Supplementary materials

Computational study of the post-transition state dynamics for the OH + CH_3OH reaction probed by photodetachment of the $CH_3O^-(H_2O)$ anion

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S1 Figures and Tables for the supporting information

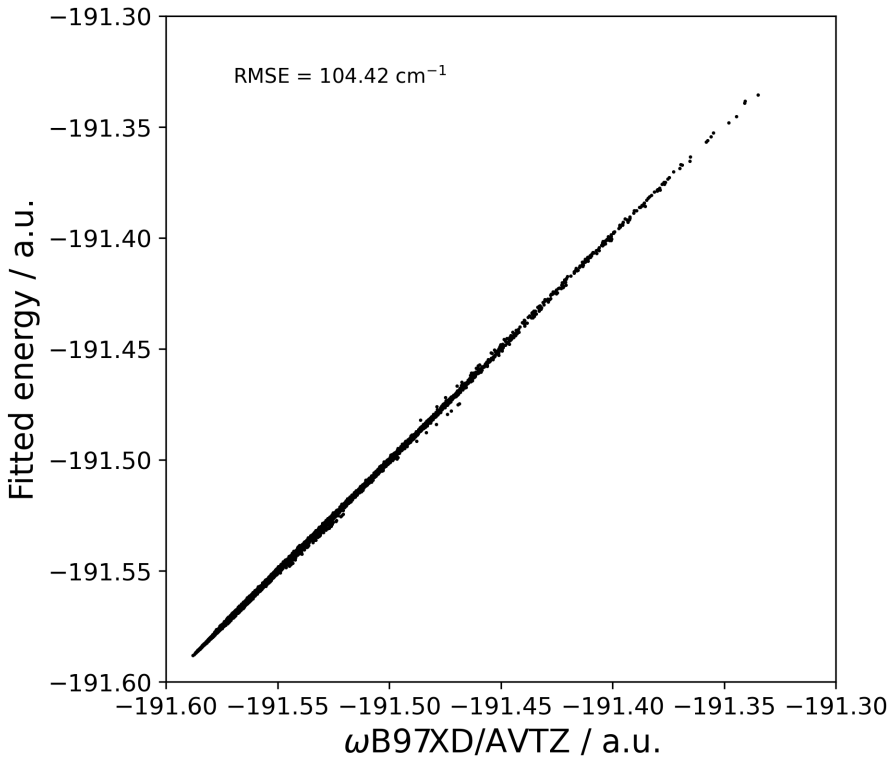

Figure S1: The potential energy fitted with respect to ωB97XD/AVTZ energy

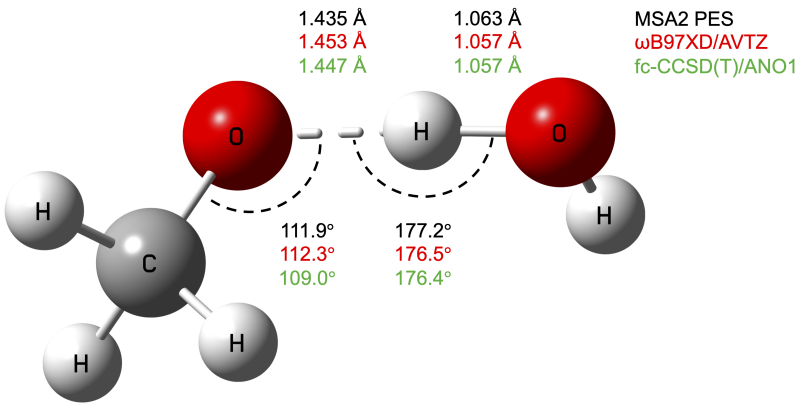

Figure S2: Comparison of the equilibrium geometry of the $CH_3O^-(H_2O)$ anion. The geometric parameters in black, red, blue, and green correspond to the fitted PES, ωB97XD/aug-cc-pVTZ(AVTZ) outcomes, and the CCSD(T) results taken from Ref. 11, respectively.

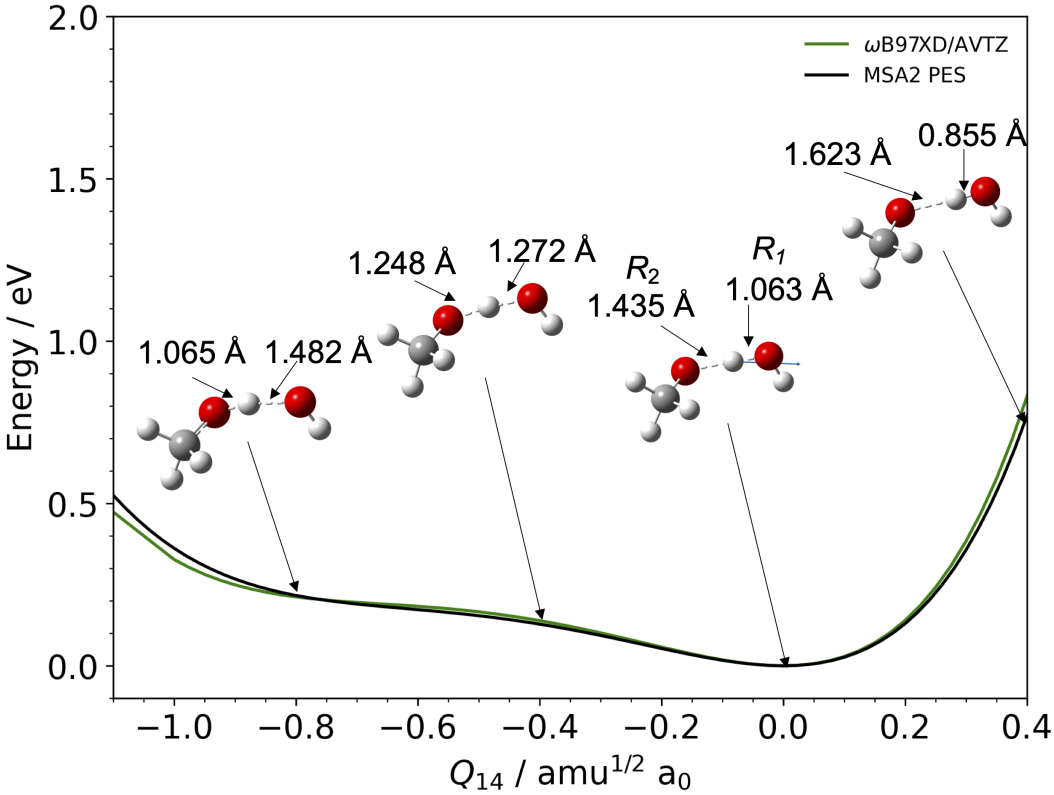

Figure S3: Potential energy curves of the MSA2 PES(black line) and the ωB97XD/aug-cc-pVTZ(AVTZ) PES (green line) along hydrogen transfer mode, Q_{14}

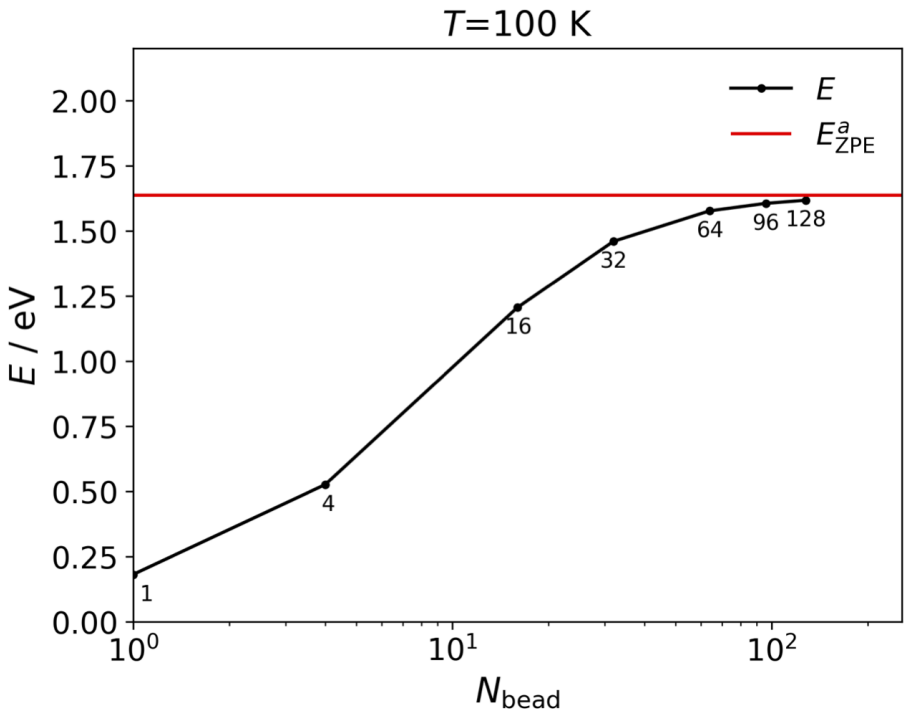

Figure S4: Convergence analysis of the number of beads at the temperature $T = 100$ K. Here, E denotes the internal energy of the anion system, while E^a_{ZPE} represents the zero-point vibrational energy.

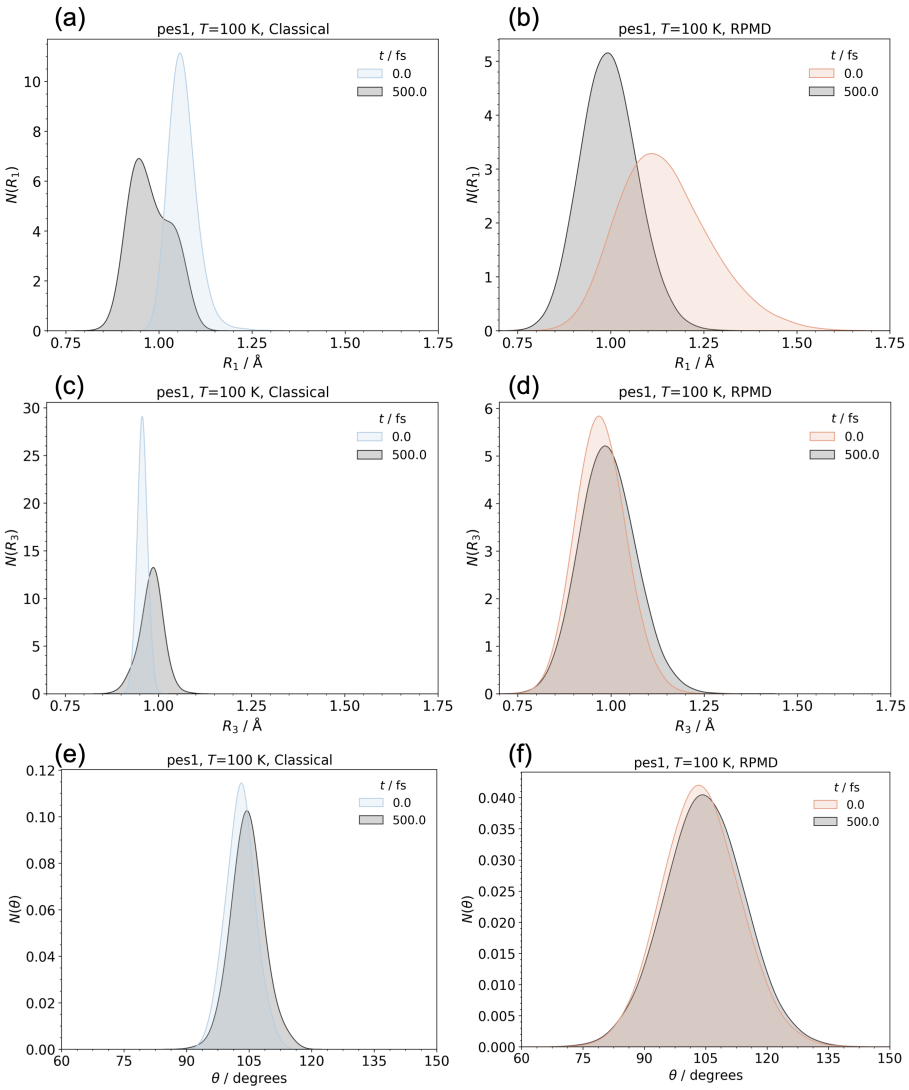

Figure S5: Time-dependent probability densities of (a) R_1, (c) R_3, and (e) θ at t=0 and 500 fs for classical MD, and (b) R_1, (d) R_3, and (f) θ at t=0 and 500 fs for RPMD on PES1.

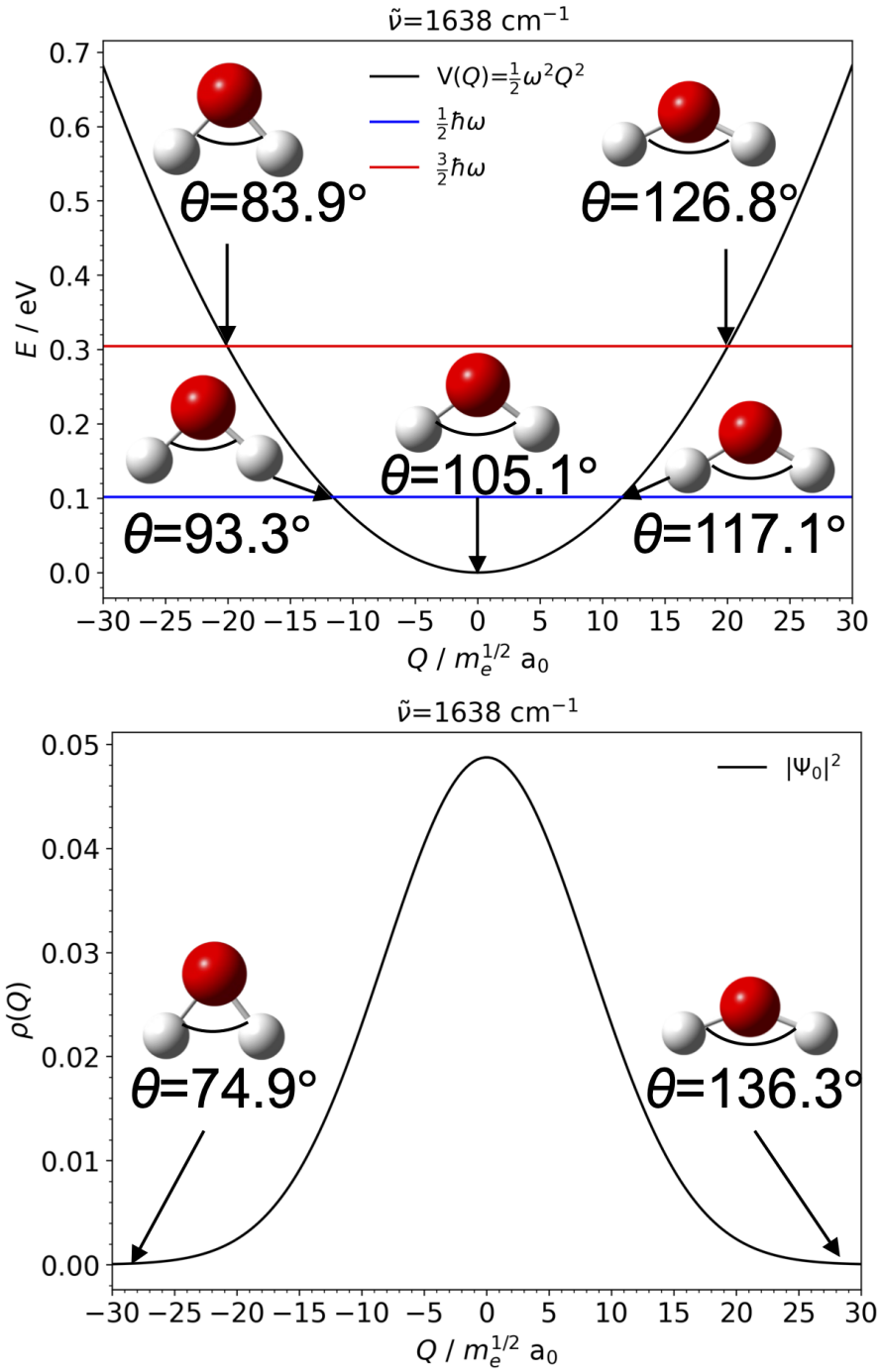

Figure S6: Harmonic potential curve (upper panel) and probability density of the zero-point wave function $|\Psi_0|^2$ for bending motion computed using the ωB97XD/aug-cc-pVTZ level of theory (lower panel), with bending angles at key geometries

Table S1: Relative energies (in eV) for the $CH_3O^-(H_2O)$ anion equilibrium structure, $CH_3OH + OH^-$ and $CH_3O^- + H_2O$ fragments calculated by the ωB97XD/AVTZ and the mHEAT-345(Q) methods. The latter is based on the high-accuracy extrapolated *ab initio* thermochemistry (HEAT) model, as used in Ref. 11. The potential energy of the equilibrium structure is set to zero.

method	$CH_3OH + OH^-$	$CH_3O^-(H_2O)$	$CH_3O^- + H_2O$
ωB97XD	1.363	0.000	1.071
mHEAT-345(Q)	1.35	0.00	1.00

Table S2: Comparison of harmonic vibrational frequencies (in cm^{-1}) for the equilibrium structure of the $CH_3O^-(H_2O)$ anion, computed using the fitted MSA2 PES function, ωB97XD/AVTZ, and fc-CCSD(T)/ANO1 as reported in Ref. 11

$\tilde{\nu}_\alpha$	MSA2 PES	ωB97XD	CCSD(T)
$\tilde{\nu}_1$	54.3	43.8	76.5
$\tilde{\nu}_2$	92.1	111.2	106.6
$\tilde{\nu}_3$	141.7	146.7	149.8
$\tilde{\nu}_4$	350.5	350.6	379.7
$\tilde{\nu}_5$	603.0	559.9	567.4
$\tilde{\nu}_6$	1151.5	1153.5	1144.0
$\tilde{\nu}_7$	1176.3	1177.9	1184.7
$\tilde{\nu}_8$	1181.2	1181.2	1186.8
$\tilde{\nu}_9$	1313.7	1278.0	1325.7
$\tilde{\nu}_{10}$	1459.6	1460.4	1469.0
$\tilde{\nu}_{11}$	1474.2	1470.3	1484.6
$\tilde{\nu}_{12}$	1480.3	1477.9	1494.8
$\tilde{\nu}_{13}$	1697.0	1679.1	1721.2
$\tilde{\nu}_{14}$	2030.3	2112.0	2179.2
$\tilde{\nu}_{15}$	2717.9	2706.9	2708.5
$\tilde{\nu}_{16}$	2748.3	2736.2	2738.1
$\tilde{\nu}_{17}$	2784.2	2776.5	2782.3
$\tilde{\nu}_{18}$	3939.9	3932.4	3869.2

Table S3: Optimized geometry (in xyz format) of the $CH_3O^-(H_2O)$ anion obtained using the MSA2 PES function

```
    8
MSA2 PES
H        -2.06358100    0.38414200    0.90022100
H        -0.93682300    1.35061100   -0.06453600
H        -2.11364200    0.29976900   -0.86560200
H         2.04306600    0.28843500    0.81841600
H         0.84208400   -0.20543700   -0.08078600
C        -1.40351100    0.33828300   -0.00231300
O        -0.50829600   -0.67897500    0.02020700
O         1.83954100    0.16057300   -0.10693700
```

Table S4: Optimized geometry (xyz format) of the $CH_3O^-(H_2O)$ anion calculated by the ωB97XD/AVTZ level

```
    8
wB97XD/AVTZ
C        -1.413488    0.334595    0.002951
O        -0.510128   -0.674738    0.010885
H        -2.151495    0.289333    0.842552
H        -0.958214    1.351600    0.079158
H        -2.045405    0.377341   -0.919978
H         0.855910   -0.191656   -0.093030
O         1.849097    0.169213   -0.104796
H         2.068378    0.210020    0.824882
```

Table S5: Optimized geometry (in xyz format) of the TS structure obtained from calculations using PES1

```
8
PES1 TS
C          -1.521974183487          -0.281836043022           0.000014212562
O          -0.384039621394           0.569809798126          -0.000043119817
H          -2.436900051327           0.307785505085           0.000827286400
H          -1.518949370792          -0.916935219470          -0.883999696368
H          -1.518051930528          -0.917730097457           0.883391078140
H           0.697939310835           0.221379086905          -0.000178673717
O           1.878117292047          -0.065758580358          -0.000318570178
H           1.955202554646          -1.035903449809           0.000287482978
```

Table S6: Optimized geometry (in xyz format) of the RC structure obtained from calculations using PES1

```
8
PES1 RC
C          -2.060474609404          -0.208374488638          -0.001225384932
O          -0.883601392144           0.587853332970          -0.005805404687
H          -2.946720685445           0.424428653558          -0.015810301564
H          -2.083234173041          -0.856738937206          -0.876019979427
H          -2.093836093060          -0.830609344396           0.891946821107
H          -0.041941582257           0.127757780296           0.006282285329
O           2.925500895811          -0.227156281087           0.005657302264
H           1.975498459490          -0.020785212240           0.005466635479
```

Table S7: Optimized geometry (in xyz format) of the PC structure obtained from calculations using PES1

```
8
PES1 PC
C          -2.296073114156           0.137648880576          -0.033906780875
O          -0.919139033148           0.107242536099           0.074211607198
H          -2.589459749023           0.501717104649          -1.009121270912
H          -2.706547592957          -0.853805983479           0.100955790045
H          -2.718547569102           0.789935920896           0.718144371674
H           3.293513683933          -0.534328473741          -0.264930043893
O           2.963819835459          -0.068245370524           0.521647846473
H           2.000291183862          -0.024340768648           0.397236884644
```

Table S8: Optimized geometry (in xyz format) of the TS structure obtained from calculations using PES2

```
8
PES2 TS
C          -1.416748129657          -0.284225659340          -0.060221351227
O          -0.313991127701           0.053226519467           0.766862521567
H          -2.248638927592           0.338443343701           0.272796498686
H          -1.195215486678          -0.062161191832          -1.104360866585
H          -1.667646646501          -1.332779391054           0.033735985540
H           0.624090904851          -0.595583446566           0.539999801373
O           1.600238877906          -0.596979043701          -0.205762621176
H           1.769254535375           0.360869869328          -0.243069968180
```

Table S9: Optimized geometry (in xyz format) of the RC structure obtained from calculations using PES2

```
8
PES2 RC
C          -1.832271739778          -0.014983016841           0.369198571322
O          -0.458400947439          -0.333422253350           0.194588088859
H          -2.079271895168           0.810715878744          -0.290104775768
H          -2.438128727461          -0.882009183468           0.120327653608
H          -1.997894971934           0.277434622940           1.397475623130
H          -0.229678929765          -1.056190792971           0.750356036480
O           2.229230345183          -0.429503536257          -0.100461857624
H           1.283724944924          -0.168548588597          -0.180771533557
```

Table S10: Optimized geometry (in xyz format) of the PC structure obtained from calculations using PES2

```
8
PES2 PC
C          -0.750386086034          -0.273466094211           0.317323945512
O          -1.600819920314           0.430927836592           1.060816865367
H          -0.999789076573          -0.238054130085          -0.745729250406
H           0.303419750104           0.103362354742           0.461976627968
H          -0.794762710336          -1.364073113146           0.633655183661
H           1.237597011336          -0.883442282662          -0.354411311432
O           2.071177274127          -0.810481547796          -0.769132438502
H           2.549893378220          -1.643070262896          -0.715937892471
```