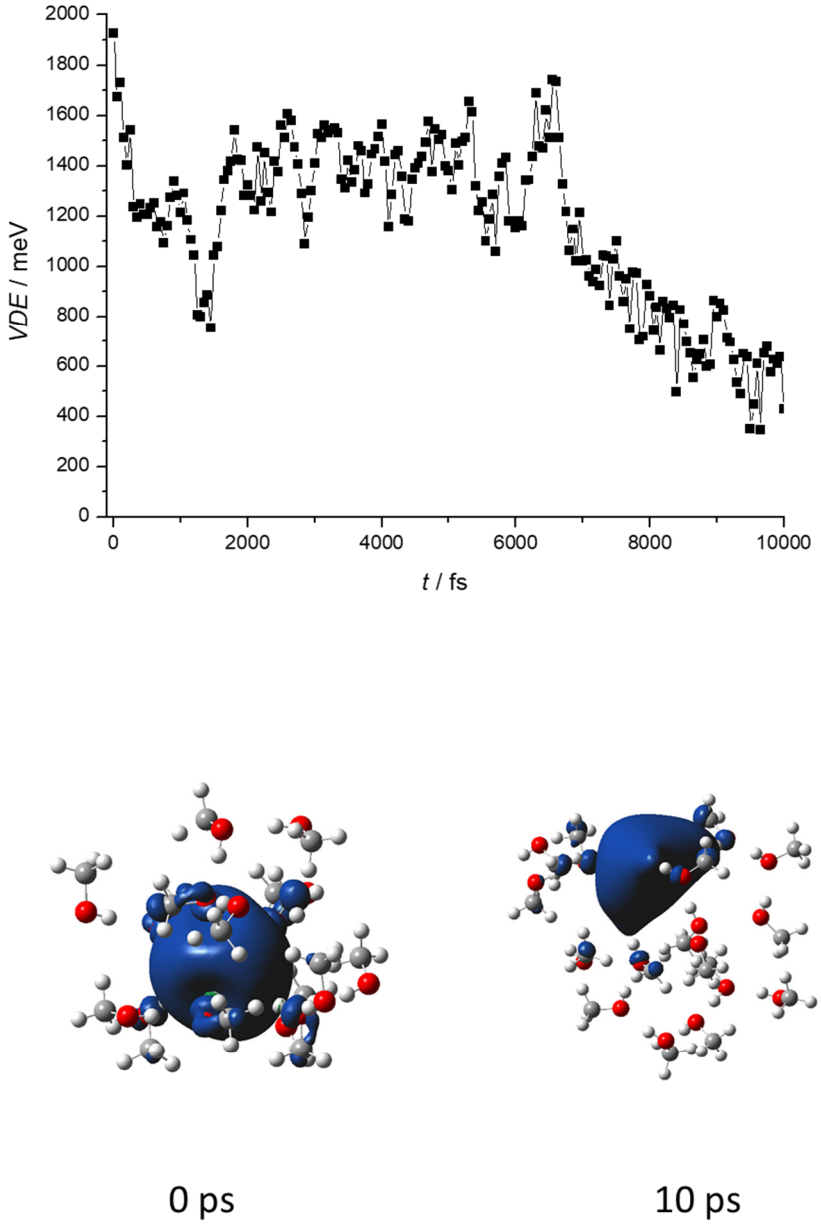
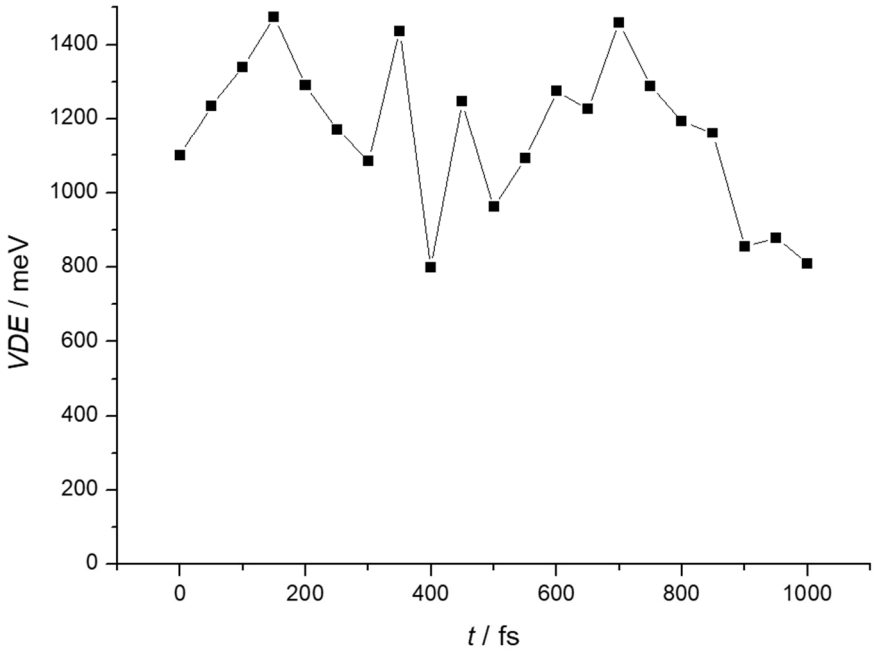
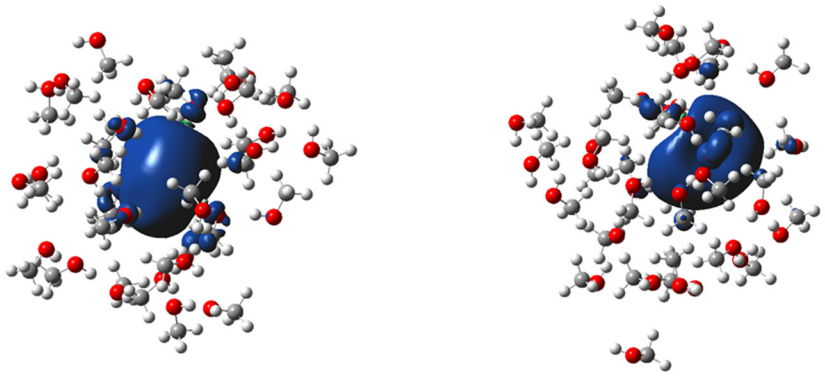


Figure S6. The time evolution of the VDE of a methanol cluster anion with n = 32 molecules for a 1 ps long trajectory. The excess electron starts the dynamics from a preformed interior state and remains in an interior state, although clearly displaced toward the surface. The initial and the final structures of the dynamics are also shown.





0 ps 1 ps

Figure S7. The time evolution of the VDE of methanol cluster anions with n = 8 molecules. The excess electron starts the dynamics from a preformed surface state and ends up in a surface state.

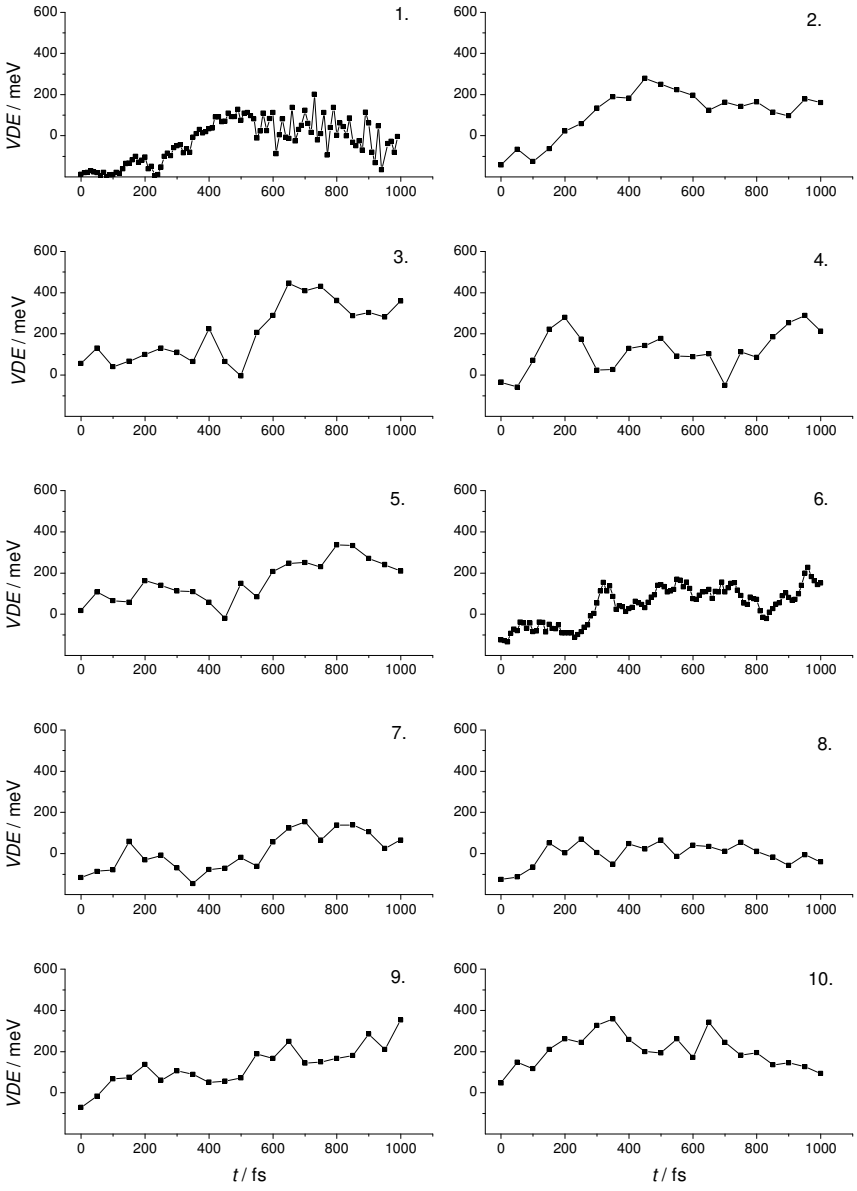


Figure S8. The time evolution of the VDE of methanol cluster anions with n = 16 molecules. The excess electron starts the dynamics from a preformed surface state and ends up in a surface state.

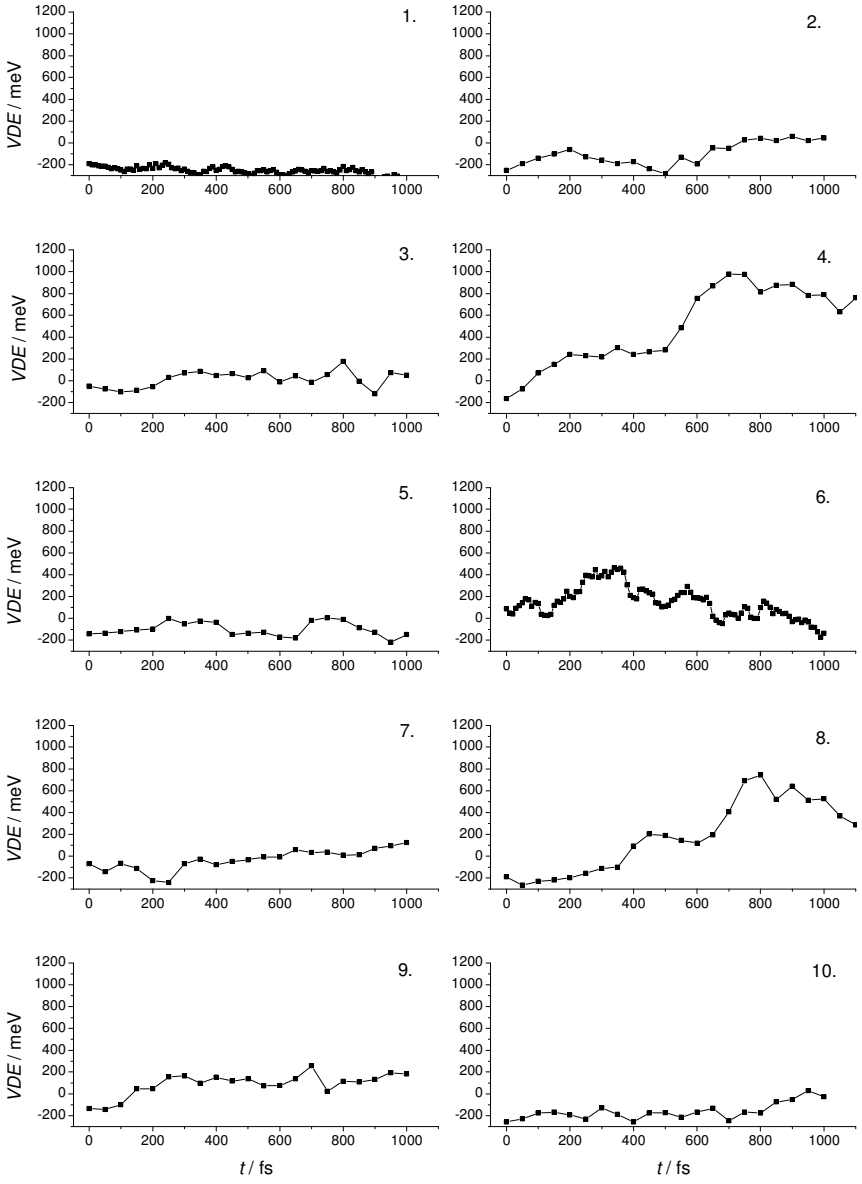
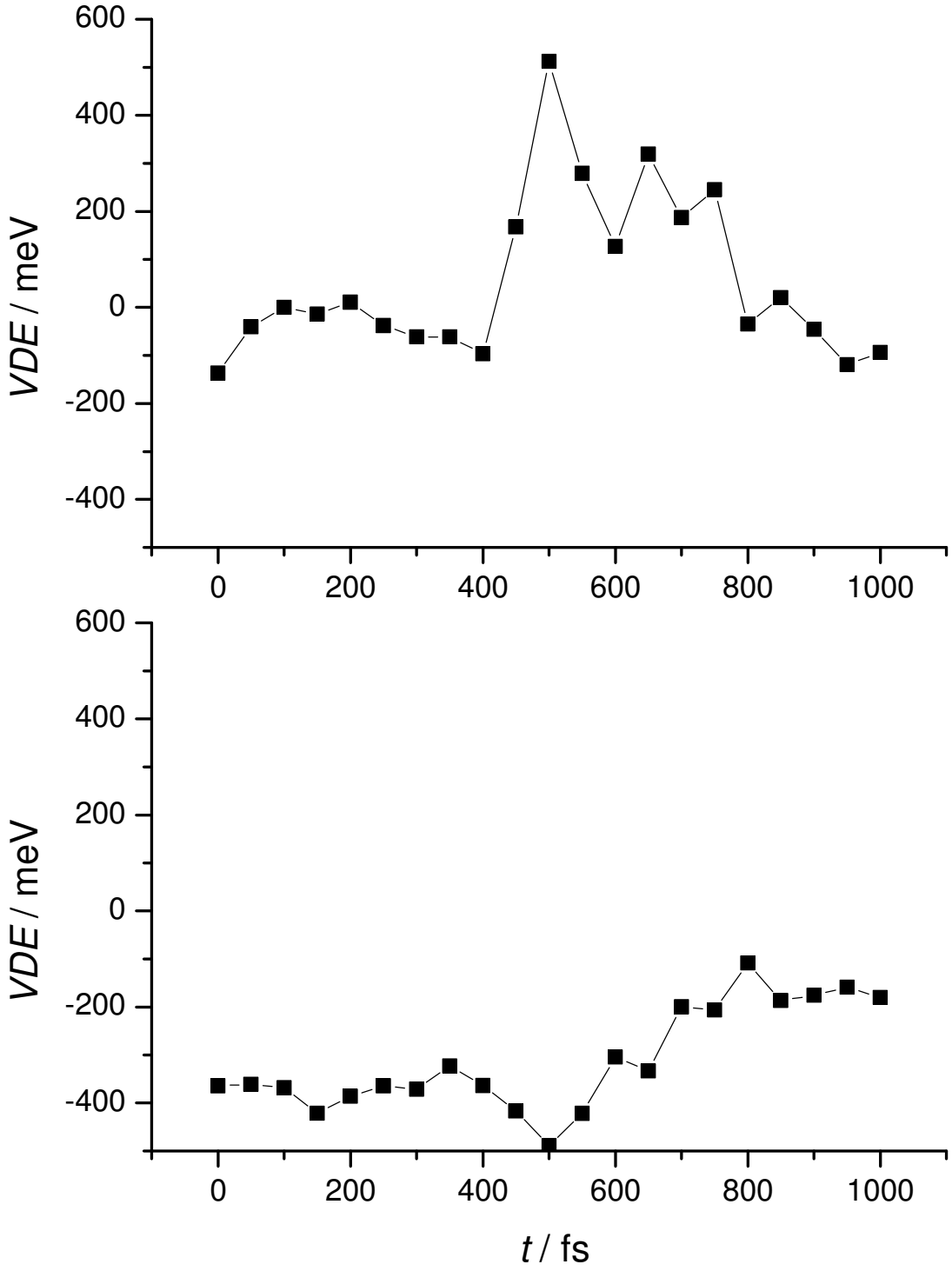


Figure S9. The time evolution of the VDE of a methanol cluster anion with $n = 32$ molecules. The excess electron starts the dynamics from a preformed surface state and ends up in a surface state.



References

[1] L. Mones, P. J. Rossky and L. Turi, *J. Chem. Phys.*, 2011, **135**, 084501.

[2] G. Pohl, L. Mones and L. Turi, *J. Chem. Phys.*, 2016, **145**, 164313.