

Supporting Information for

Dissociative photodetachment of H_3O_2^- : a full-dimensional quantum dynamics study

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SI. Anion potential energy surface

The *ab initio* method, the sampling scheme, and the fitting (or interpolation) tool are the pivotal factors in developing accurate PES. To keep consistent with the neutral PES, the *ab initio* method employed here is the same as for the neutral PES, *i.e.* the energies of all sampled points are calculated at the level of FC-UCCSD(T)-F12a/aug-cc-pVTZ,¹⁻² implemented by the software MOLPRO 2012. 1.³ FC denotes “frozen-core” treatment in the post-Hartree–Fock calculations.

The sampling scheme is as follows: the Atom Centered Density Matrix Propagation molecular dynamics is first performed by Gaussian 09, Revision E.01⁴ at the level of B3LYP/6-311G* to sample the first batch of data points. A raw PES is then generated by fitting these data points. Batches of quasiclassical trajectories are then launched on the raw PES from different initial conditions. New points whose geometries are not close to the existing data set are added to the data set to patch up the unphysical regions of the PES. The closeness between two points $\{\vec{r}_i\}$ and $\{\vec{r}'_i\}$ is

judged by the Euclidean distance, which is defined as $\chi = \sqrt{\sum_{i=1}^{10} |\vec{r}_i - \vec{r}'_i|^2}$. The

permutationally equivalent points are also included in such a screening. The points that satisfy $\chi > 0.1 \text{ \AA}$ are retained in the data set and finally a total of 35222 points are sampled by repeating the procedure dozens of times.

The fundamental-invariant neural network (FI-NN) method is applied in the fitting.⁵ The permutation invariance of the fitted PES with respect to identical atoms is enforced by using fundamental invariants as the input vector of the neural network.⁶⁻⁷ The Morse-like variables, $P_{ij} = \exp\left(\frac{r_{ij}}{\alpha}\right) \exp\left(-\frac{r_{ij}}{\alpha}\right)$, are used to construct the monomials with α as an adjustable parameters ($\alpha = 2.0 \text{ \AA}$ in this work), in which r_{ij} is the internuclear

distance between the i th and j th atoms. The architecture of the NN is the same as that used for the neutral PES, *i.e.* 26-30-70-1, which contains 26 invariant polynomials in the input layer, 30 and 70 neurons in the two hidden layers, and 1 potential energy in the output layers, with a total of 3051 parameters. The training data is fitted by the backward propagation neural network with the Levenberg–Marquardt algorithm.⁸ The “early stopping” method is used to avoid overfitting.⁹ The root mean square error

(RMSE), defined as
$$RMSE = \sqrt{\sum_{i=1}^{N_{data}} (E_{fit} - E_{ab\ initio})^2 / N_{data}}$$
, is used to assess the quality of

each fitting. The data set is randomly divided into two groups, 95% of the points as the training set and the rest 5% as the validating set. To avoid false extrapolation, only fits with a similar RMSE for both sets are reasonable. Finally, the so-called ensemble approach is implemented to minimize random errors.¹⁰ The final PES by averaging three best fits has an overall RMSE of 0.758 meV.

Figure S1 show the potential energy curves of H_3O_2^- along the central hydrogen atom transfer coordinate and the hindered rotor coordinate. The fitted values reproduce well *ab initio* calculations for both curves. There exists a C_2 -saddle point along the minimum energy path, which separates two asymmetric, minimum equilibrium structures. The global minimum structure has a C_1 symmetry with the bridging hydrogen slightly closer to one of the two oxygen atoms. The torsional potential of the two OH groups is presented on the lower panel, for which the bridging hydrogen is in the middle of the two oxygen atoms and the two OH fragments rotate along the O-H-O axis. The torsional motion is somewhat floppy, with the ‘TS’ barrier flanked by two second order saddle points, ‘cis’ and ‘trans’ barriers.

The optimized geometries of stationary points for H_3O_2^- at the level of FC-UCCSD(T)-F12a/aug-cc-pVTZ and on the fitted PES are list in Table S1. The

optimized geometries on the fitted PES are in good consistent with *ab initio* calculations. The bond lengths differ by less than 0.001 Å, and the angles differ by less than 0.2°. The energies and harmonic frequencies of the stationary points are given in Table S2. The fitted energies agree well with the *ab initio* values. The frequency difference is less than 10 cm⁻¹.

Table S1. Geometries (bond length in angstrom and angle in degree) of the stationary points for H_3O_2^- . The corresponding atom labels are shown in Figure S1.

Species	Method	R_{O1H2}	R_{O1H3}	R_{H2O4}	R_{O4H5}	θ_{H2O1H3}	θ_{O1H2O4}	θ_{H2O4H5}	Φ_{O4H5H2O1}	Φ_{O1H3H2O4}
H_2O	ab initio ^a	0.959	0.959			104.45				
	PES ^b	0.959	0.959			104.26				
OH^-	ab initio ^a				0.965					
	PES ^b				0.965					
TS	ab initio ^a	1.218	0.960	1.218	0.960	103.35	179.36	103.36	179.10	179.11
	PES ^b	1.218	0.960	1.218	0.960	103.36	179.36	103.35	179.10	179.11
GM^-	ab initio ^a	1.084	0.959	1.407	0.961	101.97	177.05	105.56	174.29	-178.88
	PES ^b	1.084	0.959	1.407	0.961	101.97	177.05	105.56	174.29	-178.89
trans-TS	ab initio ^a	1.219	0.960	1.219	0.960	104.00	180.00	104.01	-180.00	-180.00
	PES ^b	1.219	0.960	1.219	0.960	104.00	179.99	104.01	-180.00	-180.00
cis-TS	ab initio ^a	1.220	0.960	1.220	0.960	104.48	178.84	104.49	179.96	180.00
	PES ^b	1.220	0.960	1.220	0.960	104.48	178.85	104.49	179.96	179.99

^aUCCSD(T)-F12/aug-cc-pVTZ by Molpro 2012.

^bFI-NN PES.

Table S2. Energies (in eV) and harmonic frequencies (in cm^{-1}) of the stationary points for H_3O_2^- .

Species	Method	E (eV)	Frequency (cm^{-1})								
			1	2	3	4	5	6	7	8	9
$\text{H}_2\text{O}+\text{OH}^-$	Ab initio ^a	1.1830	3942	3832	3749	1646					
	PES ^b	1.1761	3940	3825	3742	1648					
TS (C_2)	Ab initio ^a	0.0110	3838	3837	1618	1517	632	573	570	210	682i
	PES ^b	0.0110	3838	3835	1618	1517	632	573	569	210	680i
GM (C_1)	Ab initio ^a	0.0000	3865	3811	1746	1617	1343	580	471	327	201
	PES ^b	0.0000	3864	3811	1748	1619	1342	580	470	327	201
trans-TS (C_{2h})	Ab initio ^a	0.0330	3842	3838	1792	1255	737	605	496	187i	702i
	PES ^b	0.0329	3840	3837	1790	1258	737	606	495	187i	700i
cis-TS (C_{2v})	Ab initio ^a	0.0609	3836	3833	1787	1253	751	612	500	236i	744i
	PES ^b	0.0608	3841	3834	1786	1256	750	612	501	239i	741i

^aUCCSD(T)-F12/aug-cc-pVTZ by Molpro 2012.

^bFI-NN PES.

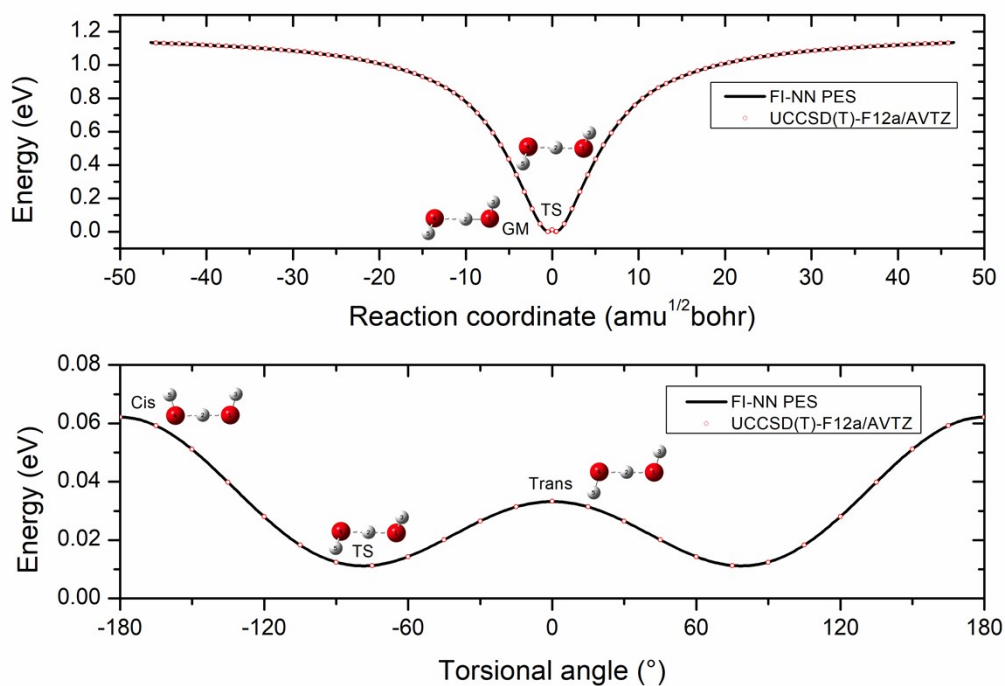


Figure S1: Potential energy curves for the anion H_3O_2^- along the central hydrogen atom transfer coordinate in the upper panel and the hindered rotor coordinate in the lower panel. The other coordinates are fixed at the TS geometry in the lower panel. All energies are given in kcal mol^{-1} and relative to the global minimum.

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