

On the existence of CO₃²⁻ microsolvated clusters: a theoretical study

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S1. Global optimization: PSO, CK, SAMD

This Special Section provides additional information on Global Optimization techniques.

We used the DFT-driven-PSO algorithm^{s1} as a main global optimization driver to obtain global minimum structures of the $[\text{CO}_3 \cdot (\text{H}_2\text{O})_n]^{2-}$ ($n = 1-9$) microsolvated clusters. The level of theory was PBE0/def2-SVP.^{s2-s4} Number of generations represents how much consequent optimization cycles were performed. Generation size is the number of molecular replicas within one generation which developed its own unique locally optimized geometry. Survived population represents the number of replicas which geometries were saved during a one generation step and transferred to another generation. **Table S1-A** contains the used parameters for each simulation.

Table S1-A. Population size and number of generations in DFT-driven-PSO Global Optimization

Stoichiometry	Generation Size	Survived Population	Number of Generations
$[\text{CO}_3 \cdot \text{H}_2\text{O}]^{2-}$	10	5	9
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_2]^{2-}$	10	5	9
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_3]^{2-}$	10	5	9
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_4]^{2-}$	20	10	9
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$	20	10	9
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^-$	20	10	14
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-}$	20	10	14
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-}$	20	10	14
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-}$	20	10	19
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-}$	20	10	19

Figure S1-A represents the evolution of Global Minimum geometry and the first low-lying isomer during DFT-driven-PSO global optimization for $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$. It may be vividly seen that global minimum structure was found almost immediately during first optimization cycle and was presented in each generation.

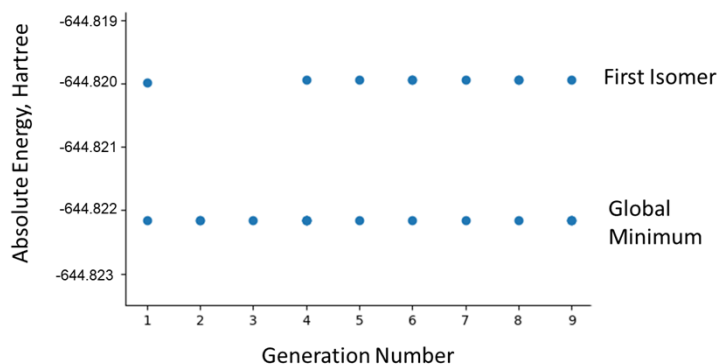


Figure S1-A. An example of global minimum structure and first low-lying isomer energy evolution during DFT-driven-PSO global optimization for $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ cluster.

In addition, we carried out global optimization with the Coalescence Kick (CK) strategy^{s5} for the $[\text{CO}_3\cdot(\text{H}_2\text{O})_n]^{2-}$ ($n = 4-5$) microsolvated clusters. The main goal of the CK optimization was to confirm obtained geometries via the DFT-driven-PSO approach with the same level of theory. The information regarding population size in CK simulations is placed in **Table S1-B**.

Table S1-B. Population size in the Coalescence Kick simulations

Stoichiometry	Population Size
$[\text{CO}_3\cdot(\text{H}_2\text{O})_4]^{2-}$	1000
$[\text{CO}_3\cdot(\text{H}_2\text{O})_5]^{2-}$	2000

The last global optimization algorithm – Simulated Annealing Molecular Dynamics^{s6} (SAMD) – was used to generate global minimum structure of dissociated single-charged anions: $[\text{HCO}_3\cdot(\text{H}_2\text{O})_m]^-$ and $[\text{OH}\cdot(\text{H}_2\text{O})_m]^-$ ($m = 1-8$). Here we used more accurate D3-L-M06/def2-SVPD level of theory^{s4,s7-s10}. We provide an execution script written on SANSscript language which can be executed in the ORCA 5.x suite and the example of the minimization trajectory for $[\text{OH}\cdot(\text{H}_2\text{O})_2]^-$ cluster.

```
%md

Cell Cube 12 Spring 20
# Cell cube creates cubic wall around center of mass
# Spring is an elastic constant (kJ/mol) within quadratic potential

Minimize LBFGS Steps 20 Noise 0.5 StepLimit 0.05
# L-BFGS minimization is only needed for generating adequate initial
# structure. Noise generates random atomic displacements. StepLimit prevents
# L-BFGS minimization converge to local minimum fastly.

# The next block is an MD Block
Initvel 1000_K
# Velocities generation for concrete temperature
Thermostat CSVR 1000_K Timecon 1_fs Massive # Thermostat settings
Timestep 0.5_fs # Integrand step length
Run 300 # How much steps in MD trajectory

# The next block is an annealing block

Minimize Anneal Steps 3000 TempConv 950_K Noise 0.1
# TempConv is a convergence temperature. We set up cooling factor as 50K but
# it can be adjusted in multiplication fashion (0.9 - 0.95 works good).
Dump Position Format XYZ Stride 0 Filename "Geometry_1000.xyz"
# Put the final geometry in the new trjectory file.

Initvel 950_K # New random velocities for the next temperature step
Thermostat CSVR 950_K Timecon 1_fs Massive
Run 300
Timestep 0.5_fs
Minimize Anneal Steps 3000 TempConv 900_K Noise 0.1
Dump Position Format XYZ Stride 0 Filename "Geometry_950.xyz"
```

```

Initvel 900_K
Thermostat CSVR 900_K Timecon 1_fs Massive
Run 300
Timestep 0.5_fs
Minimize Anneal Steps 3000 TempConv 850_K Noise 0.1
Dump Position Format XYZ Stride 0 Filename "Geometry_900.xyz"

... # repeat printing iterations with the chosen cooling factor

Initvel 100_K
Thermostat CSVR 100_K Timecon 1_fs Massive
Run 100
Timestep 0.5_fs
Minimize Anneal Steps 3000 TempConv 50_K Noise 0.025
Dump Position Format XYZ Stride 0 Filename "Geometry_100.xyz"

Initvel 50_K
Thermostat CSVR 50_K Timecon 1_fs Massive
Run 100
Timestep 0.5_fs
Minimize Anneal Steps 3000 TempConv 1_K Noise 0.025
Dump Position Format XYZ Stride 0 Filename "Geometry_50.xyz"

Initvel 0.5_K
Thermostat CSVR 0.5_K Timecon 1_fs Massive
Timestep 0.5_fs
Run 100
Minimize Anneal Steps 3000 TempConv 1_K Noise 0.01
Dump Position Format XYZ Stride 0 Filename "Geometry_005.xyz"

# Final L-BFGS geometry optimization
Minimize LBFGS Steps 3000 StepLimit 0.1
Dump Position Format XYZ Stride 0 Filename "Geometry_Final.xyz"

End

```

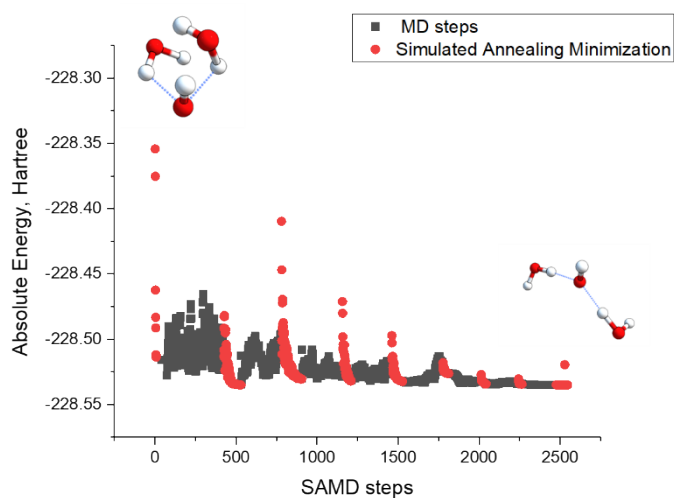


Figure S1-B. Global Optimization trajectory of $[\text{OH}\cdot(\text{H}_2\text{O})_2]^-$ cluster: red dots correspond to simulated annealing blocks, black dots correspond to MD blocks

S2. Computation of electron Detachment Energies

There are a lot of ways how to accurately simulate Vertical/Adiabatic Detachment Energies (VDE/ADE), therefore, we used some of them to compare; however, without experiment there is no adequate reference for comparison. This special section is a technical one and performed mainly for experimental and computational specialists. As an example, we took the microsolvated cluster $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ which is the first stable specie toward autoionization process. It is important to note that our calculations were carried out using Gaussian16 (Rev C.01) and ORCA 5.03 program packages,^{s11-s14} therefore, we used methods which are available there. Also, we used C1 point group symmetry.

First VDE_1 and ADE_1 values usually correspond to the most intensive peaks in the photodetachment spectra. Generally, it is an energy difference between initial and ionized electronically ground states. This energy difference can be obtained by two main computational strategies: 1) calculate the absolute energies of both states by two separate calculations, 2) calculate the ionized state as an excitation to the initial state. The first strategy is mainly presented by very accurate coupled clusters calculations which results are usually used as an accurate reference in quantum chemistry community (CCSD(T) is the golden standard of accuracy). Although, they can be applied only for single reference systems. The second strategy can deal with VDE values only, however, can provide ionized electronically excited states directly.

We compared the following approaches (**Table S2-A**):

- Domain-based local pair natural orbital coupled clusters with single and double and improved perturbative triple excitations using exact correlation wavefunction ansatz^{s15-s19} and cc-pVTZ-F12 basis set^{s20} (abbreviation is DLPNO-CCSD(T)-F12/cc-pVTZ-F12). Corresponding reference wavefunction was an open-shell Hartree-Fock (UHF) Slater Determinant with quasi-restricted orbitals projection^{s21}. F12 ansatz was performed with the resolution-of-identity approximation (F12/D); corresponding auxiliary basis sets were cc-pVTZ-F12-CABS and cc-pVQZ-F12-MP2fit.^{s22}
- DFT calculations with different density functionals and def2-QZVPPD basis set.^{s4,s10} Double Hybrid density functional utilized resolution-of-identity approximation in conjunction with def2-QZVPPD/C basis set.^{s23,s24} All DFT calculations utilized open-shell Kohn-Sham (UKS) Slater determinants.
- Ionization potential equation-of-motion coupled clusters with single and double excitations utilizing the back-transferred pair natural orbital strategy^{s25} and aug-cc-pVTZ basis set^{s26,s27} (abbreviation is bt-PNO-IP-EOM-CCSD/aug-cc-pVTZ). This approach utilized closed-shell RHF reference wavefunction of the initial "2-" state.
- Electron Propagator Theory (EPT) in form of outer-valence Green's functions^{s28} (OVGF) and renormalized partial third order quasi-particle approximation^{s29,s30} (P3+) and aug-cc-pVTZ basis set. Reference wavefunction was a closed-shell RHF Slater determinant of the initial "2-" state.

Here DLPNO-CCSD(T)-F12/cc-pVTZ-F12 serves as a main reference. ADE_1 values include ZPE correction obtained at D3-M06-2X/def2-QZVPPD level of theory.

Table S2-A. $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ VDE_1 and ADE_1 values calculated by different approaches

Method/basis	VDE_1	ADE_1
DLPNO-CCSD(T)-F12/cc-pVTZ-F12	1.179	0.220
bt-PNO-IP-EOM-CCSD/aug-cc-pVTZ	0.745	N/A
OVGF/ aug-cc-pVTZ	1.265	N/A
P3+/ aug-cc-pVTZ	0.669	N/A
DFT with B3LYP ^{s31} /def2-QZVPPD	0.518	-0.127
DFT with PBE0 ^{s2,s3} /def2-QZVPPD	0.599	-0.057
DFT with M06-2X ^{s7} /def2-QZVPPD	1.146	0.309
DFT with ω B97M-V ^{s32} /def2-QZVPPD	0.895	0.131
DFT with SCS-DSD-PBEP86 ^{s33} /def2-QZVPPD	1.319	0.335
DFT with ω B97X-2 ^{s34} /def2-QZVPPD	1.116	0.185

It can be seen that M06-2X/def2-QZVPPD, OVGF/ aug-cc-pVTZ and double hybrid density functionals with def2-QZVPPD basis set provide the results very close to DLPNO-CCSD(T)-F12/cc-pVTZ-F12 level of theory, thus, may be recommended. Moreover, the very common B3LYP and PBE0 density functional are not accurate enough to capture correct detachment energies.

At the same moment, calculations of ionized electronically excited states are not so straightforward. There is no appropriate common reference calculation as CCSD(T) and results may vary a lot. Again, we have two different strategies: 1) calculate energy difference of the initial and ionized ground state, perform an excited states calculation on the ionized state wavefunction; 2) use IP-EOM-CCSD or EPT formulations which are capable to produce excited ionized states starting from initial ground state. Only the first five excited states will be presented.

We tested following approaches (**Table S2-B**):

- Linear response time-dependent DFT (LR-TD-DFT) with the Tamm-Dankoff approximation. We tried different density functional, and double-hybrid density functionals utilized so-called perturbative correction for double excitations in the CIS(D) fashion^{s35,s36} and the spin-component scaling procedure (SCS)^{s37}. Basis set was set to def2-TZVPPD, double hybrid functionals utilized resolution-of-identity approximation with def2-TZVPPD/C basis set. Energy differences between ground states were taken from DLPNO-CCSD(T)-F12/cc-pVTZ-F12 calculations.
- State-averaged CASSCF wavefunction obtained with electrons and orbitals involved to TD-DFT excited states with CIS(D) correction. The overall active space size was 13 electrons and 7 orbitals which formed first six TD-DFT excited states. After CASSCF energies were corrected by different multireference approaches: Spectroscopy Oriented Configuration Interaction^{s38} (SORCI) with

special truncation scheme of excitation classes, Multireference Average Quadratic Coupled Clusters^{s39} (MR-ACCQ), multistate Fully Internally Contracted N-Electron Valence second-order Perturbation Theory^{s40–s42} (MS-FIC-NEVPT2), and the most rigorous multireference equation-of-motion coupled clusters with CAS, 2h,1h,1p excitations in the diagonalization manifold^{s43} (MR-EOM-T|T[†]|SXD-h-v). All multireference calculations utilized def2-TZVPD basis set^{s4,s10} as being quite sensitive to the basis set size. Only limited number of methods were applied to ADE calculations due to tremendous computational cost. Energy differences between ground states were taken from DLPNO-CCSD(T)-F12/cc-pVTZ-F12 calculations.

- Ionization potential equation-of-motion coupled clusters with single and double excitations utilizing the back-transferred pair natural orbital strategy and aug-cc-pVTZ basis set (abbreviation is bt-PNO-IP-EOM-CCSD/aug-cc-pVTZ). This approach utilized closed-shell RHF reference wavefunction of the initial “2-” state.
- Electron Propagator Theory (EPT) in form of outer-valence Green’s functions (OVGF) and renormalized partial third order approximation (P3+) and aug-cc-pVTZ basis set. Reference wavefunction was a closed-shell RHF Slater determinant of the initial “2-” state.

Table S2-B. $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ VDE and ADE values calculated by different approaches. Excited ionized energies are included.

Method/basis	Root Number	VDE ₁ , eV	ADE ₁ , eV
bt-PNO-IP-EOM-CCSD/aug-cc-pVTZ	1	0.745	N/A
	2	1.764	
	3	1.914	
	4	2.151	
	5	2.305	
OVGF/ aug-cc-pVTZ	1	1.265	N/A
	2	2.110	
	3	2.263	
	4	2.616	
	5	2.766	
P3+/ aug-cc-pVTZ	1	0.669	N/A
	2	1.697	
	3	1.865	
	4	2.070	
	5	2.240	
TD-DFT/TDA with CAM-B3LYP	1*	1.179	0.220
	2	2.124	1.170
	3	2.279	2.246
	4	2.317	2.590
	5	2.490	2.746
TD-DFT/TDA with M06-2X/def2-TZVPPD	1*	1.179	0.220
	2	1.948	0.694
	3	2.138	2.308
	4	2.576	3.067
	5	2.721	3.155

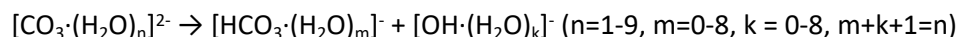
TD-DFT/TDA with ω B97M-D4/def2-TZVPPD	1*	1.179	0.220
	2	2.186	1.222
	3	2.337	2.473
	4	2.752	2.690
	5	2.910	3.057
TD-DFT/TDA with SCS-B2GP-PLYP21 /def2-TZVPPD	1*	1.179	0.220
	2	2.729	1.147
	3	2.653	2.557
	4	3.440	2.855
	5	3.852	2.935
TD-DFT/TDA with SCS-RSX-QIDH /def2-TZVPPD	1*	1.179	0.220
	2	1.581	1.138
	3	1.735	2.541
	4	2.006	2.635
	5	2.356	2.655
SORCI on CASSCF(13e,7o)/def2-TZVPD	1*	1.179	0.220
	2	2.133	1.044
	3	2.148	2.366
	4	2.235	2.592
	5	2.589	2.833
ACCQ on CASSCF(13e,7o)/def2-TZVPD	1*	1.179	Not calculated
	2	2.045	
	3	2.276	
	4	3.001	
	5	3.057	
MS-FIC-NEVPT2 on CASSCF(13e,7o) /def2-TZVPD	1*	1.179	0.220
	2	2.554	1.552
	3	2.687	2.570
	4	2.741	2.708
	5	2.863	2.834
MR-EOM-T T ⁺ SXD-h-v on CASSCF(13e,7o)/def2-TZVPD	1*	1.179	Not calculated
	2	2.104	
	3	2.278	
	4	2.574	
	5	2.746	

* first state correspond to energy difference obtained at DLPNO-CCSD(T)-F12/cc-pVTZ-F12 level of theory.

As was said above, for excited states there is no common golden reference albeit the experimental data. We may see some trends: multistate multireference second order perturbation theory (in form of MS-FIC-NEVPT2) provides results similar to double hybrid functionals, all MRCI-like calculations are close to MR-EOM-CC and M06-2X or ω B97M-D4 calculations. IP-EOM-CCSD and P3+ methods provide similar results, while OVGf is closer to MRCI calculations.

S3. Deprotonation and dissociation reaction energies

In the main text we mentioned the reaction energies of the protonation and dissociation process:



were calculated for all investigated $[\text{CO}_3 \cdot (\text{H}_2\text{O})_n]^{2-}$ ($n = 1-9$) microsolvated clusters. We used globally optimized geometries refined at D3-M06-2X/def2-QZVPPD level of theory; Grimme's third-order dispersion correction^{s8,s9} was used without damping function. Here we provide results for $n = 1-9$ altogether (**Table S3**).

Table S3. $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ VDE and ADE values calculated by different approaches. Excited ionized energies are included.

Reaction	$\Delta_r E + \Delta_r \text{ZPE}$, kcal/mol
$[\text{CO}_3 \cdot \text{H}_2\text{O}]^{2-} \rightarrow \text{HCO}_3^- + \text{OH}^-$	-56.667
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_2]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + \text{OH}^-$	-40.153
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_2]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-53.896
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_3]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + \text{OH}^-$	-27.671
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_3]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-41.662
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_3]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-45.897
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_4]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + \text{OH}^-$	-16.681
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_4]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-35.193
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_4]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-39.676
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_4]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]^-$	-40.941
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_4]^- + \text{OH}^-$	-9.506
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-26.367
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-35.371
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]^-$	-36.884
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_4]^-$	-37.253
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_5]^- + \text{OH}^-$	0.410
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_4]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-21.127
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-28.480
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]^-$	-34.514
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_4]^-$	-35.131
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_6]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_5]^-$	-32.159
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_6]^- + \text{OH}^-$	4.388
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_5]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-11.107
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_4]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-23.135
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]^-$	-27.519
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot (\text{H}_2\text{O})_4]^-$	-32.656
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_5]^-$	-29.933
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_7]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_6]^-$	-26.601
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_7]^- + \text{OH}^-$	6.731
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_6]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-9.964
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_5]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]^-$	-15.951
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_4]^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]^-$	-25.009
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + [\text{OH} \cdot (\text{H}_2\text{O})_4]^-$	-28.496
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot (\text{H}_2\text{O})_5]^-$	-30.293
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_6]^-$	-27.210
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_8]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_7]^-$	-23.862

$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_8]^- + \text{OH}^-$	9.547
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_7]^- + [\text{OH} \cdot \text{H}_2\text{O}]^-$	-8.917
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_6]^- + [\text{OH} \cdot (\text{H}_2\text{O})_2]$	-16.105
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_5]^- + [\text{OH} \cdot (\text{H}_2\text{O})_3]$	-19.121
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_4]^- + [\text{OH} \cdot (\text{H}_2\text{O})_4]$	-27.283
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_3]^- + [\text{OH} \cdot (\text{H}_2\text{O})_5]$	-27.430
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot (\text{H}_2\text{O})_2]^- + [\text{OH} \cdot (\text{H}_2\text{O})_6]$	-28.867
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow [\text{HCO}_3 \cdot \text{H}_2\text{O}]^- + [\text{OH} \cdot (\text{H}_2\text{O})_7]$	-25.768
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_9]^{2-} \rightarrow \text{HCO}_3^- + [\text{OH} \cdot (\text{H}_2\text{O})_8]$	-21.080

It should be noted that the global trend is the increase of the reaction energy difference upon hydration; meanwhile, protonation and dissociation is still energetically preferable in a bulk water solvent.

S4. Relaxed scans of protonation potential surfaces

To prove that protonation state is stabilized by an internal motion of atoms, we made a several protonation scans in mean of static DFT relaxed scans of potential energy surface. We moved each uniquely coordinated Hydrogen atom of water molecule toward a neighbor Oxygen atom. As an example, we used the $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ microsolvated cluster in the global minimum geometry and in the geometry which was taken as a “snapshot” during the production run of the BOMD simulation under 300K. The scans utilized D3-M06-2X/def2-TZVPPD level of theory.

1) Global minimum geometry scans (Figure S4-A):

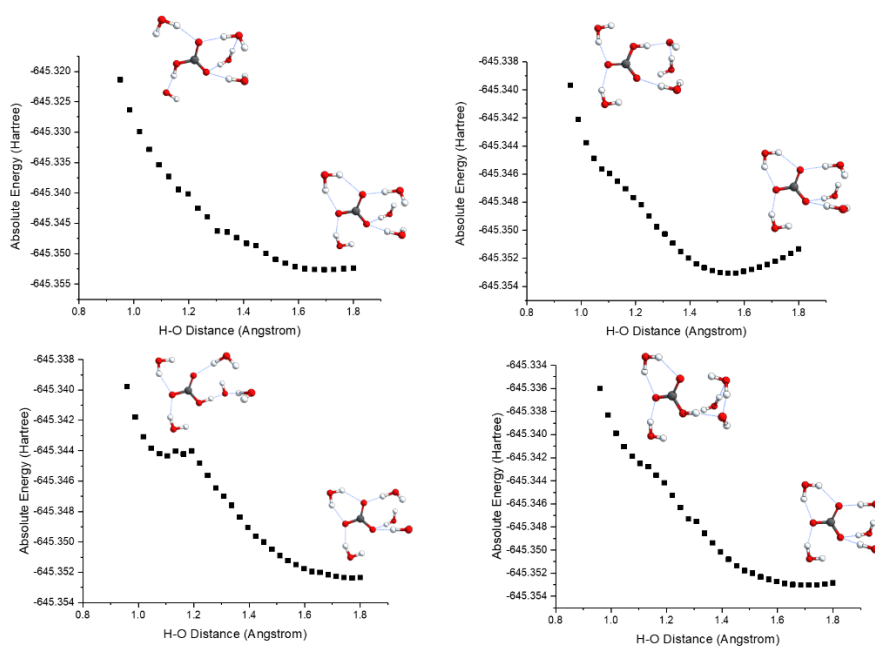


Figure S4-A. Potential energy relaxed scans of global minimum structure toward protonation

The scans show that some kind of stabilization can be achieved only if the protonated form is separated from the OH^- anion by a distance, and OH^- anion is solvated by another water molecule. Although, this

configuration possesses a diminished reaction barrier for the backward deprotonation process, therefore, cannot be assumed to be stable. Moreover, this geometry is not a true minimum due to the presence of imaginary frequency in the nuclear Hessian upon local optimization. Thus, only additional movement of nuclei can stabilize the protonated state, moreover, while the full stabilization can be observed only upon dissociation.

2) “snapshot” geometry scans (**Figure S4-B**):

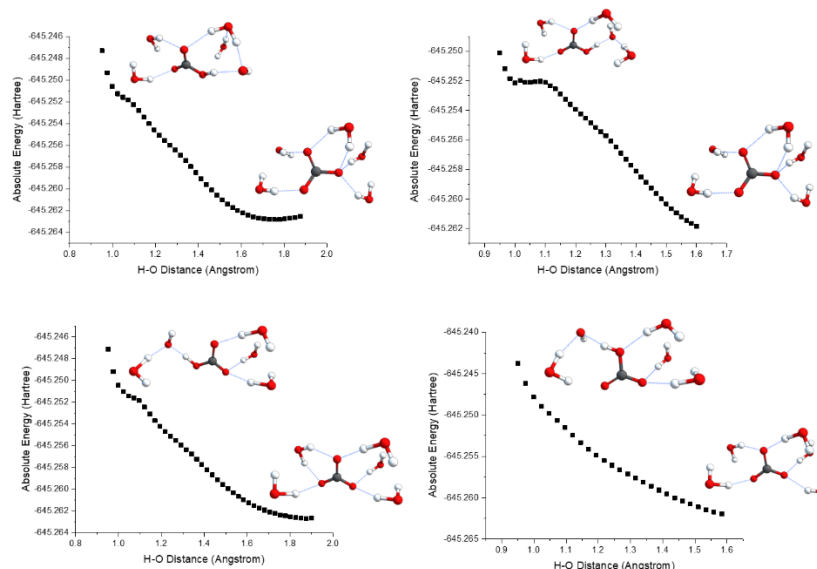


Figure S4-B. Potential energy relaxed scans of the BOMD “snapshot” structure toward protonation

We may see the very same trend which was observed in the previous case with a global minimum structure.

S5. Globally optimized structures and low-lying isomers: energy ordering

CK and DFT-driven-PSO algorithms can provide not only information on a non-dissociated global minimum structure but also other low-lying isomers in terms of energy. We recalculated obtained geometries using D3-M06-2X/def2-QZVPPD level of theory including ZPE correction. The energy ordering obtained by this density functional is similar to DLPNO-CCSD(T)-F12/cc-pVTZ-F12 energy ordering which was tested for the $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ molecular cluster. Also, we will present isomers of $[\text{CO}_3 \cdot (\text{H}_2\text{O})_n]^{2-}$ ($n = 4-9$) structures (**Figure S5-A**) due to strict autoionization instability for $n = 1-3$ clusters. It should be strictly outlined that real global minimum geometries for all clusters are protonated and dissociated single-charged anions.

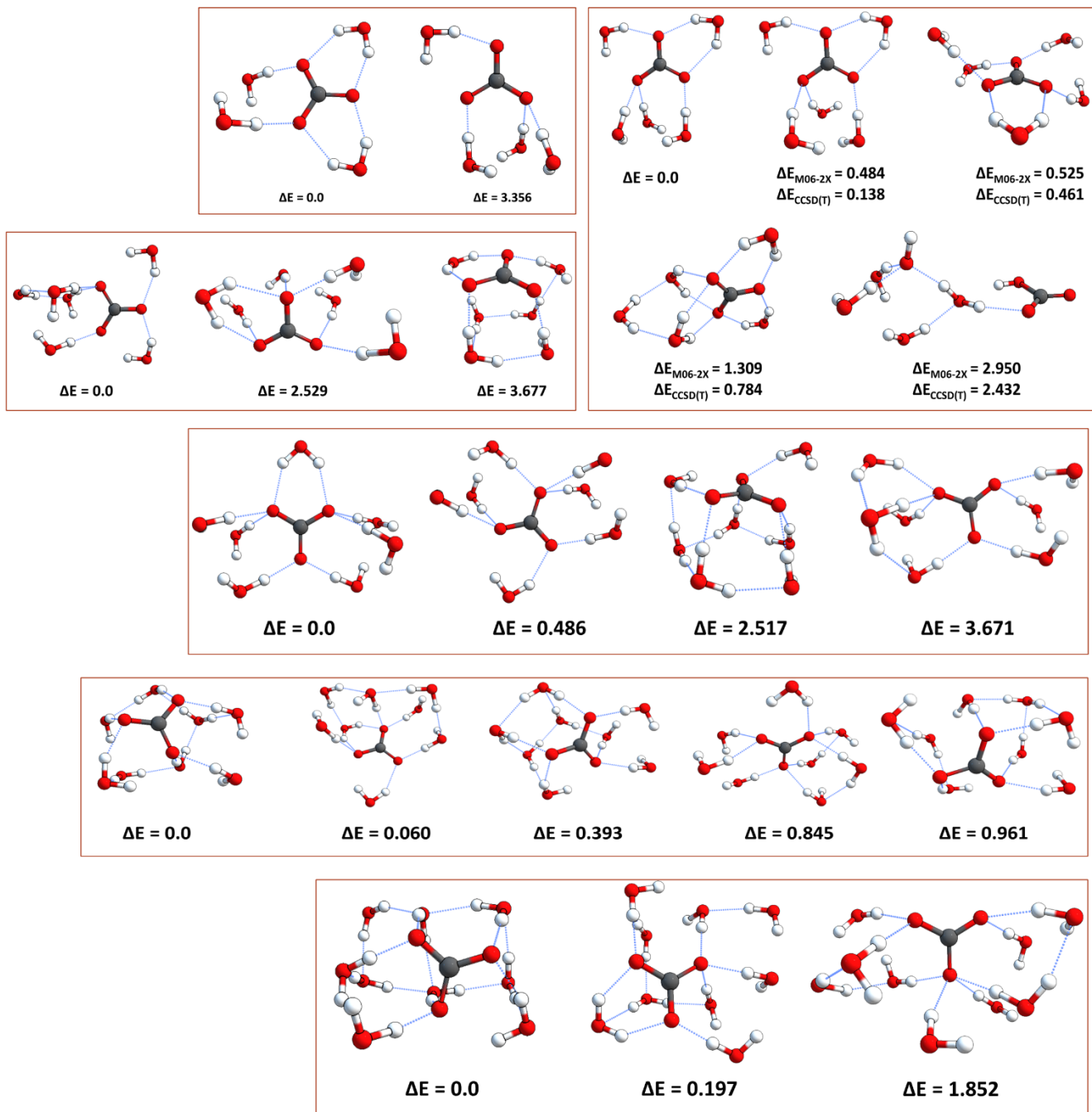


Figure S5-A. Global minimum structures and low-lying isomers. ΔE corresponds to D3-M06-2X/def2-QZVPPD level of theory including ZPE correction.

As an addition, we show the geometry of $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$ isomer which is unstable toward auto-ionization process (**Figure S5-B**). This isomer lies above global minimum geometry by 5.6 kcal/mol (DLPNO-CCSD(T)-F12 and ZPE correction obtained at D3-M06-2X/def2-QZVPPD level of theory). VDE_1 is 0.53 eV while ADE_1 is slightly negative (-0.02 eV) at the same level of theory.

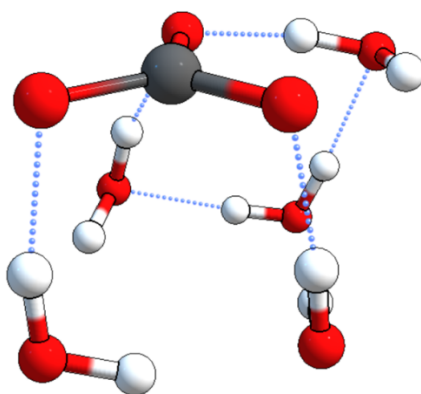


Figure S5-B. Unstable toward auto-ionization isomer of $[\text{CO}_3 \cdot (\text{H}_2\text{O})_5]^{2-}$. While VDE value is positive, ADE value is slightly negative which designates formal instability.

S6. Globally optimized structures: cartesian coordinates (xyz coordinates)

Table S6. Calculated non-dissociated global minimum geometries.

Stoichiometry	XYZ coordinates			
$[\text{CO}_3 \cdot \text{H}_2\text{O}]^{2-}$	8	1.476628913	-1.263462251	-0.548706349
	1	0.530408668	-1.525611389	-0.364254685
	1	1.222739048	-0.308461455	-0.410335435
	6	-1.113225765	0.224588343	0.149092642
	8	-0.002619359	0.883813928	-0.038272884
	8	-1.102321819	-1.075507404	0.032073170
	8	-2.195476686	0.842193228	0.443281541
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_2]^{2-}$	8	-2.726180005	0.481655130	-1.403882373
	1	-2.004129313	0.914811931	-0.827330490
	1	-2.171874598	-0.296070536	-1.577320785
	8	2.182586345	-2.155473655	-0.529493191
	1	1.307696608	-2.164732042	-0.950696888
	1	2.015875682	-1.236925675	-0.119204388
	6	0.137769747	0.161389439	-0.249139817
	8	1.316001982	0.142435802	0.284814035
	8	-0.261642118	-0.826444754	-0.979958841
	8	-0.638343331	1.176498359	-0.046909263
$[\text{CO}_3 \cdot (\text{H}_2\text{O})_3]^{2-}$	8	-2.988549497	-2.385647619	0.204469009
	1	-2.178473904	-2.727449006	-0.220606427
	1	-2.572015605	-1.509682136	0.397228314
	8	2.098334338	-2.537095995	-1.675106410
	1	2.071839817	-1.627849143	-1.318518337
	1	1.163192813	-2.716144751	-1.410248970
	8	0.230577683	1.947630384	0.718499859
	1	-0.561910106	1.381897441	0.791749588
	1	0.748091119	1.241344749	0.258229034
	6	-0.221988919	-0.994247057	-0.249349301
	8	0.907181452	-0.389858944	-0.426209605

	8	-0.376793199	-2.208351808	-0.664518900
	8	-1.195490993	-0.383943114	0.342776146
[CO ₃ · (H ₂ O) ₄] ²⁻	6	-0.989536870	0.386016162	0.217125032
	8	-1.820049951	-0.263849421	0.949725568
	8	0.027220607	0.980554600	0.748078767
	8	-1.172789412	0.455080417	-1.062861754
	8	0.211719478	2.409644151	-1.984223736
	1	-0.355789871	1.603936503	-1.695897613
	1	0.484502284	2.707961245	-1.111705896
	8	-0.708377402	0.326560278	3.358769217
	1	-0.128687109	0.745939662	2.698251349
	1	-1.318801567	-0.044216196	2.682538634
	8	2.360813622	0.953274632	-0.568804559
	1	1.968372566	1.260240547	-1.393225134
	1	1.536773749	0.889425713	-0.010968629
	8	-3.515807834	-1.059127362	-1.014683523
	1	-3.107612176	-0.931427034	-0.127754362
	1	-2.829181114	-0.546960897	-1.476067362
[CO ₃ · (H ₂ O) ₅] ²⁻	8	2.596723852	0.803486600	-1.264303719
	1	3.010204315	0.754400248	-0.394954495
	1	1.643098823	0.820063851	-0.983921016
	8	-3.168501452	-2.029125396	-0.042413740
	1	-3.041760013	-1.055924816	-0.029035166
	1	-2.217234219	-2.228518343	-0.038209816
	8	2.349799371	0.132368059	1.612022376
	1	1.525560653	0.474918407	1.190155173
	1	2.371058712	-0.757991681	1.229734194
	8	1.990003501	-2.007728623	-0.303384827
	1	2.312518510	-1.300894823	-0.874016440
	1	1.016202075	-1.739005903	-0.177081695
	8	-1.543197265	3.086120311	0.020762190
	1	-1.943417351	2.183846375	0.012724612
	1	-0.627913082	2.770872913	0.018741525
	6	-0.736552305	0.001311354	-0.006041921
8	-0.473948082	-1.257934884	-0.013823087	
8	-1.946554722	0.414996140	-0.005447142	
8	0.242613680	0.860566210	0.005572994	
[CO ₃ · (H ₂ O) ₅] ⁻	8	-0.383847638	-0.525879656	-3.079458701
	1	-0.557360613	-0.925805303	-2.204851825
	1	-0.883191795	0.294191615	-3.018325116
	8	1.873514515	-0.838245110	0.408669078
	1	1.729146102	-0.042174004	0.949797458
	1	0.975420193	-1.155520101	0.227626643
	8	0.706738119	2.553063973	-0.952772033
	1	1.272982613	1.907461382	-1.417571474
	1	-0.177603871	2.159558782	-0.975257597
	8	1.044292342	1.585775302	1.679699469
	1	0.135571180	1.270773643	1.776252731
	1	1.025407173	2.073244137	0.835356867
	8	2.158457878	0.433918126	-2.111072782
	1	2.192500831	-0.064300750	-1.273648865

	1	1.399928189	0.057705022	-2.585552496
	6	-1.364347779	-0.040253147	-0.041649053
	8	-1.569915143	0.315172462	1.180903189
	8	-0.890795647	-1.124121098	-0.402387521
	8	-1.723262650	0.934950724	-0.783658973
[CO ₃ · (H ₂ O) ₆] ²⁻	8	-3.025027858	2.196972884	2.156477113
	1	-2.177950415	1.746167556	2.017534983
	1	-3.510441675	1.685741650	1.472458852
	8	-5.051040480	-1.252676934	-1.481580750
	1	-4.142063464	-1.590842164	-1.530240858
	1	-4.838540178	-0.524370000	-0.860675940
	8	-0.149244919	-1.762524933	-2.132391979
	1	0.536604874	-1.958363526	-1.482812060
	1	-0.960333977	-1.541182019	-1.591653300
	8	1.980494993	-1.637753258	0.135695249
	1	1.712487361	-0.733756431	-0.108391228
	1	1.193734478	-1.955241019	0.621071120
	8	-0.511985370	-2.183759642	1.267923842
	1	-0.770997937	-1.217189380	1.253096129
	1	-1.089296940	-2.468609544	0.545870624
	8	0.644769698	0.727254541	-0.769668635
	1	-0.135641848	0.621399095	-0.158556747
	1	0.384965027	0.169995180	-1.516131210
	6	-2.496824817	-0.172954543	0.075773712
	8	-1.480973066	0.233622707	0.795156113
8	-2.327420482	-1.176354859	-0.720447691	
8	-3.625017007	0.402943641	0.180304663	
[CO ₃ · (H ₂ O) ₇] ²⁻	8	-0.320602637	2.377862809	2.393591621
	1	-0.684023114	1.562033827	1.985767655
	1	0.434508712	2.539399775	1.808720179
	8	0.446768241	-3.210709324	-1.739749216
	1	-0.098429288	-2.667804219	-1.129065858
	1	1.324126291	-2.842388694	-1.558168057
	8	1.237673655	2.471177085	-0.044092411
	1	0.368700013	2.753022456	-0.353413611
	1	1.129944124	1.478721631	0.008194667
	8	0.739099599	-3.987977464	1.084322861
	1	0.231613616	-3.144625148	1.052639579
	1	0.706491052	-4.228038277	0.150630709
	8	-3.361783065	-1.478626039	1.153217780
	1	-2.945120827	-0.600955031	1.125613565
	1	-2.569602163	-1.968729451	0.875445743
	8	2.635858963	-2.056622255	-0.240190314
	1	1.985201885	-1.305950524	-0.128315787
	1	2.296909770	-2.710910499	0.382117979
	8	-1.746672706	2.871037230	-0.136934692
	1	-1.636986454	1.897774707	-0.029472343
	1	-1.503211552	3.158372741	0.750982471
	6	-0.374541864	-0.527662542	0.401954946
	8	0.816434703	-0.149553804	0.107882019
	8	-0.683853611	-1.777839135	0.356218112
	8	-1.261490344	0.342625145	0.744075404

[CO ₃ · (H ₂ O) ₈] ²⁻	8	1.794093943	-0.977000642	-1.179775477
	1	0.891242011	-0.609949898	-1.350154251
	1	1.907171272	-0.732304996	-0.254315454
	8	-3.470442918	1.324506069	1.832773132
	1	-2.632471953	1.750512185	2.067321191
	1	-3.333620677	1.107999714	0.881952629
	8	-0.141574913	-3.078827672	-0.421010544
	1	0.630931354	-2.574691187	-0.706370270
	1	-0.900012708	-2.443464658	-0.593269056
	8	-0.562272593	-2.353900594	2.282268821
	1	-1.501064118	-2.093273205	2.226888226
	1	-0.371906625	-2.717458242	1.396675056
	8	0.583259253	0.098776187	1.354939089
	1	0.121403963	0.159710078	0.487066708
	1	0.207305136	-0.698818388	1.769507047
	8	-1.239555198	2.926013828	-0.819925579
	1	-0.545045199	2.301375054	-1.073308243
	1	-1.973813881	2.250330477	-0.801920416
	8	-0.796830723	2.554084884	1.971677352
	1	-0.290391541	1.726534526	1.910588539
	1	-0.940062260	2.797213848	1.037518664
	8	-3.244804799	-1.564274238	1.794671191
	1	-2.980277304	-1.538283968	0.843664690
	1	-3.366925507	-0.626426372	2.008581406
6	-1.835784496	-0.145648178	-0.841871246	
8	-0.614169977	0.200363660	-1.112019080	
8	-2.128492764	-1.380812353	-0.668831985	
8	-2.738661776	0.757834081	-0.723823139	
[CO ₃ · (H ₂ O) ₉] ²⁻	8	0.730194906	-2.181142139	3.120951457
	1	1.072775537	-2.455057222	2.249519261
	1	-0.205631753	-1.969436595	2.948119134
	8	1.570614695	0.500894016	2.661517416
	1	1.358003602	-0.407350134	2.941724181
	1	1.618069492	0.441138449	1.682513639
	8	1.536676403	-2.719346317	0.449890374
	1	0.656752723	-2.301772304	0.233626327
	1	2.065796943	-1.927154575	0.284349096
	8	0.893069272	3.266668374	0.313568254
	1	0.302467224	2.465154635	0.220411756
	1	1.639870061	3.020878423	-0.243404238
	8	2.039436234	1.776458674	-1.936488348
	1	1.148183639	2.077796669	-2.126428875
	1	1.865876297	1.088551043	-1.228147884
	8	1.745341026	3.353433572	2.955035217
	1	1.822163403	2.397284690	3.084363086
	1	1.442407886	3.411429114	2.025282098
	8	-1.207757393	1.423460928	2.619362349
	1	-0.282026837	1.209977896	2.822183946
	1	-1.196386852	1.387873373	1.636819512
	8	-0.810381694	3.846154083	4.185540806
	1	0.107027937	3.830718227	3.868324064
	1	-1.193913028	3.115795163	3.678654028

	8	-1.905803469	-1.370692124	2.356741714
	1	-1.864983499	-0.447149958	2.644739478
	1	-1.537284641	-1.311503696	1.441970108
	6	0.065729709	-0.002611424	-0.022844337
	8	1.363442757	0.044569398	-0.074992855
	8	-0.526522714	-1.134319173	0.055237102
	8	-0.604856866	1.092257933	-0.022320867
[HCO ₃ · H ₂ O] ⁻	6	2.602744563	2.855187348	1.072098000
	8	3.704383439	3.271638156	1.396898163
	8	1.531980597	3.296564002	1.857763791
	8	2.285526863	2.078668699	0.125950676
	1	-0.188096414	0.647607012	0.764222138
	8	-0.194573372	1.441889604	0.230616883
	1	0.733551842	2.896792178	1.493379776
	1	0.790511483	1.647915001	0.087852573
[HCO ₃ · (H ₂ O) ₂] ⁻	1	-1.082592673	-0.832118876	1.327582236
	8	1.507723917	-2.889625757	-2.240570850
	1	1.720869374	-1.974129357	-2.016199831
	1	0.805564293	-3.029801434	-1.587245088
	8	1.184447143	2.116822003	0.242388834
	1	0.482098143	1.883008888	0.852912624
	1	1.306479243	1.257196730	-0.206045217
	6	0.194120220	-1.068390383	-0.035838916
	8	1.096578868	-0.506392157	-0.672870206
	8	-0.254952604	-2.221415746	-0.115985847
8	-0.418135427	-0.260076870	0.937220837	
[HCO ₃ · (H ₂ O) ₃] ⁻	8	2.483959685	1.230009287	-1.356602536
	1	1.537183177	0.995934782	-1.194547823
	1	2.584344551	2.073278081	-0.914978175
	1	-0.383515399	-1.159622549	1.411984512
	8	3.127151305	-0.820853983	0.562044164
	1	3.151762341	-0.153632124	-0.138244916
	1	2.178451500	-0.902517520	0.719205732
	8	-2.560999054	2.274446395	-1.293204842
	1	-2.678884661	1.611359120	-0.596669934
	1	-1.639062789	2.089645492	-1.510639749
	6	-0.661322633	0.151571287	0.084998122
	8	0.180340309	-0.744310744	0.755069335
	8	-1.833847392	0.168862137	0.475336481
8	-0.103330584	0.804665956	-0.813181206	
[HCO ₃ · (H ₂ O) ₄] ⁻	8	2.753505536	1.075654364	-1.067251062
	1	2.866686996	0.118841859	-1.003564336
	1	1.813614518	1.189642152	-0.844927509
	1	-0.992422553	-1.362097801	-1.234730958
	8	2.328517731	0.646205496	1.797307815
	1	2.857762495	1.023978036	1.083893069
	1	1.430040102	0.773557658	1.448885892
	8	2.389897184	-1.650079897	0.015751207
	1	2.434444521	-1.081027872	0.798243146
	1	1.492222475	-1.503975863	-0.314965948
	8	-1.971512481	3.027462376	0.734334778
	1	-1.031190792	2.817748509	0.731167586

	1	-2.312926808	2.210107453	0.342307899
	6	-0.744769150	0.310010716	-0.379310698
	8	-0.226040668	-0.872535454	-0.925983413
	8	-1.969066668	0.427642404	-0.430601679
	8	0.128341223	1.072452170	0.079410296
[HCO ₃ · (H ₂ O) ₅] ⁻	8	0.935614791	1.798098931	-1.499926538
	1	0.203740229	1.333776149	-1.062721174
	1	1.602272497	1.103042895	-1.572015094
	1	-1.409565271	-2.017075111	-1.304050916
	8	1.439499347	-0.244644774	1.446597460
	1	1.168657681	-0.929977036	2.058363486
	1	0.600836274	0.041612890	1.004950227
	8	2.101500263	-0.876834277	-1.253205327
	1	1.170732579	-1.119647902	-1.349730061
	1	2.175266700	-0.739569677	-0.298001664
	8	0.012770055	3.101048012	0.934165100
	1	-0.572851625	2.331217160	0.912636776
	1	0.563659207	2.962543570	0.151781237
	6	-1.559164031	-0.448648314	-0.248777581
	8	-0.779749469	-1.380189962	-0.957530707
	8	-2.760232365	-0.649179970	-0.220605963
	[HCO ₃ · (H ₂ O) ₆] ⁻	8	-0.861543739	0.467928943
8		1.889503182	2.263638597	2.966881535
1		1.252555710	2.731525429	2.407358475
1		1.929369490	1.399713271	2.539764210
8		1.836759906	0.739200300	-0.458481198
1		0.883316519	0.943846849	-0.388217169
1		2.112702175	1.249235390	-1.233173855
1		-1.257160328	-1.510906364	1.292334461
8		1.539491426	0.108864475	2.377830075
1		0.689817751	0.572221587	2.361031695
1		1.913165896	0.278115498	1.503231907
8		0.748374006	-1.731623873	-1.508582950
1		1.351558254	-1.055029870	-1.167067982
1		-0.001206493	-1.669786892	-0.898395464
8		1.628754673	2.235007173	-2.904560663
1		0.884374237	1.600042058	-3.011582546
1		1.216493539	3.022316790	-2.546478689
6	-1.164124957	0.318600456	0.734057885	
8	-1.273138286	-1.030339932	0.448676817	
8	-1.276566552	0.658727858	1.923768870	
8	-0.928077146	1.038022641	-0.256049844	
8	-0.661708801	-1.713108457	3.170203617	
1	-1.048421726	-0.826376825	3.062983267	
1	0.272092950	-1.536180562	2.996465908	
8	-0.445044175	0.451778134	-2.903203791	
1	-0.803513593	0.665359953	-2.018604552	
1	-0.039157688	-0.414041056	-2.743268449	
[HCO ₃ · (H ₂ O) ₇] ⁻	8	3.731662674	0.213063358	-1.374099604
	1	3.445144880	-0.157567594	-0.528144665
	1	3.284459747	1.076249044	-1.421414822
	1	-2.541904262	1.595184674	-0.650775493

	8	2.172640705	-1.054831665	0.788927146
	1	1.432453800	-0.457655715	0.545187375
	1	2.002311958	-1.850262212	0.279356121
	8	1.292654329	-0.801244374	-2.482943701
	1	2.218277902	-0.567455683	-2.305652660
	1	0.829728626	-0.455009822	-1.704471009
	8	-4.020356323	1.463715575	0.607338861
	1	-4.110294525	2.231317348	1.172223263
	1	-3.256981404	0.962284198	0.974806022
	6	-0.975880317	0.744820851	0.046247789
	8	-1.620320459	1.459300817	-0.925862604
	8	-1.625051409	0.387095651	1.041124511
	8	0.233152146	0.531204656	-0.197049604
	8	-0.049960347	-1.235150792	2.861776321
	1	0.804775442	-1.251714451	2.420767948
	1	-0.607235543	-0.695276436	2.280557966
	8	0.036213666	1.601482456	-3.437014584
	1	-0.593657768	1.617669443	-2.704975205
	1	0.461238977	0.732815821	-3.356246064
	8	1.956417311	2.416314432	-1.449400692
	1	1.485996211	2.386098550	-2.295326183
	1	1.355073739	1.916135267	-0.874701103
	8	2.778344861	0.689066242	-0.300941951
	1	3.714914899	0.827496352	-0.149679732
	1	2.575781615	-0.249633158	-0.013294823
	1	-2.513581852	1.530949667	-0.588411943
	8	0.057646612	-2.658276099	-1.050642925
	1	-0.673482011	-2.544027883	-0.429424440
	1	-0.126343287	-1.899517652	-1.648788481
	8	1.458515252	1.155593866	-2.811620835
	1	1.985389973	0.937100608	-2.026808568
	1	0.670938097	0.582718406	-2.735107031
	8	-2.378500525	1.786633972	1.297547683
	1	-2.289876511	0.823904549	1.206544507
	1	-1.459560568	2.092312166	1.315722176
	6	-1.542485903	0.030777278	-1.259267788
	8	-2.123846834	1.256344760	-1.438770350
	8	-1.824495127	-0.580353426	-0.199757788
	8	-0.797102736	-0.347417891	-2.181056026
	8	0.020153500	-0.352693894	1.821377648
	1	-0.646280497	-0.620727867	1.158663506
	1	0.186214825	0.568511162	1.565064945
	8	-0.147931234	3.233982247	-1.935288892
	1	0.521036696	2.665607191	-2.366611092
	1	-0.953362494	2.698073011	-2.001217960
	8	0.524878819	2.199560764	0.575534688
	1	0.231915341	2.638052858	-0.250318649
	1	1.372601526	1.788843171	0.334578781
	8	2.084991300	-1.675916641	0.563952142
	1	1.514990440	-2.122297145	-0.097311141
	1	1.430063148	-1.305315198	1.190669154
[HCO ₃ ·(H ₂ O) ₈] ⁻				

[OH · H ₂ O] ⁻	8	-3.642088348	-0.423188473	1.008078874
	1	-3.808946058	0.458272126	0.675242871
	1	-2.537220847	-0.587386565	0.763881920
	8	-1.272996562	-0.736345046	0.472586654
	1	-0.814104041	-0.623722654	1.305538171
[OH · (H ₂ O) ₂] ⁻	8	-4.751355143	-0.141541606	-0.005166493
	1	-3.866698656	-0.635872319	-0.234749599
	1	-4.442927085	0.633925120	0.462157147
	8	-0.327269590	-0.995108813	0.657959315
	1	-0.242020716	-1.847971067	1.082116752
	8	-2.544922439	-1.285326281	-0.535389215
	1	-2.390040205	-1.218472818	-1.477435793
[OH · (H ₂ O) ₃] ⁻	1	-1.238182266	-1.074926932	0.158182769
	8	-3.931570462	-1.019405394	-0.152588650
	1	-3.715135938	-0.170634202	-0.550542279
	1	-3.374904123	-0.968606271	0.673674458
	8	-2.106620144	-0.542093064	1.675353846
	1	-2.034754217	-0.595807162	2.625202162
	8	-0.896866924	-1.586189364	-0.404330953
	1	-1.172438310	-1.259900352	0.498144604
	1	-1.760507351	-1.769056926	-0.786470040
	8	-1.920766452	1.318520404	-0.164191364
	1	-1.359867799	0.725421242	-0.673172012
1	-2.013877680	0.788785088	0.676770829	
[OH · (H ₂ O) ₄] ⁻	8	-2.598292998	-0.957669367	1.611967165
	1	-3.273378220	-1.376987757	1.074219531
	1	-1.810599701	-0.902091524	0.964427541
	8	-0.835845171	-0.692195608	-0.214102935
	1	-0.726291216	0.732965351	-0.783898919
	1	-0.059403753	-1.246986987	-0.250931858
	8	-3.186543408	-0.627616152	-1.575476219
	1	-3.479537787	0.133245648	-1.058931735
	1	-2.294521287	-0.804320916	-1.198949497
	8	-0.860784452	1.663349277	-1.186178016
	1	-1.377234023	1.473010252	-1.971996346
	8	-3.230219155	1.610947814	0.454803750
	1	-2.397404817	1.788072157	-0.013802665
	1	-3.028962022	0.838568627	1.008806995
[OH · (H ₂ O) ₅] ⁻	8	-3.217131443	0.490624208	2.304286374
	1	-3.515003974	-0.043893955	1.554713368
	1	-2.367389945	0.828242327	1.988169446
	8	-1.059857423	-1.403712743	-0.164221178
	1	-0.828785769	0.168031264	0.519894772
	1	-0.755369935	-2.128855476	0.378008388
	8	-3.481257538	-0.912239682	-0.202721409
	1	-3.951927543	-1.595814390	-0.676900148
	1	-2.463869663	-1.212888466	-0.164736150
	8	-0.816784604	1.136765239	0.720790676
	1	-1.370031585	1.498377589	0.015485695
	8	-2.422296695	1.224283600	-1.777864530
	1	-1.617874827	0.768770098	-2.069424771
	1	-2.919978047	0.541781818	-1.296323586

	8	0.187428020	-0.079708259	-2.029097931
	1	0.508385903	0.611083279	-1.443867642
	1	-0.217031932	-0.726229452	-1.381197374
[OH · (H ₂ O) ₆] ⁻	8	-3.274288338	0.742492371	0.897761103
	1	-3.908518563	0.719224778	0.174976403
	1	-2.774140126	-0.115390982	0.764579192
	8	-1.905326319	-1.358349201	0.177228339
	1	-0.057390603	0.915807014	0.785203289
	1	-2.005509566	-2.235970129	0.542949350
	8	-3.656956964	-0.603705683	-1.748970545
	1	-3.078455717	-1.013000238	-1.062135869
	1	-3.024973501	-0.207545569	-2.352411680
	8	0.107713366	0.125572437	1.316636674
	1	-0.576295773	-0.500979353	0.988219945
	8	-1.137390175	1.904067387	-0.676542424
	1	-0.975642279	1.114138617	-1.215145985
	1	-1.902792788	1.666297466	-0.128582993
	8	-0.398265559	-0.664442428	-1.812636662
	1	-0.951029259	-1.065647158	-1.074669222
	1	0.463940225	-0.553341738	-1.406462805
	8	-1.764466508	1.025598571	3.383094232
1	-2.473415081	1.077824400	2.731449732	
1	-1.013655729	0.717526009	2.855070633	
[OH · (H ₂ O) ₇] ⁻	8	-1.316875240	2.525232165	0.430665458
	1	-1.764307281	2.735075612	1.253188132
	1	-3.003869787	-1.567695145	0.614577294
	8	-0.368890328	-1.732398728	-0.768476966
	1	-0.723560866	0.766934908	1.115174789
	1	-0.280875603	-0.914361298	-1.287489073
	8	-2.981731514	0.966013909	-0.842856474
	1	-3.669514832	1.331587611	-1.398877489
	1	-2.618090130	0.341641499	2.025728165
	8	-0.723922320	-0.097630354	1.553696564
	1	-0.510644277	-0.730089046	0.846279774
	8	-5.634504812	-1.133306343	1.336664616
	1	-5.028848430	-0.467276223	1.694939154
	1	-5.151287400	-1.457448562	0.568609533
	8	-0.560373598	0.826623534	-1.947161132
	1	-1.511830625	0.853214521	-1.658837080
	1	-0.150809373	1.487846240	-1.383429895
	8	-3.482563446	0.738368311	1.845867897
	1	-2.012749833	2.033466397	-0.097630767
	1	-3.442970108	0.889795491	0.875212683
8	-3.190752579	-1.600227227	-0.328226815	
1	-1.325350643	-1.896024442	-0.772723699	
1	-3.152042155	-0.634129975	-0.599475951	
[OH · (H ₂ O) ₈] ⁻	8	-3.248422720	3.220858578	-0.017249879
	1	-2.334158175	3.206699160	0.310332382
	1	-3.094560081	-1.599791877	1.025150768
	8	-0.240247172	-1.206071400	0.125990424
	1	-2.230918923	0.428989435	2.052642335
1	-0.227113427	-0.508961779	-0.546999337	

	8	-3.229165396	0.482879913	-1.068493915
	1	-3.882652169	0.402884110	-1.763423148
	1	-4.049174773	1.726709788	1.505981635
	8	-1.297687691	0.337899227	2.302810569
	1	-0.898461715	-0.238681379	1.629340214
	8	-5.899665110	-1.379127231	0.795170738
	1	-5.160043082	-1.822868433	0.366214364
	1	-5.495644990	-0.566813122	1.129502192
	8	-0.809073797	0.978202999	-1.581461410
	1	-1.815073770	0.789421560	-1.467613997
	1	-0.692926919	1.424505576	-2.418761380
	8	-4.020707007	0.768190020	1.405666275
	1	-3.297160132	2.406416122	-0.541645921
	1	-3.789583634	0.679315900	0.435784262
	8	-3.019133975	-1.870686919	0.105135736
	1	-1.092050763	-1.648235186	-0.012142239
	1	-3.098876332	-1.012722967	-0.405835570
	8	-0.563444293	2.621980435	0.744135556
	1	-0.718738991	1.963663690	1.440889608
	1	-0.515721677	2.081290662	-0.060699701

References

- S1. N. V. Tkachenko, A. A. Tkachenko, V. A. Kulyukin and A. I. Boldyrev, *J. Phys. Chem. A*, 2021, **125**, 8899–8906.
- S2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- S3. M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029–5036.
- S4. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- S5. M. Saunders, *Journal of Computational Chemistry*, 2004, **25**, 621–626.
- S6. P. Rublev, N. V. Tkachenko, A. S. Pozdeev and A. I. Boldyrev, *Dalton Trans.*, 2022, **52**, 29–36.
- S7. Y. Zhao and D. G. Truhlar, *Theor Chem Account*, 2008, **120**, 215–241.
- S8. S. Grimme, *Journal of Computational Chemistry*, 2006, **27**, 1787–1799.
- S9. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- S10. D. Rappoport and F. Furche, *J. Chem. Phys.*, 2010, **133**, 134105.
- S11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. C.01* 2016.
- S12. F. Neese, *WIREs Computational Molecular Science*, 2012, **2**, 73–78.
- S13. F. Neese, *WIREs Computational Molecular Science*, 2018, **8**, e1327.
- S14. F. Neese, *WIREs Computational Molecular Science*, 2022, **12**, e1606.
- S15. C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
- S16. C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.

- S17. C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, *J. Chem. Phys.*, 2016, **144**, 024109.
- S18. Y. Guo, C. Riplinger, U. Becker, D. G. Liakos, Y. Minenkov, L. Cavallo and F. Neese, *J. Chem. Phys.*, 2018, **148**, 011101.
- S19. A. Kumar, F. Neese and E. F. Valeev, *J. Chem. Phys.*, 2020, **153**, 094105.
- S20. K. A. Peterson, T. B. Adler and H.-J. Werner, *J. Chem. Phys.*, 2008, **128**, 084102.
- S21. F. Neese, *J. Am. Chem. Soc.*, 2006, **128**, 10213–10222.
- S22. K. E. Yousaf and K. A. Peterson, *J. Chem. Phys.*, 2008, **129**, 184108.
- S23. F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chemical Physics Letters*, 1998, **294**, 143–152.
- S24. A. Hellweg and D. Rappoport, *Phys. Chem. Chem. Phys.*, 2014, **17**, 1010–1017.
- S25. A. K. Dutta, F. Neese and R. Izsák, *J. Chem. Phys.*, 2016, **145**, 034102.
- S26. T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- S27. R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806.
- S28. W. von Niessen, J. Schirmer and L. S. Cederbaum, *Computer Physics Reports*, 1984, **1**, 57–125.
- S29. J. V. Ortiz, *J. Chem. Phys.*, 1998, **108**, 1008–1014.
- S30. J. V. Ortiz, *Journal of Chemical Physics*, 1996, **104**, 7599–7605.
- S31. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.
- S32. N. Mardirossian and M. Head-Gordon, *J. Chem. Phys.*, 2016, **144**, 214110.
- S33. S. Kozuch and J. M. L. Martin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20104–20107.
- S34. J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2009, **131**, 174105.
- S35. M. Head-Gordon, R. J. Rico, M. Oumi and T. J. Lee, *Chemical Physics Letters*, 1994, **219**, 21–29.
- S36. S. Grimme and F. Neese, *J. Chem. Phys.*, 2007, **127**, 154116.
- S37. M. Casanova-Páez and L. Goerigk, *J. Chem. Phys.*, 2020, **153**, 064106.
- S38. F. Neese, *J. Chem. Phys.*, 2003, **119**, 9428–9443.
- S39. P. G. Szalay and R. J. Bartlett, *Chemical Physics Letters*, 1993, **214**, 481–488.
- S40. C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger and J.-P. Malrieu, *J. Chem. Phys.*, 2001, **114**, 10252–10264.
- S41. C. Angeli, R. Cimiraglia and J.-P. Malrieu, *J. Chem. Phys.*, 2002, **117**, 9138–9153.
- S42. C. Kollmar, K. Sivalingam, Y. Guo and F. Neese, *J. Chem. Phys.*, 2021, **155**, 234104.
- S43. L. M. J. Huntington and M. Nooijen, *J. Chem. Phys.*, 2015, **142**, 194111.