Supplementary Information

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(1) Computational details:

DFT (B3LYP, PBE, PBE0, M06-2x and WB97x) and CCSD were done using Gaussian 09, Revision D.01 program.[i] We add D3 version of Grimme's dispersion with Becke-Johnson damping[ii] to each functional except WB97x that uses a similar damping function to that used by the Grimme's GD3 (ref)[iii] model. Basis set 6-311+G(d,p) was use in all the calculations. M06-2X calculations were done with aug-cc-pVDZ basis set also.

(2) (18e/13o)/(17e/13o)/ aug-cc-pVDZ were included in the active space of the CASSCF[iv] calculations of isolated carbonate CO_3^{2-} and its anion-radical $CO_3^{\cdot -}$ (GAMESS[v] program suite).

Table 1-SI. C-O bond lengths (in Å) and vibrational frequencies ν (cm^{-1}) of the anion-radical $CO_3^{\cdot -}$ ($1^2A_2'$) and the di-anion CO_3^{2-} ($1^1A_1'$) in the D_{3h} configuration. ΔE = E($1^1A_1'$)- ($1^2A_2'$) is the energetic gap between the di-anion and the anion-radical (in eV). CAS(18/13)/aug-cc-pVDZ (CO_3^{2-}) and CAS(18/13)/aug-cc-pVDZ ($CO_3^{\cdot -}$).

	C-O, Å	ν 1e'	a_2''	a_1'	2e'	ΔE, eV
$1^1A_1'$	1.316	663	897	998	1338	4.94
$1^1A_2'$	1.279	i732	823	1080	1074	

(3) Table 2-SI. C-O bond length (in Å), frequencies and intensities of vibrational modes of CO_3 fragment, ionization potential (IP, in eV)) and corresponding charge transfer $q(H2O)_n$ of isolated vs. hydrated (SMD approximation) di-anion CO_3^{2-} and corresponding clusters $CO_3 \cdot (H_2O)_n^{2-}$ (n=3 and 6).

Mode (cm^{-1})	1e'	$1a_2''$	$1a_1'$	2e'	R(C-O), Å	IP, eV	$q(H_2O)_n$
CO_3^{2-}	658/0.4	882/7.5	1049/0.0	1388/933	1.305	-3.30	-
CO_3^{2-} - SMD					1.296	4.46	-
$CO_3(H_2O)_3^{2-}$-	686/8.	908/54.	1072/0.0	1426/772	1.298	-1.25	-0.219
SMD					1.294	5.12	-0.170
$CO_3(H_2O)_6^{2-}$	682/2.7	937/68.	1081/0.0	1451/613	1.295	0.26	-0.248
SMD					1.293	5.6	-0.223

(4) Table 3-SI. C-O bond length (in Å), frequencies and intensities of vibrational modes of CO_3 fragment analogous to high symmetric d, ionization potential (IP, in eV)) and corresponding charge transfer $q(H2O)_n$ of isolated vs. hydrated (SMD approximation) di-anion $CO_3^{\cdot-}$ and corresponding clusters $CO_3(H_2O)_n^{\cdot-}$ (n=3 and 6).

Mode (cm^{-1})	1e'	$1a_2''$	$1a_1'$	2e'	R(C-O), Å	$q(H_2O)_n$
$CO_3^{\cdot-}$	i255	847/26.	1135/0.	1234/10.	1.269	-
SMD					1.267	-
$CO_3(H_2O)_3^{\cdot-}$	i279	856/39.	1140/0.	1235/10.	1.268	-0.052
SMD					1.268	-0.045
$CO_3(H_2O)_6^{\cdot-}$	i277	857/26.	1141/0.	1233/10.	1.268	-0.064
SMD					1.268	-0.059

(5) Coordinates of optimized structure of $CO_3(H_2O)_n^{2-}$ level of theory: M062X/ 6-311+G(d,p):

(5-I) n=0:

C	-0.000001	-0.000013	-0.000010
O	1.189908	0.524502	0.000003
O	-1.049208	0.768186	0.000003
O	-0.140699	-1.292679	0.000003

(5-II) n=3:

C	-1.222377	0.008748	-0.010143
O	-1.197336	-1.161418	-0.561035
O	-1.204076	0.116204	1.278923
O	-1.183389	1.070909	-0.747352
O	1.263841	-0.726704	1.661335
H	1.370768	-1.120941	0.784452
H	0.288708	-0.472859	1.647705
O	1.287121	-1.080165	-1.437764
O	1.295237	1.782039	-0.194027
H	1.395717	-0.124125	-1.338085
H	0.319486	1.660035	-0.412663
H	0.307780	-1.192072	-1.228738
H	1.388601	1.216626	0.585347

(5-III) n=6

C	-0.000024	0.003050	-0.000680
O	-0.000498	-0.100080	1.285963
O	0.000878	1.168686	-0.554638
O	-0.000832	-1.059695	-0.733174
O	2.613574	1.740439	-0.024407
H	2.703696	1.101955	0.698170
H	1.642424	1.728222	-0.202451
O	2.609136	-0.851191	1.522729

O	2.611572	-0.894770	-1.495636
H	2.700878	-1.158869	0.609047
H	1.640146	-1.040176	-1.394881
H	1.638170	-0.688317	1.598547
H	2.704120	0.050412	-1.306386
H	-1.641659	0.426494	1.686304
O	-2.612963	0.596930	1.636011
H	-2.704785	1.044359	0.782097
H	-1.640529	1.248459	-1.213068
O	-2.611377	1.116887	-1.335811
H	-2.700282	0.153296	-1.298466
H	-2.702257	-1.202084	0.513736
O	-2.609652	-1.718214	-0.300412
H	-1.638473	-1.673994	-0.473566

(6) Coordinates of optimized structure of $CO_3(H_2O)_n^{\cdot-}$ level of theory: M062X/ 6-311+G(d,p):

(6-I) n=0:

C	0.072782	-0.000042	-0.000055
O	1.306695	-0.000088	0.000016
O	-0.680545	1.043623	0.000013
O	-0.680736	-1.043503	0.000013

(6-II) n=3:

C	1.391438	0.115013	0.009368
O	1.397940	-0.545586	1.112527
O	1.470170	-0.725788	-0.961034
O	1.287401	1.338553	-0.101269
O	-1.395832	-1.027041	-1.370100
H	-1.540821	-1.232083	-0.432703
H	-0.431377	-1.060570	-1.460107
O	-1.471617	-0.723949	1.496373

O	-1.543807	1.619340	-0.174418
H	-1.611980	0.192212	1.206367
H	-0.587438	1.788490	-0.142522
H	-0.509753	-0.785167	1.600699
H	-1.621304	0.922800	-0.844570

(6-III) n=6:

C	0.013264	-0.054149	0.000000
O	1.284509	0.140201	0.000000
O	-0.551066	-1.149665	0.000000
O	-0.564925	1.094258	0.000000
O	-0.857270	-1.445649	2.859403
H	0.088771	-1.272362	2.986721
H	-0.932419	-1.605777	1.907536
O	1.636325	0.008156	2.922734
O	-0.857270	1.417512	2.903756
H	0.985217	0.717195	3.050285
H	-0.898141	1.593510	1.954265
H	1.835813	0.050464	1.978213
H	-1.167381	0.500094	2.982098
H	1.835813	0.050464	-1.978213
O	1.636325	0.008156	-2.922734
H	0.088771	-1.272362	-2.986721
H	0.985217	0.717195	-3.050285
O	-0.857270	1.417512	-2.903756
H	-0.898141	1.593510	-1.954265
H	-0.932419	-1.605777	-1.907536
O	-0.857270	-1.445649	-2.859403
H	-1.167381	0.500094	-2.982098

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