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# Electronic Supplementary Information

## Examining Structural Evolution of Bicarbonate-Water Clusters: Insights from Photoelectron Spectroscopy, Basin-Hopping Structural Search, and Comparison with Available IR Spectra Studies

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Table S1. Optimized structures and bond parameters of $HCO_3^-(H_2O)_2$ under different DFT functionals with same basis set (6-311++G**), and compared with MP2 method.

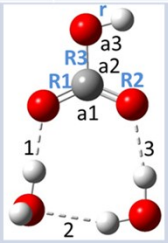
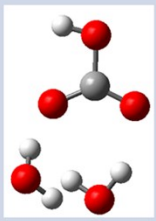
| | | Functionals | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | B3LYP | O3LYP | X3LYP | PW91 | MP2 | M06-2X | M06-L |
| Bond Length | 1 | 1.69337 | 1.75483 | 1.68651 | 1.64596 | 1.68991 | | |
| | 2 | 2.05667 | 2.25816 | 2.04236 | 1.99027 | 2.06269 | | |
| | 3 | 1.88727 | 1.94759 | 1.88042 | 1.85835 | 1.88803 | | |
| Configuration | |   | | | | |  | |

Table S2. Top 12 occupied molecular orbital e

| n | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HOMO | 4.097 | 4.844 | 5.153 | 5.541 | 5.787 | 6.097 | 6.247 | 6.380 | 6.415 | 6.528 | 6.552 | 6.605 |
| -1 | 4.662 | 5.331 | 5.662 | 6.130 | 6.454 | 6.613 | 6.762 | 6.764 | 6.877 | 6.957 | 7.009 | 7.083 |
| -2 | 5.016 | 5.677 | 6.039 | 6.472 | 6.746 | 7.012 | 6.934 | 6.938 | 6.997 | 7.127 | 7.144 | 7.332 |
| -3 | 5.875 | 6.057 | 6.094 | 6.704 | 6.853 | 7.055 | 6.974 | 7.013 | 7.095 | 7.228 | 7.338 | 7.371 |
| -4 | 8.221 | 6.547 | 6.772 | 6.807 | 6.966 | 7.200 | 7.084 | 7.134 | 7.160 | 7.299 | 7.399 | 7.515 |
| -5 | 9.183 | 8.498 | 6.823 | 7.138 | 7.147 | 7.332 | 7.183 | 7.282 | 7.298 | 7.323 | 7.438 | 7.542 |
| -6 | 9.389 | 8.876 | 8.337 | 7.158 | 7.235 | 7.544 | 7.213 | 7.315 | 7.381 | 7.418 | 7.519 | 7.604 |
| -7 | 10.094 | 9.905 | 8.677 | 8.842 | 7.410 | 7.563 | 7.402 | 7.485 | 7.046 | 7.468 | 7.543 | 7.162 |
| -8 | 12.851 | 10.083 | 9.397 | 9.068 | 9.108 | 7.838 | 7.663 | 7.736 | 7.729 | 7.525 | 7.664 | 7.723 |
| -9 | 23.562 | 10.778 | 10.238 | 9.305 | 9.209 | 9.142 | 7.816 | 7.770 | 7.973 | 7.621 | 7.714 | 7.829 |
| -10 | 24.212 | 11.504 | 10.568 | 9.636 | 9.336 | 9.424 | 8.970 | 8.000 | 7.986 | 7.711 | 7.780 | 7.847 |
| -11 | 26.795 | 13.733 | 10.940 | 10.674 | 9.553 | 9.474 | 9.126 | 8.932 | 8.394 | 8.039 | 7.809 | 7.954 |
| -12 | 277.701 | 24.201 | 11.817 | 10.824 | 9.922 | 9.763 | 9.278 | 9.198 | 9.011 | 8.113 | 7.847 | 8.023 |

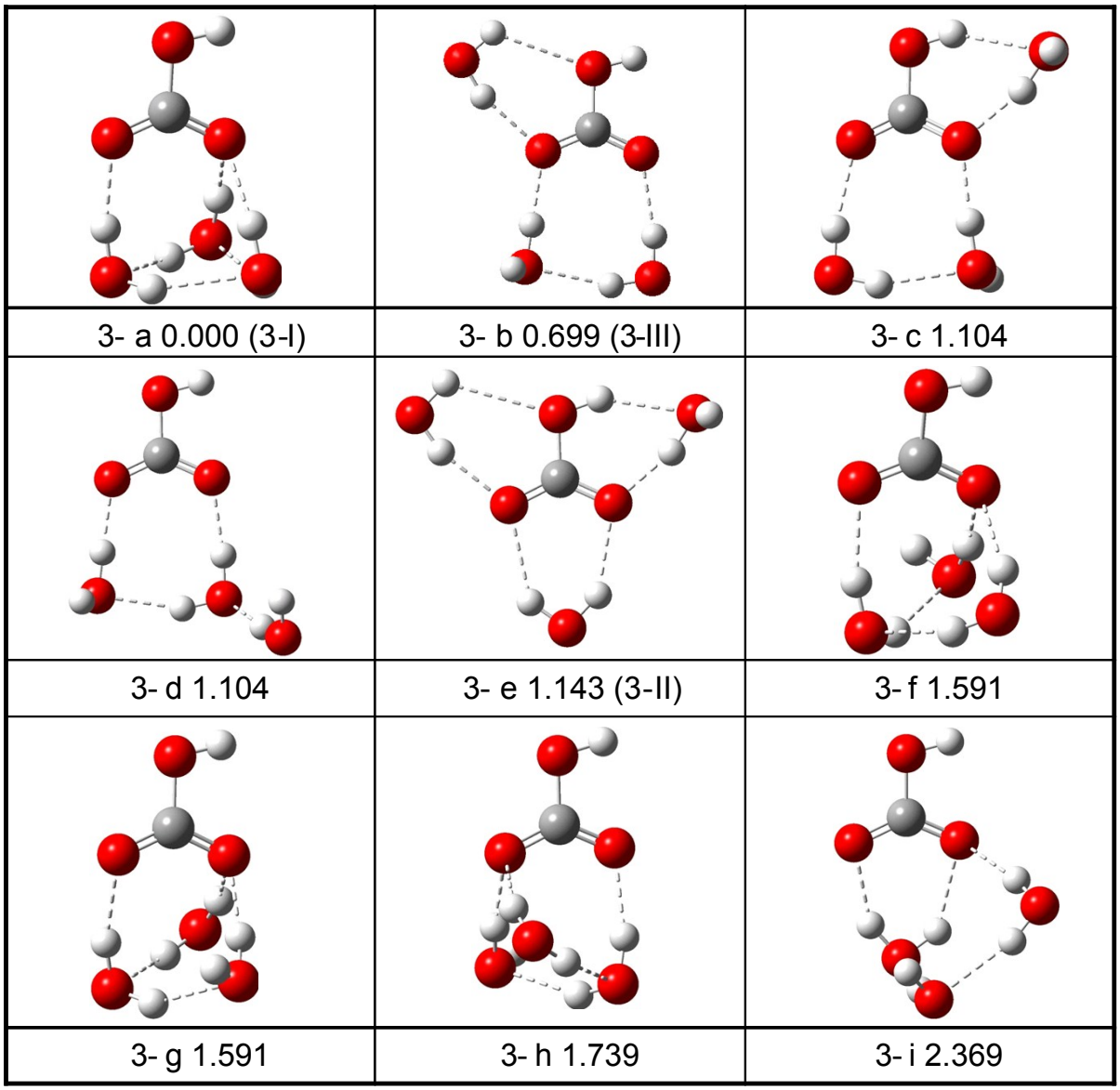



Figure S1. Low-lying isomers of $HCO_3^-(H_2O)_3$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

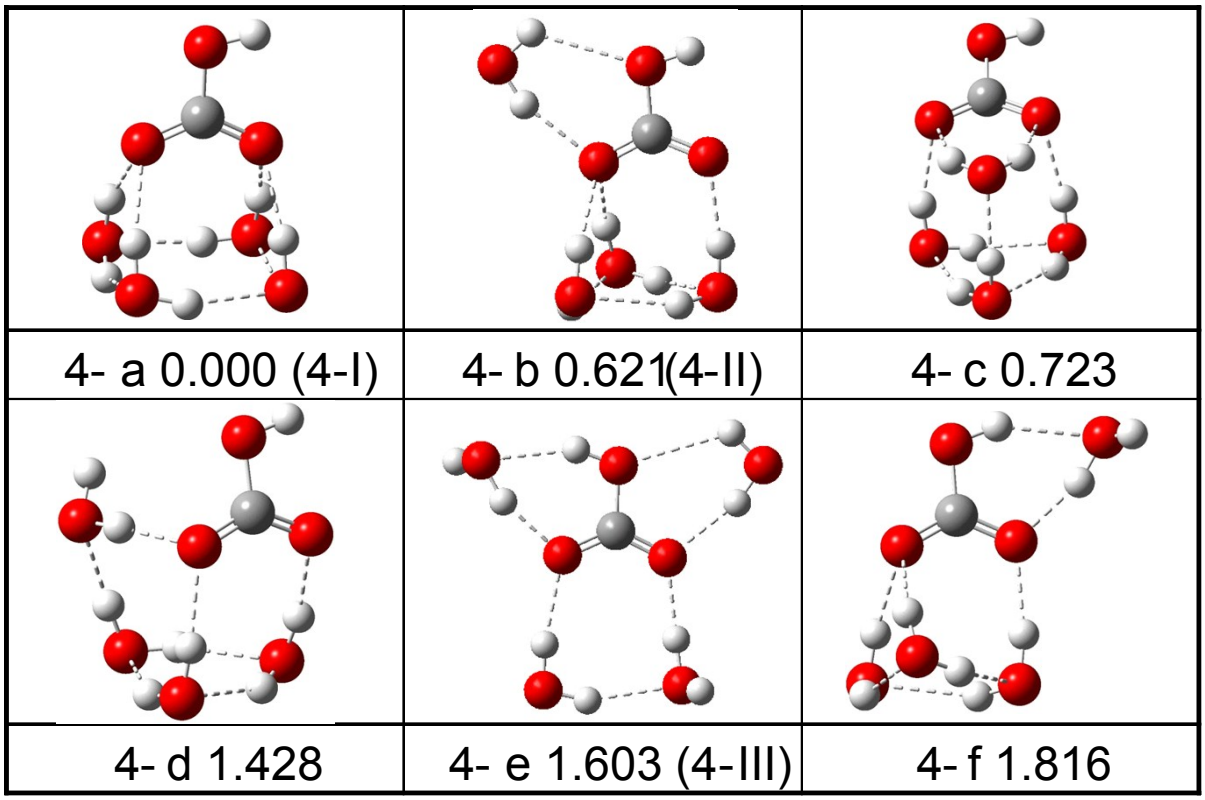



Figure S2. Low-lying isomers of $HCO_3^-(H_2O)_4$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

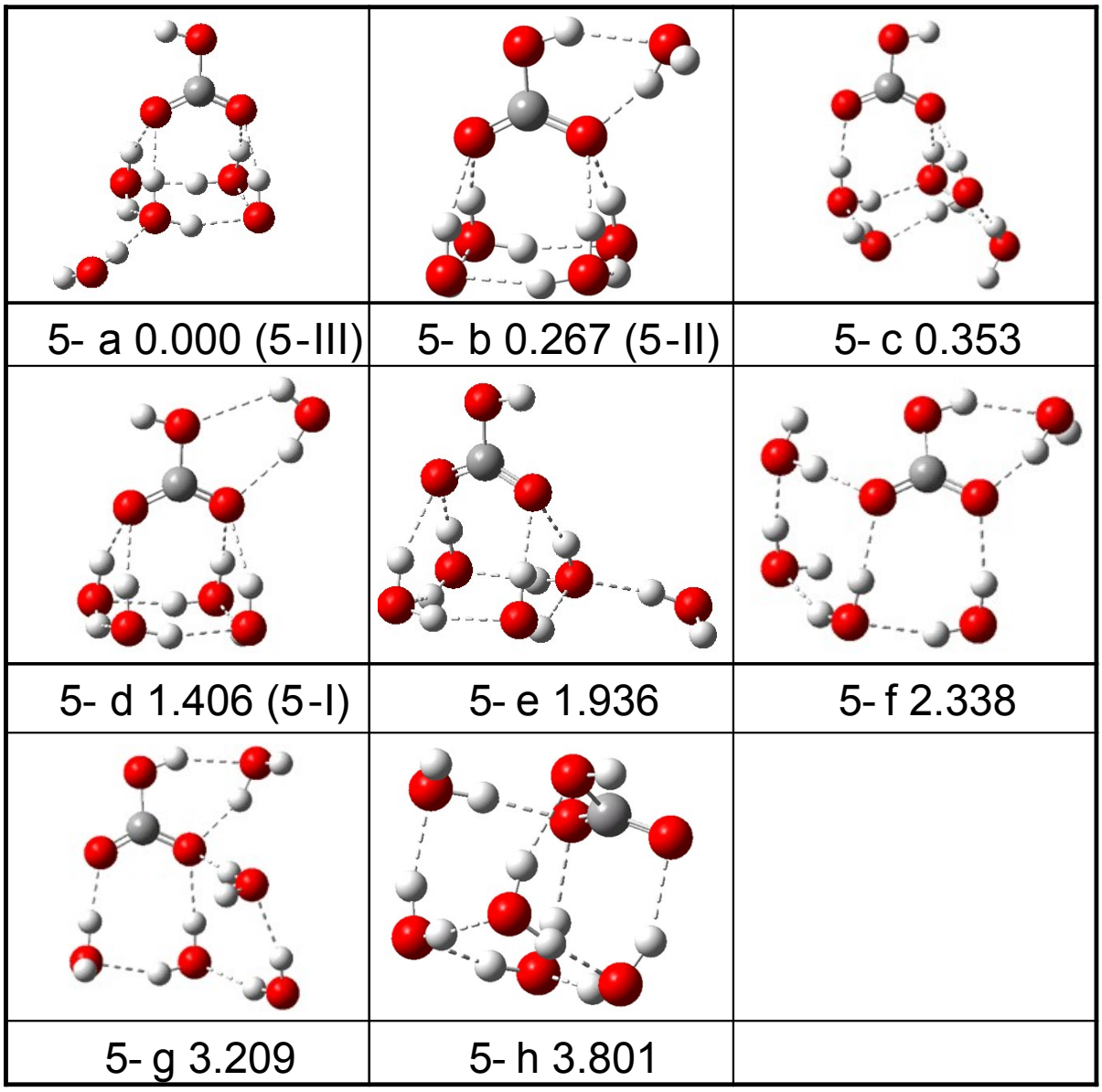



Figure S3. Low-lying isomers of $HCO_3^-(H_2O)_5$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

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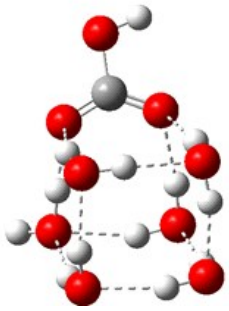
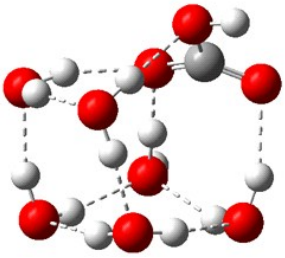
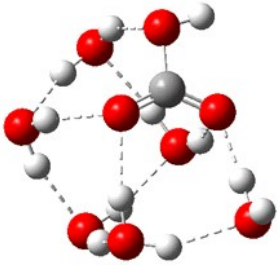
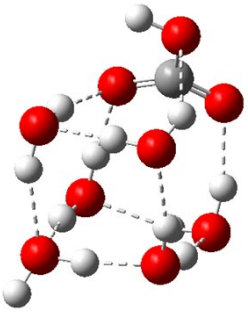
|  |  |  |  |
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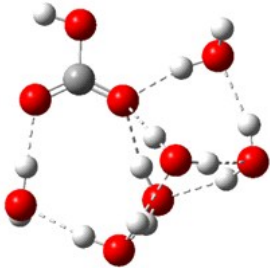
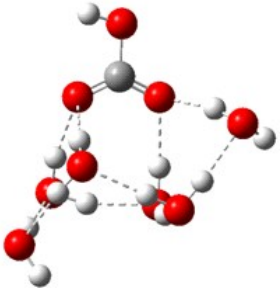
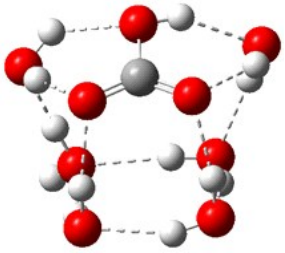
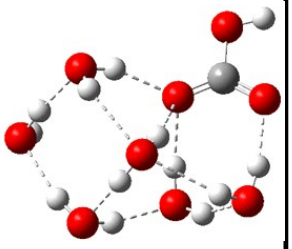
|  |  |  |  |
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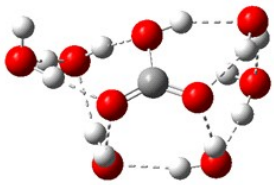
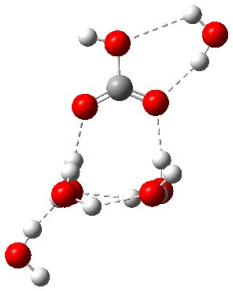
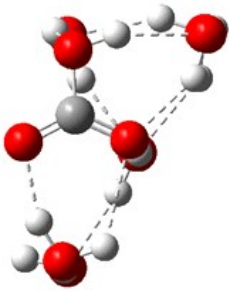
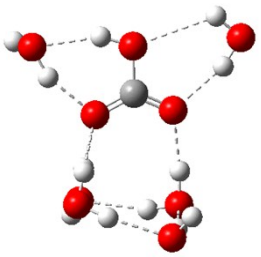
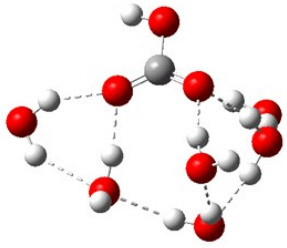
|  |  |  |  |
| 6- i 4.015 | 6- j 4.311 (6-I) | 6- k 4.819 | 6- l 5.036 (6-II) |
|  | | | |
| 6- m 8.897 | | | |

Figure S4. Low-lying isomers of $HCO_3^-(H_2O)_6$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

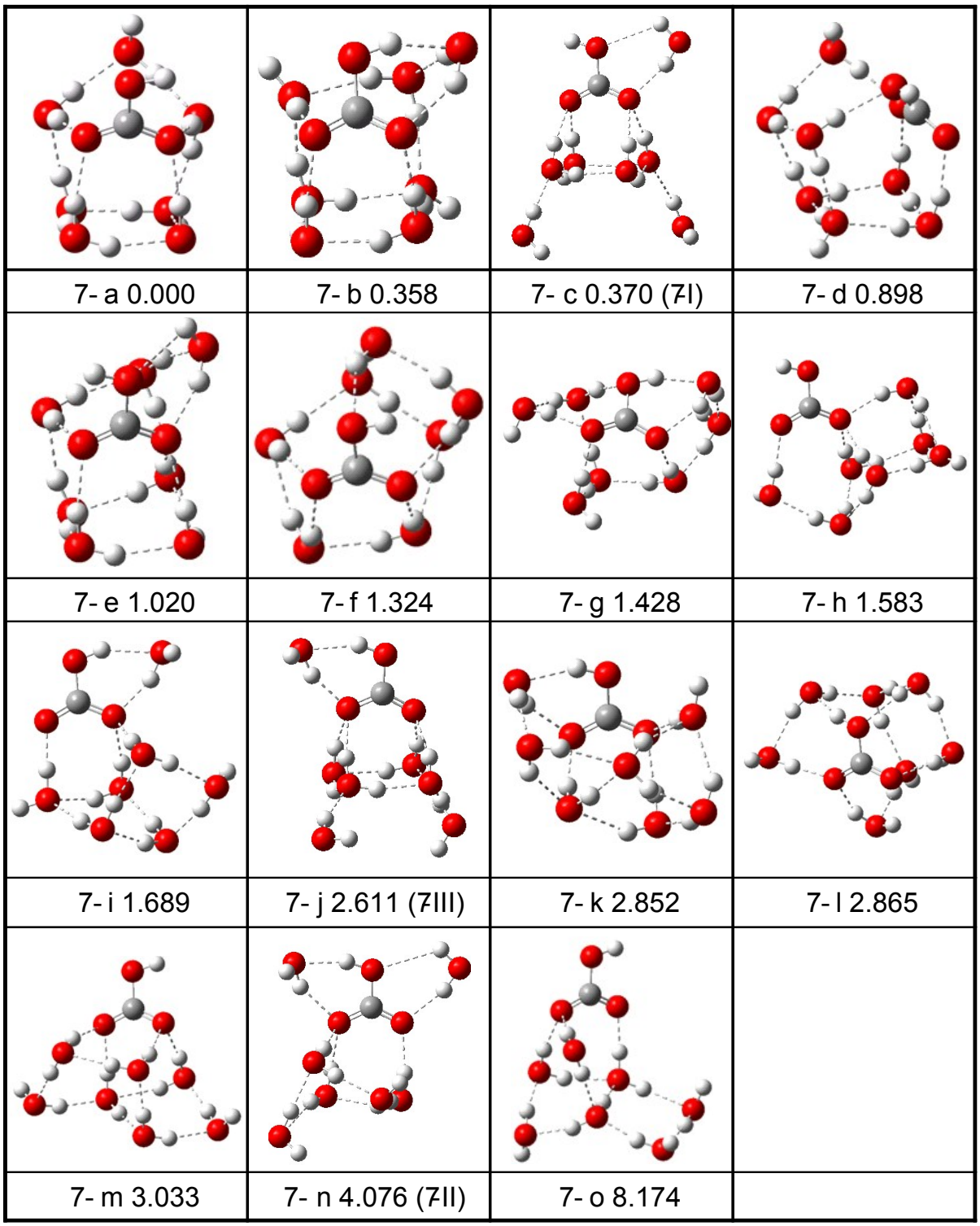



Figure S5. Low-lying isomers of $HCO_3^-(H_2O)_7$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

| | | | |
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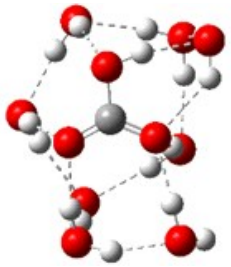
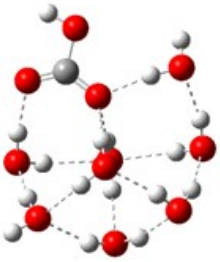
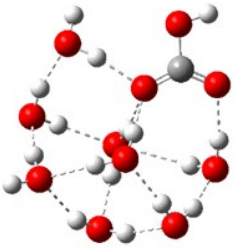
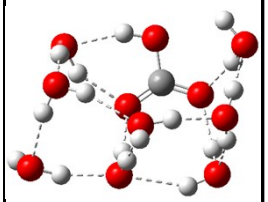
|  |  |  |  |
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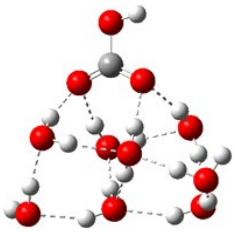
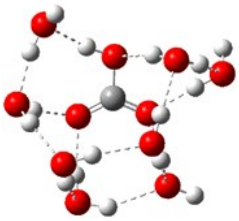
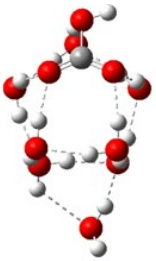
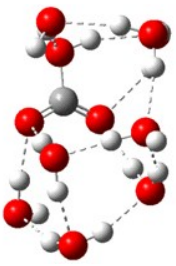
|  |  |  |  |
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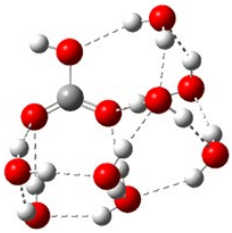
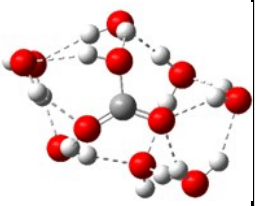
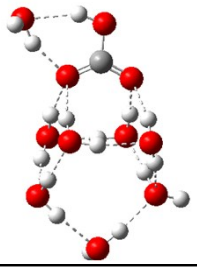
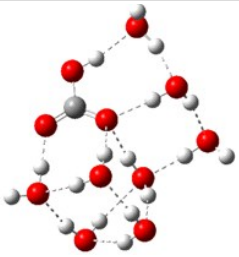
|  |  |  |  |
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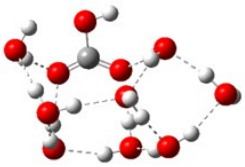
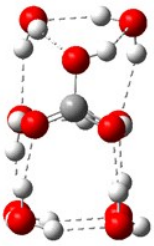
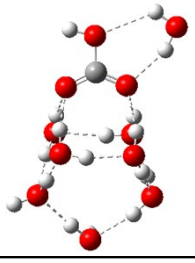
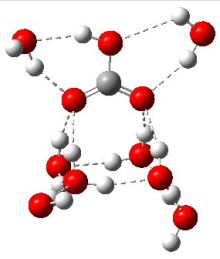
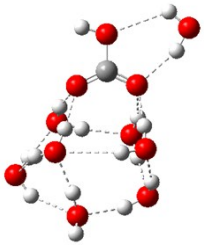
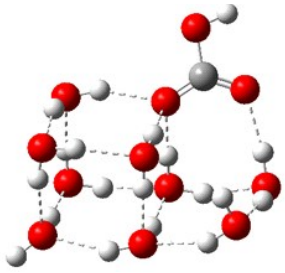
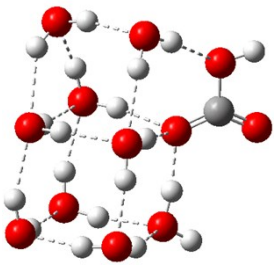
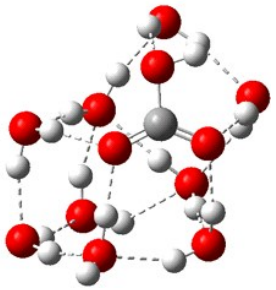
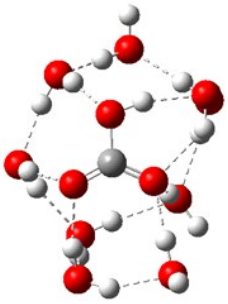
|  |  |  |  |
| 8- m 3.332 | 8- n 3.789 | 8- o 4.211 | 8- p 5.840 (8-III) |
|  | | | |
| 8- q 7.317 (8-I) | | | |

Figure S6. Low-lying isomers of $HCO_3^-(H_2O)_8$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated. The structures that are similar to those in the work of Neumark & Asmis are also labeled in parentheses.

| | | | |
|---|---|---|---|
|  |  |  |  |
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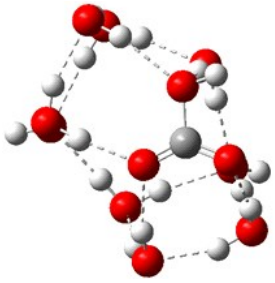
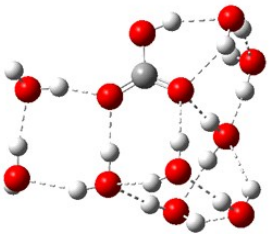
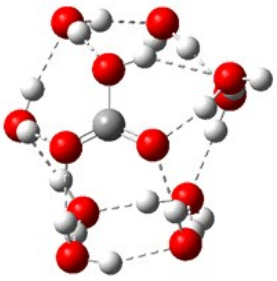
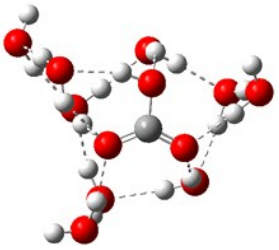
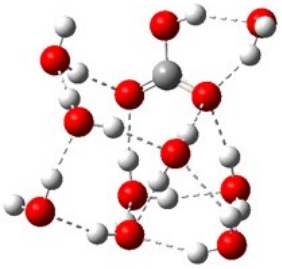
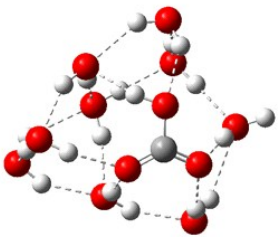
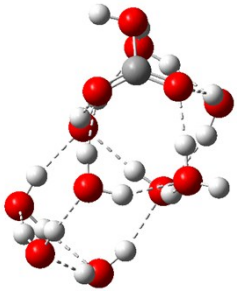
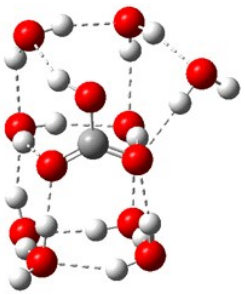
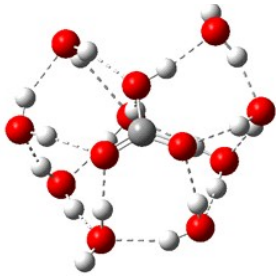
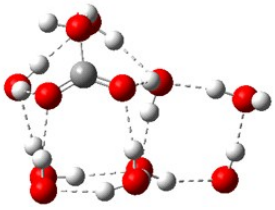
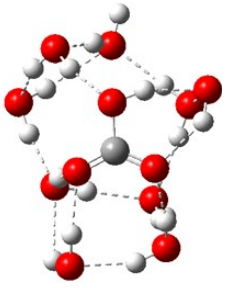
|  |  |  |  |
| 9- e 1.202 | 9- f 1.598 | 9- g 1.635 | 9- h 2.024 |
|  |  |  |  |
| 9- i 2.232 | 9- j 2.275 | 9- k 2.349 | 9- l 2.350 |
|  |  |  | |
| 9- m 2.435 | 9- n 2.639 | 9- o 2.737 | |

Figure S7. Low-lying isomers of $HCO_3^-(H_2O)_9$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated.

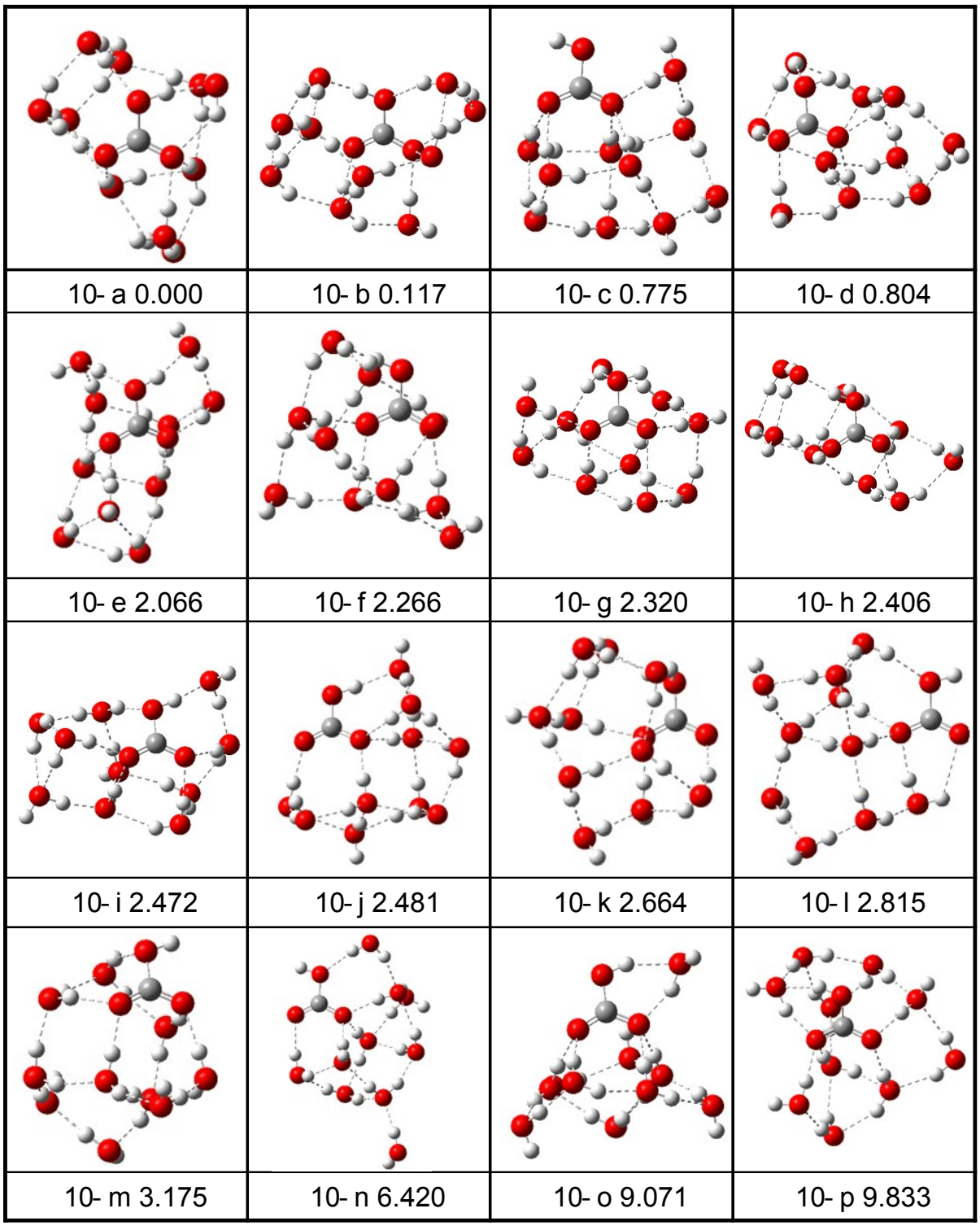



Figure S8. Low-lying isomers of $HCO_3^-(H_2O)_{10}$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated.

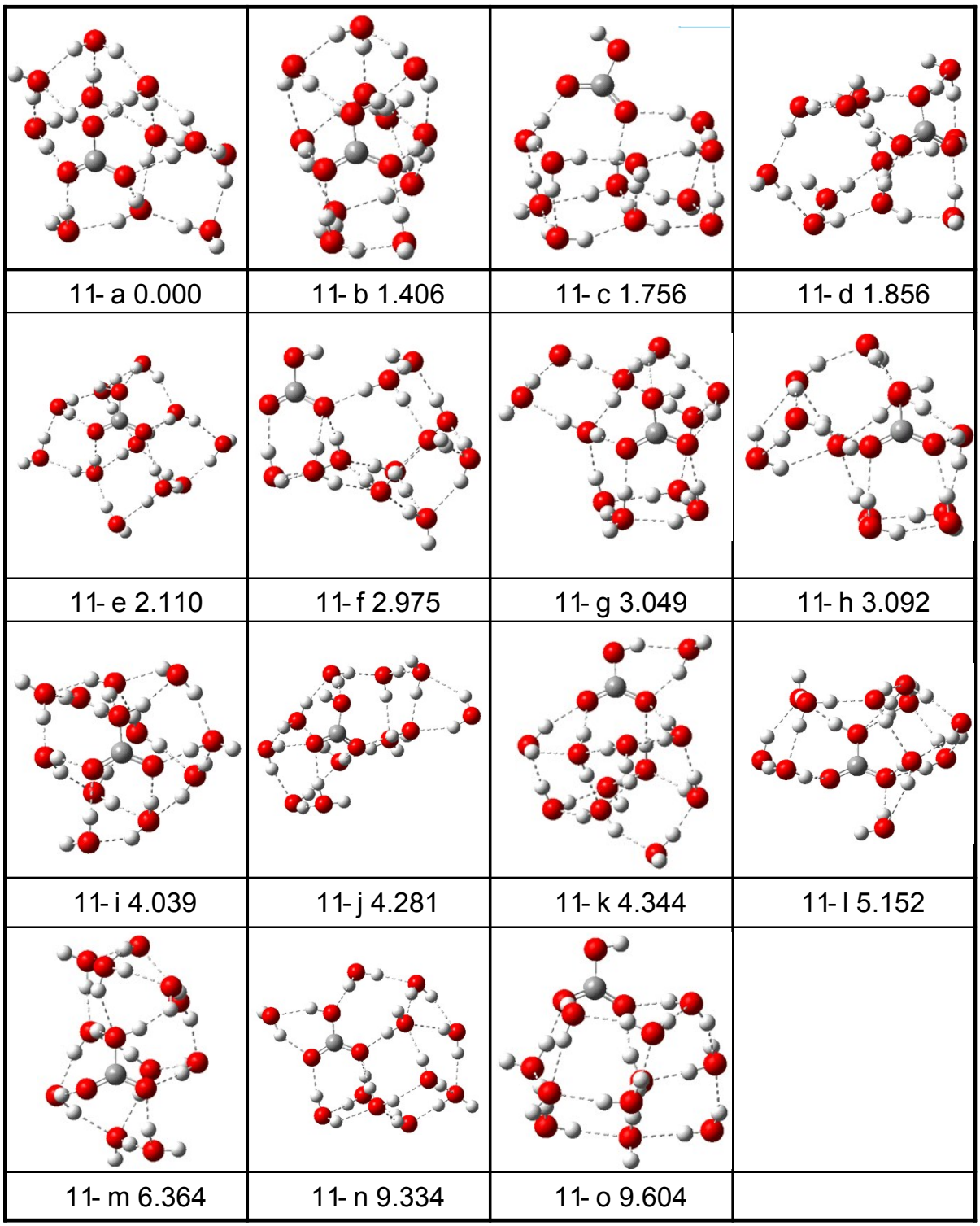



Figure S9. Low-lying isomers of $HCO_3^-(H_2O)_{11}$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated.

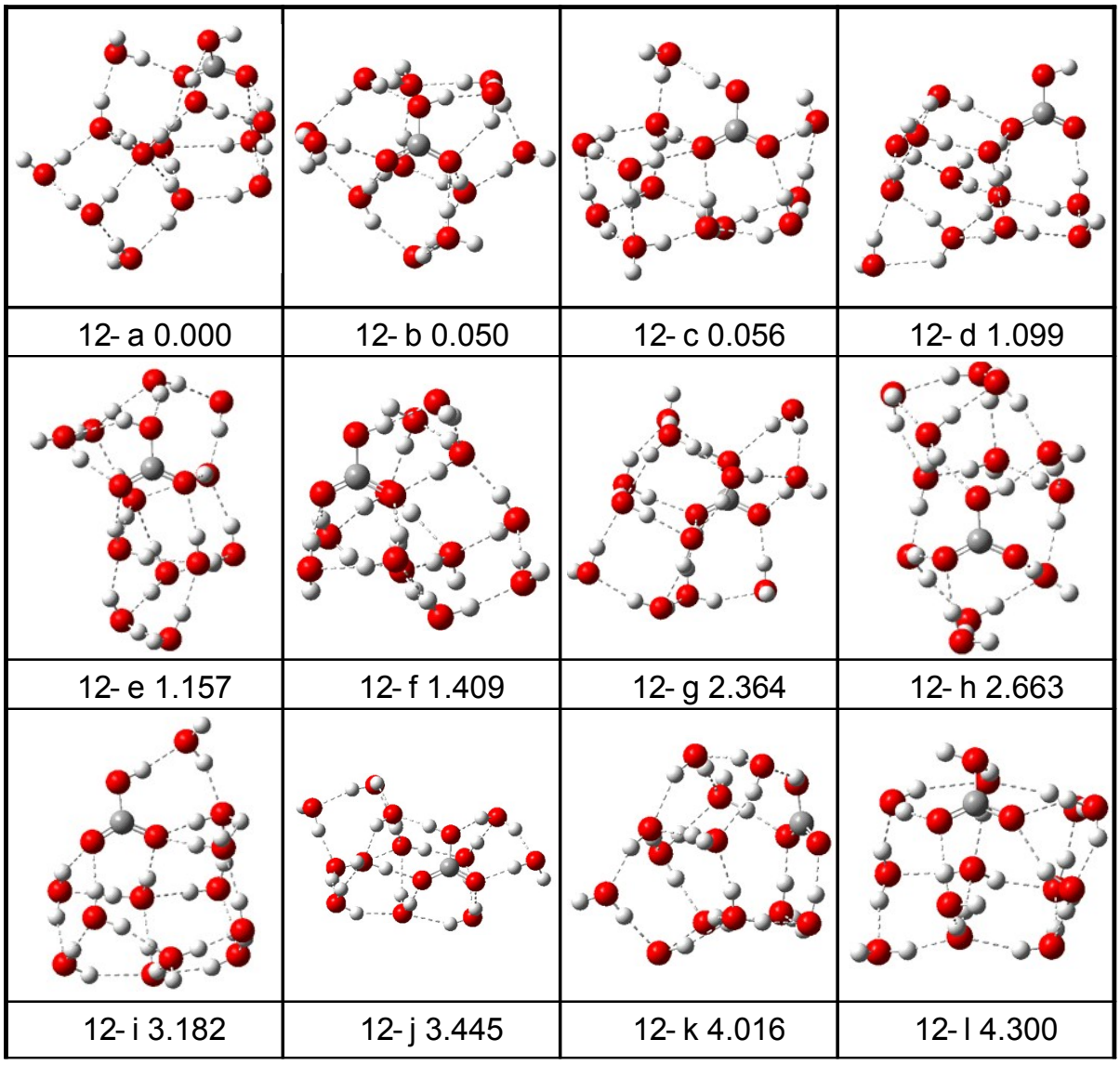



Figure S10. Low-lying isomers of $HCO_3^-(H_2O)_{12}$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated.

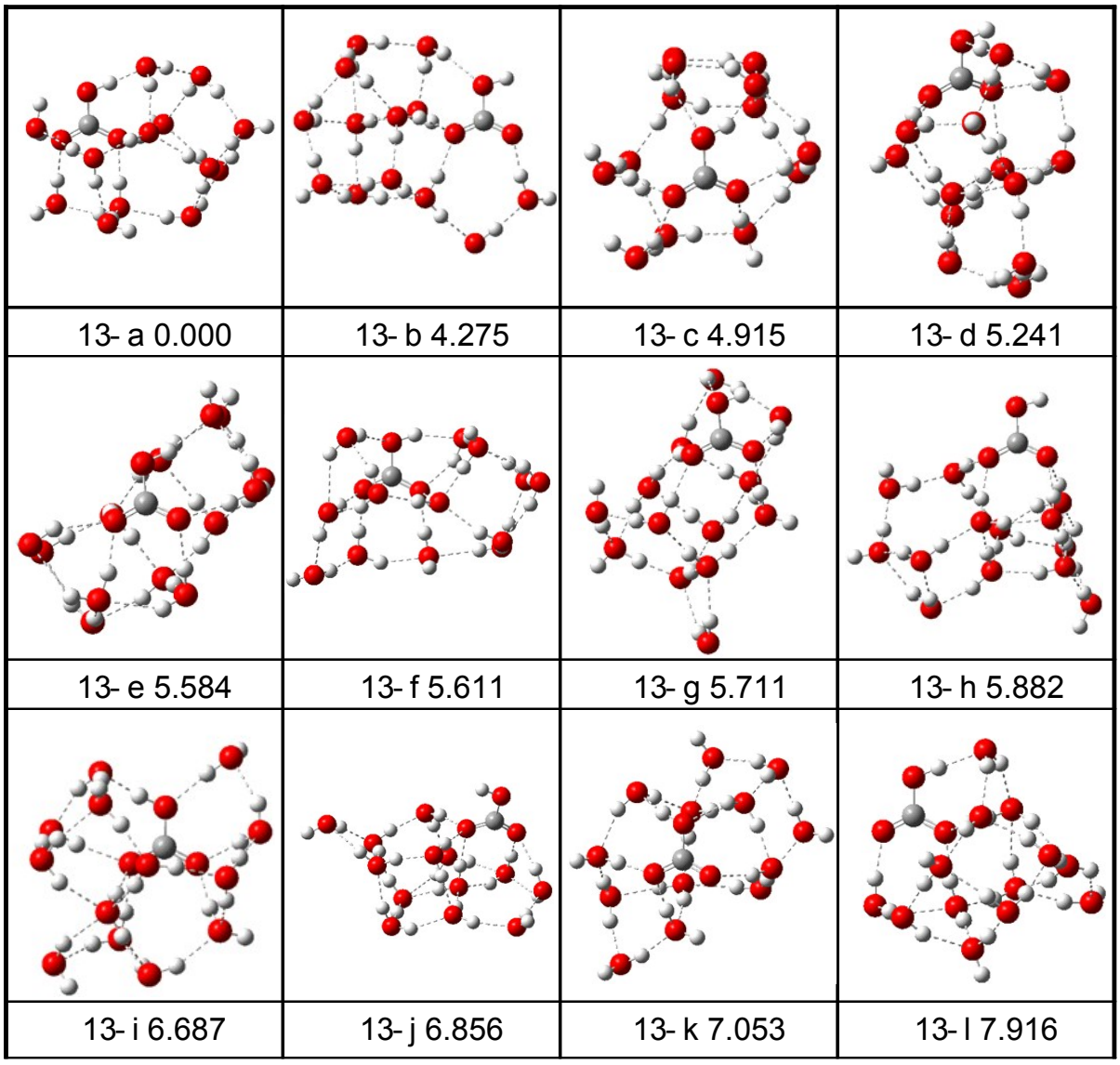



Figure S11. Low-lying isomers of $HCO_3^-(H_2O)_{13}$ under B3LYP/6-311++G(3df, 3pd) level of theory, relative energies (in kcal/mol) are indicated.

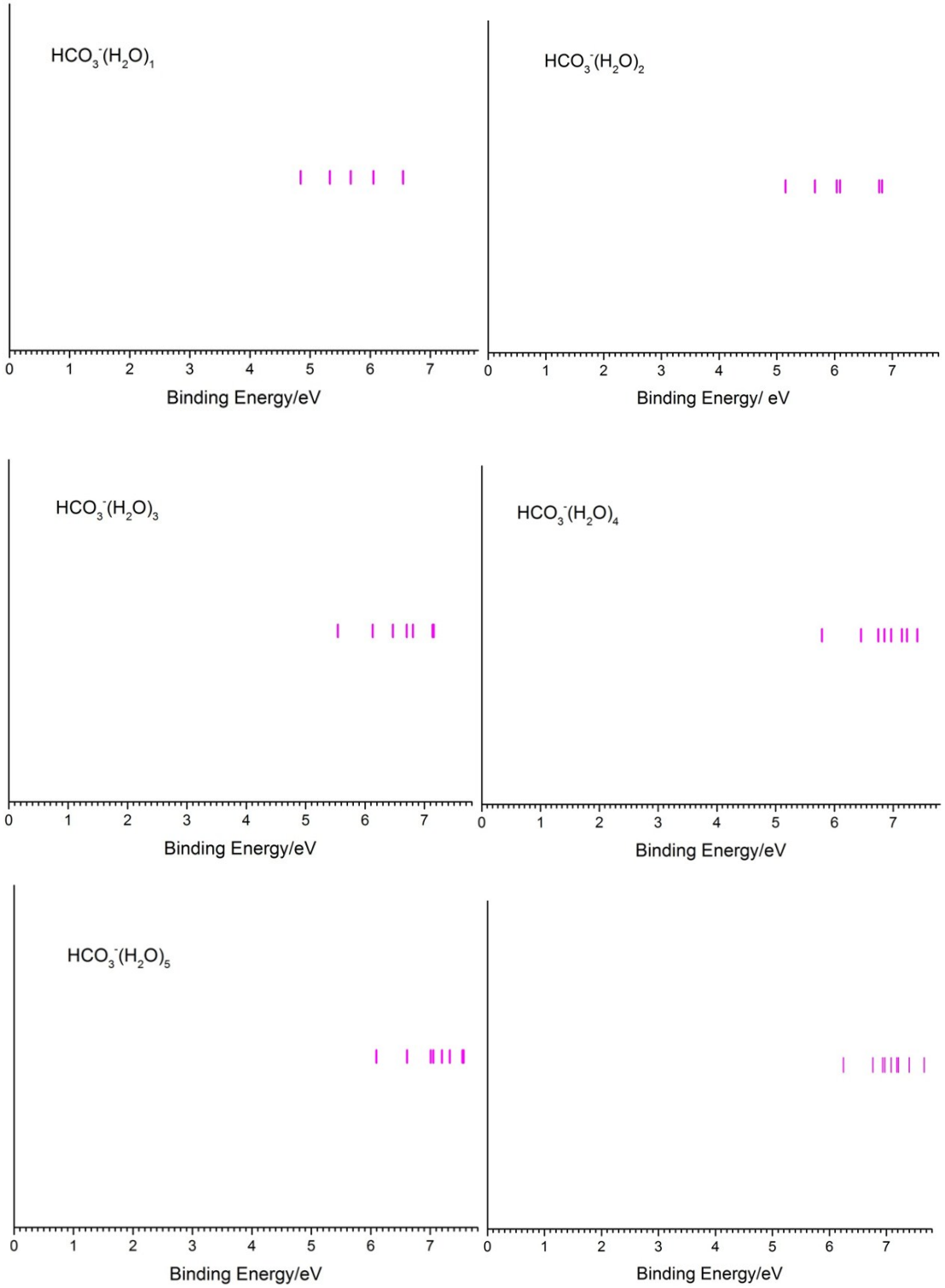



Figure S12. The stick density of states (DOS) spectra of the minimum energy isomer of $HCO_3^-(H_2O)_{1\text{-}6}$.

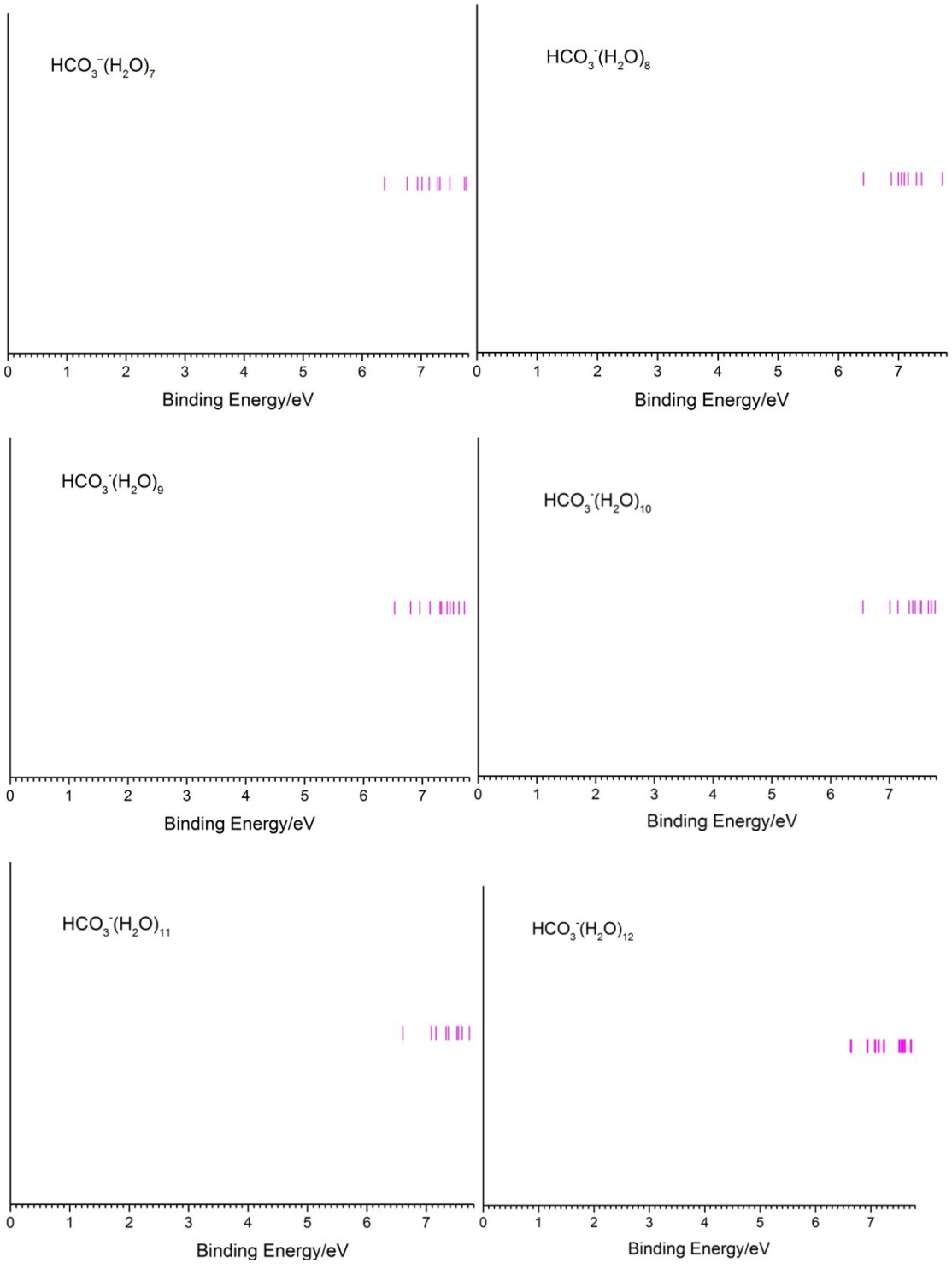



Figure S13. The stick density of states (DOS) spectra of $HCO_3^-(H_2O)_{7\text{-}12}$.

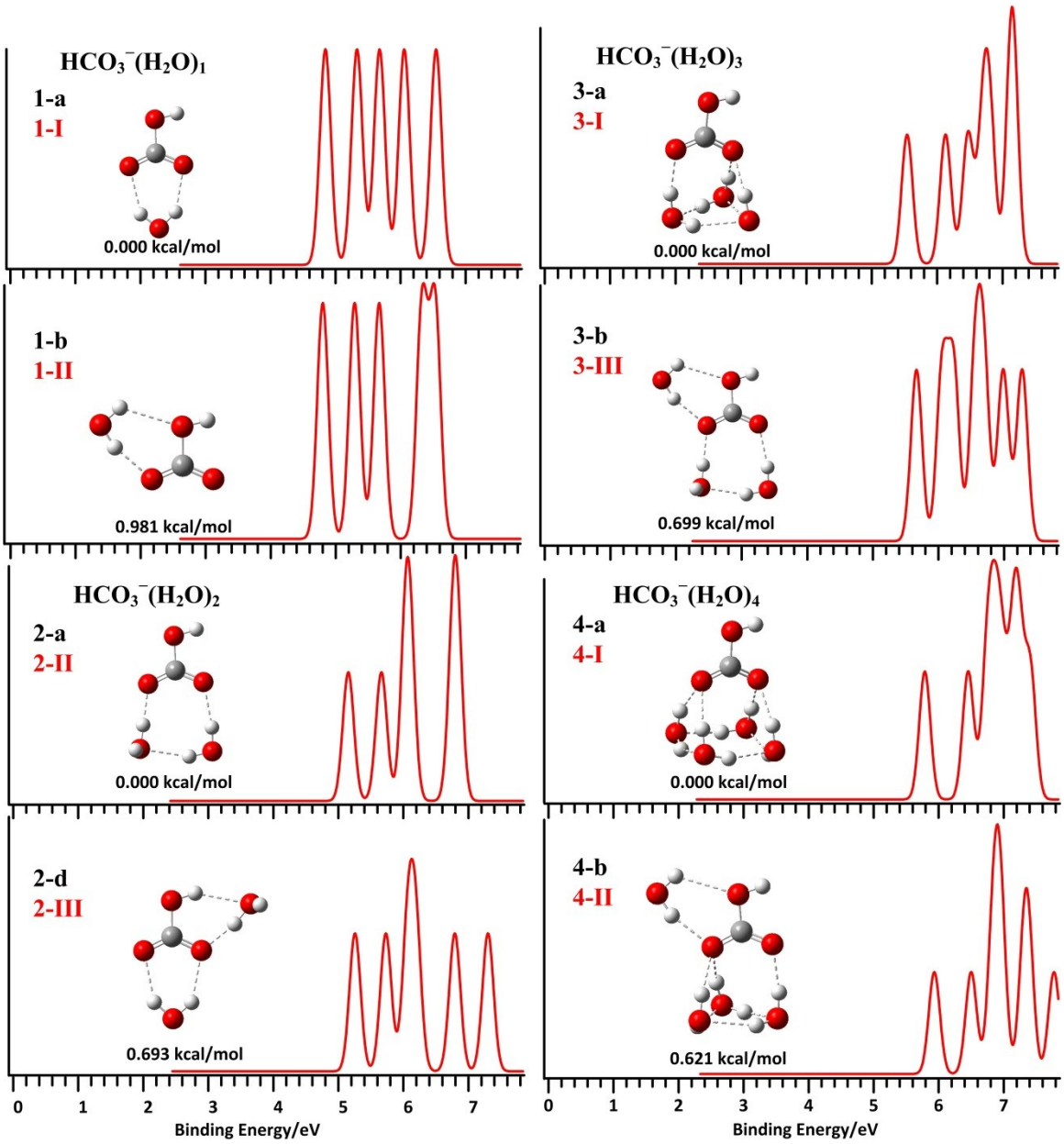



Figure S14. Simulated PES spectra of $HCO_3^-(H_2O)_n$, n=1-4 accompany with structures, and relative energies (in kcal/mol) of the low-lying isomers at the B3LYP/6-311++(3df,3pd) level of theory, marked n-a and n-b, respectively. Any structures that are similar to those in the work of Neumark and Asmis are also labeled in red.

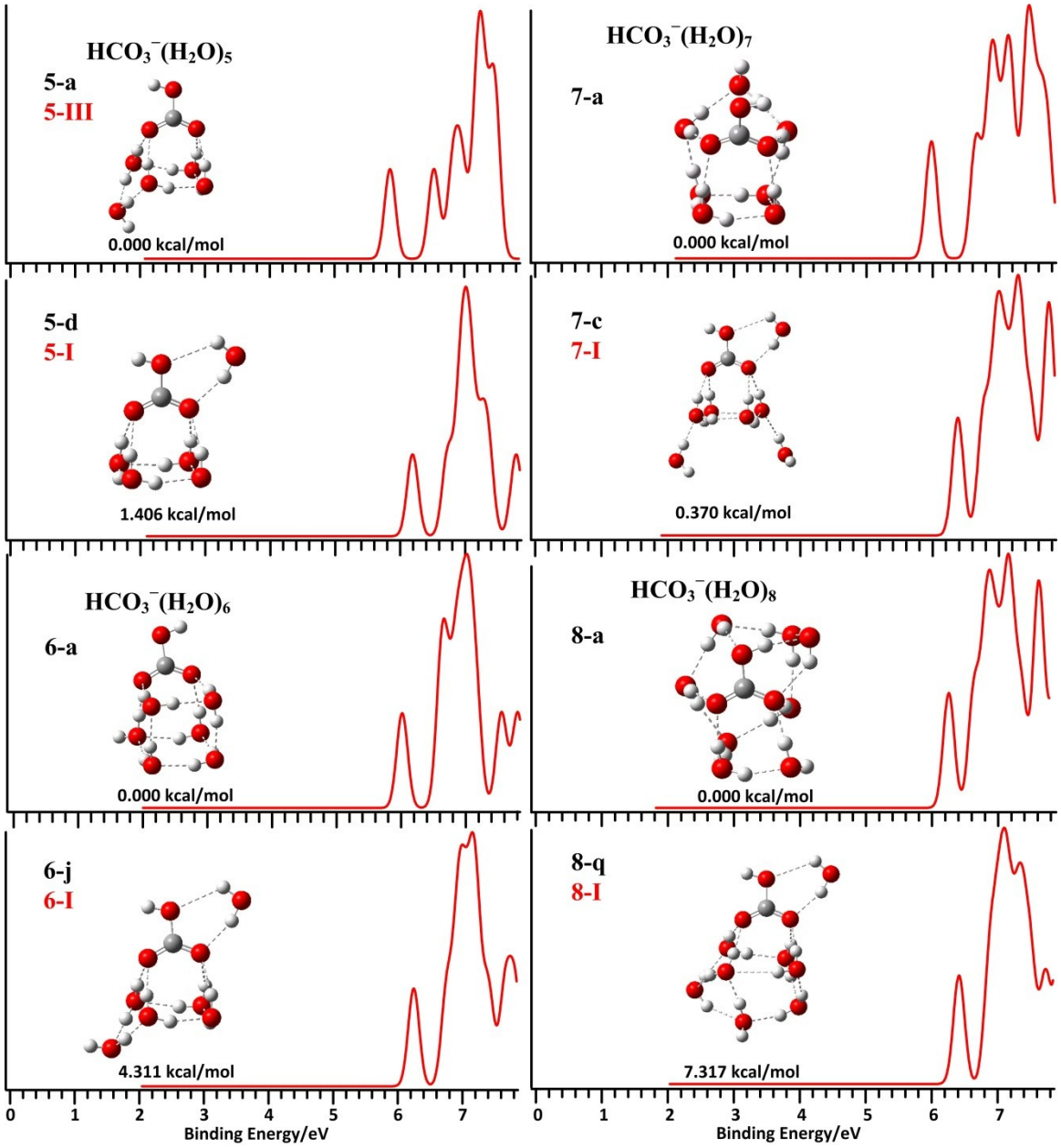



Figure S15. Simulated PES spectra of $HCO_3^-(H_2O)_n$, n=5-8 accompany with structures, and relative energies (in kcal/mol) of the low-lying isomers at the B3LYP/6-311++(3df,3pd) level of theory, marked n-a and n-b, respectively.

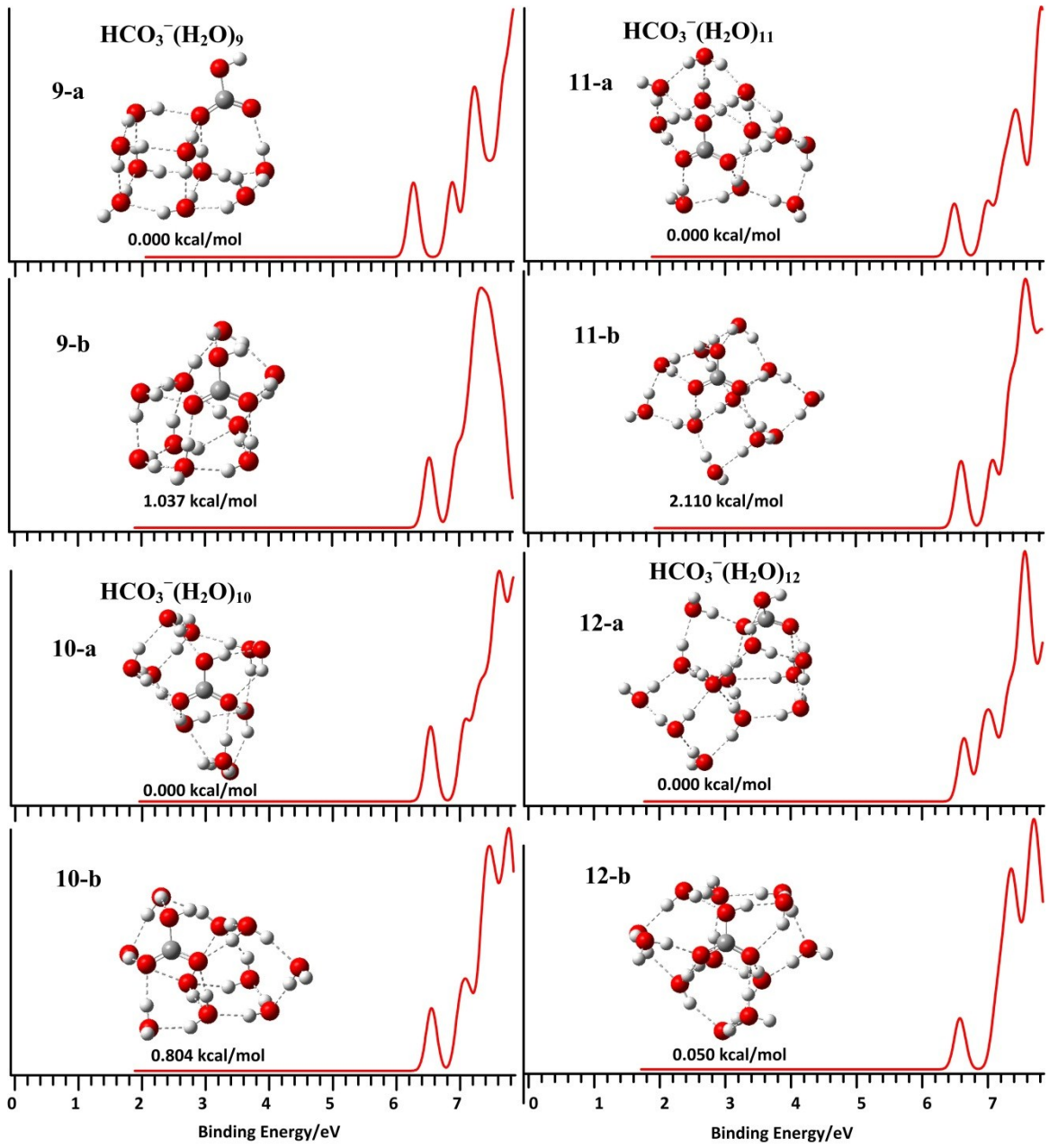



Figure S16. Simulated PES spectra of $HCO_3^-(H_2O)_n$, n=9-12 accompany with structures, and relative energies (in kcal/mol) of the low-lying isomers at the B3LYP/6-311++(3df,3pd) level of theory, marked n-a and n-b, respectively.

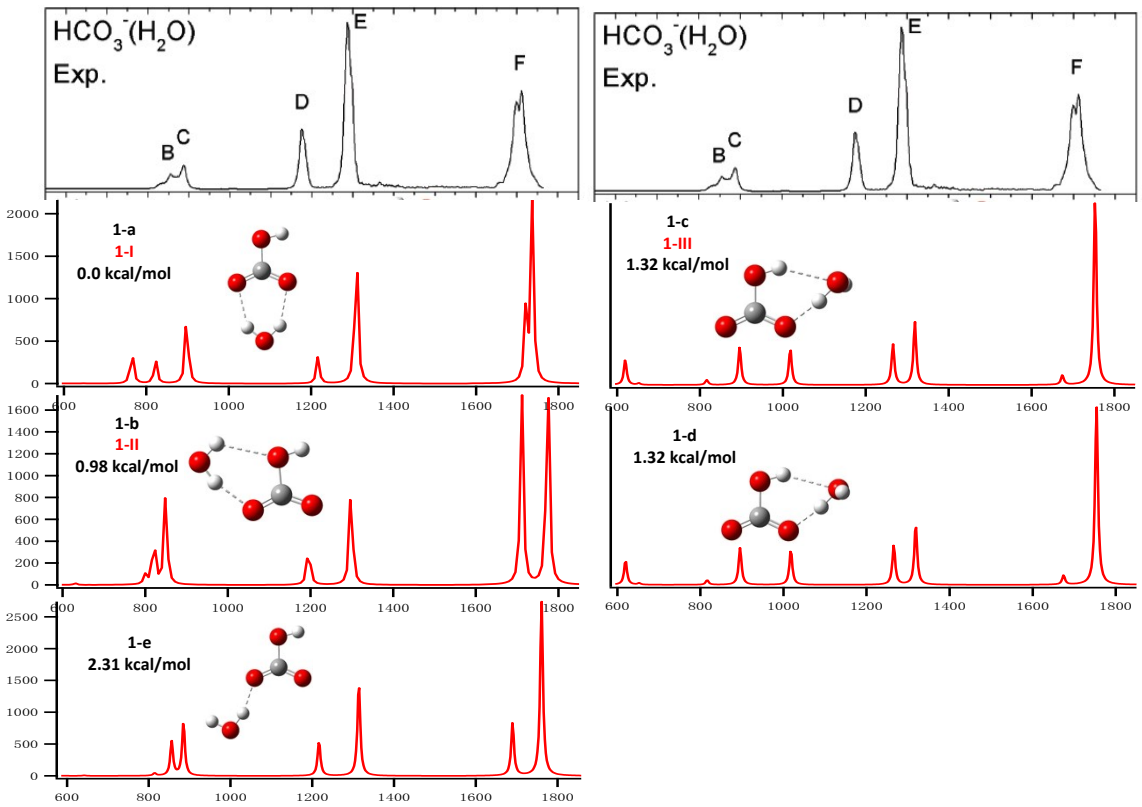



Fig. S17 Experimental (copied from Ref. 20) and theoretical infrared spectra of $HCO_3^-(H_2O)_1$, clusters.

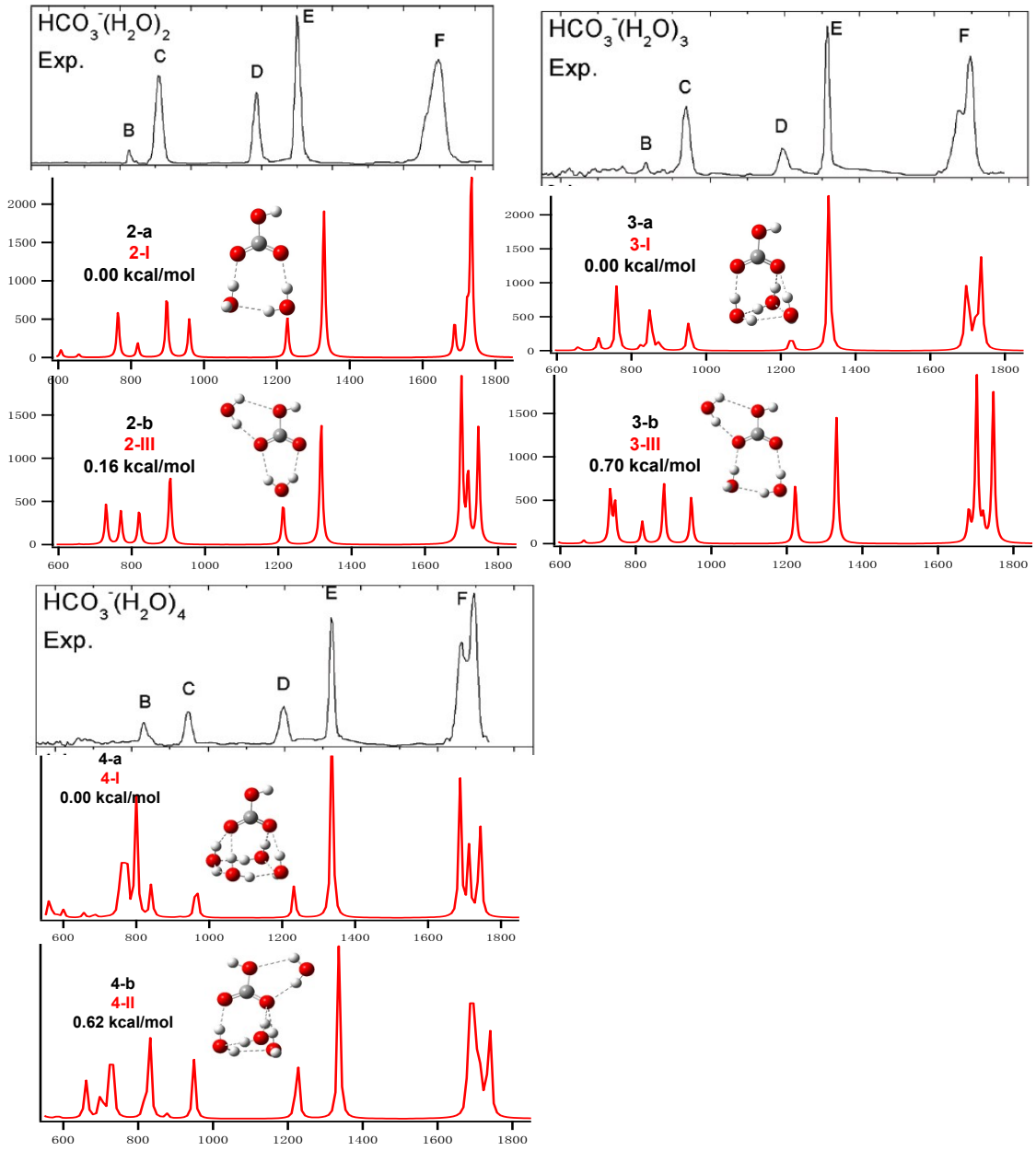



Fig. S18 Experimental (copied from Ref. 20) and theoretical infrared spectra of $HCO_3^-(H_2O)_n$, n=2-4 clusters.

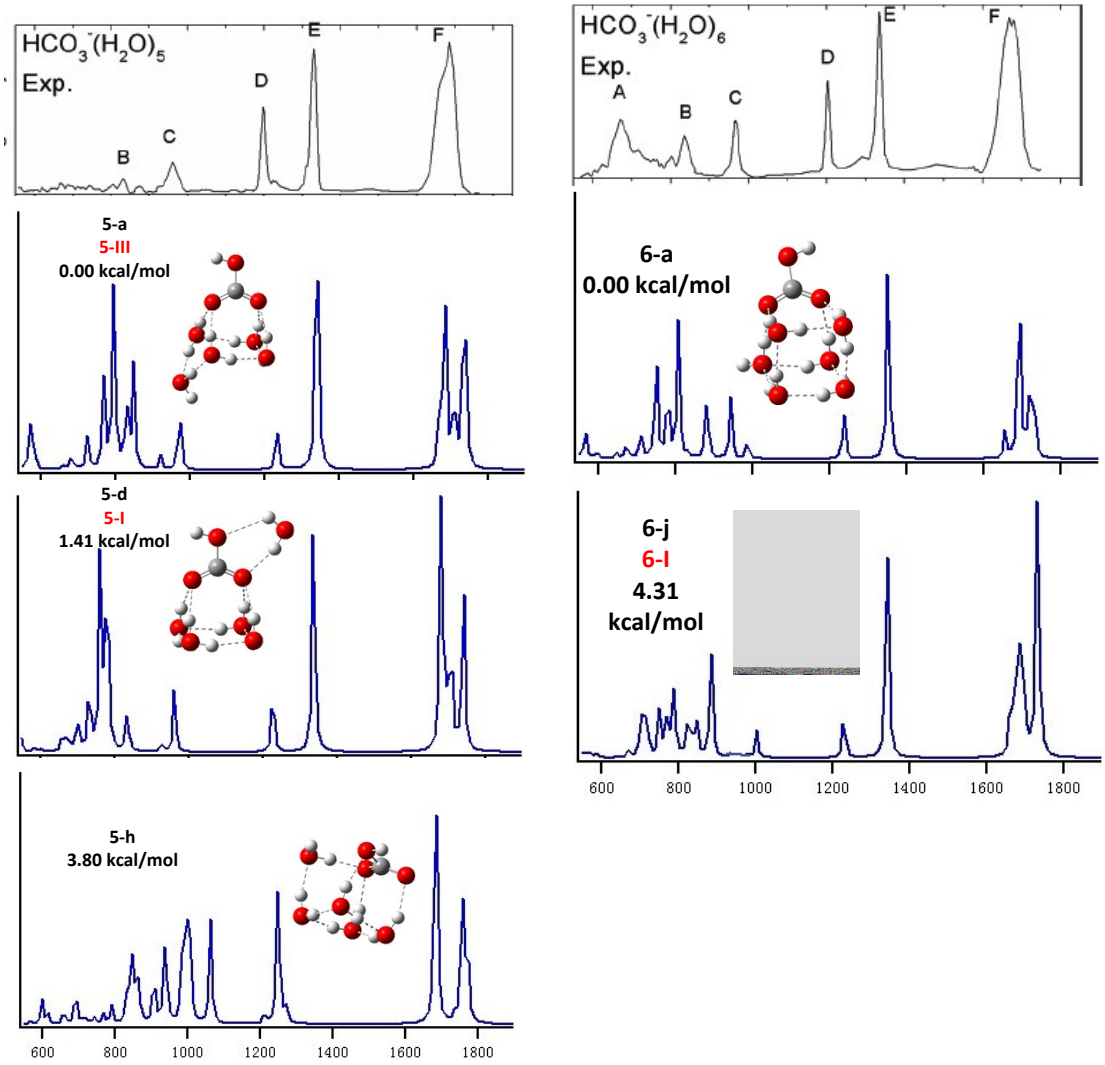



Fig. S19 Experimental (copied from Ref. 20) and theoretical infrared spectra of $HCO_3^-(H_2O)_5$ and $HCO_3^-(H_2O)_6$ clusters.

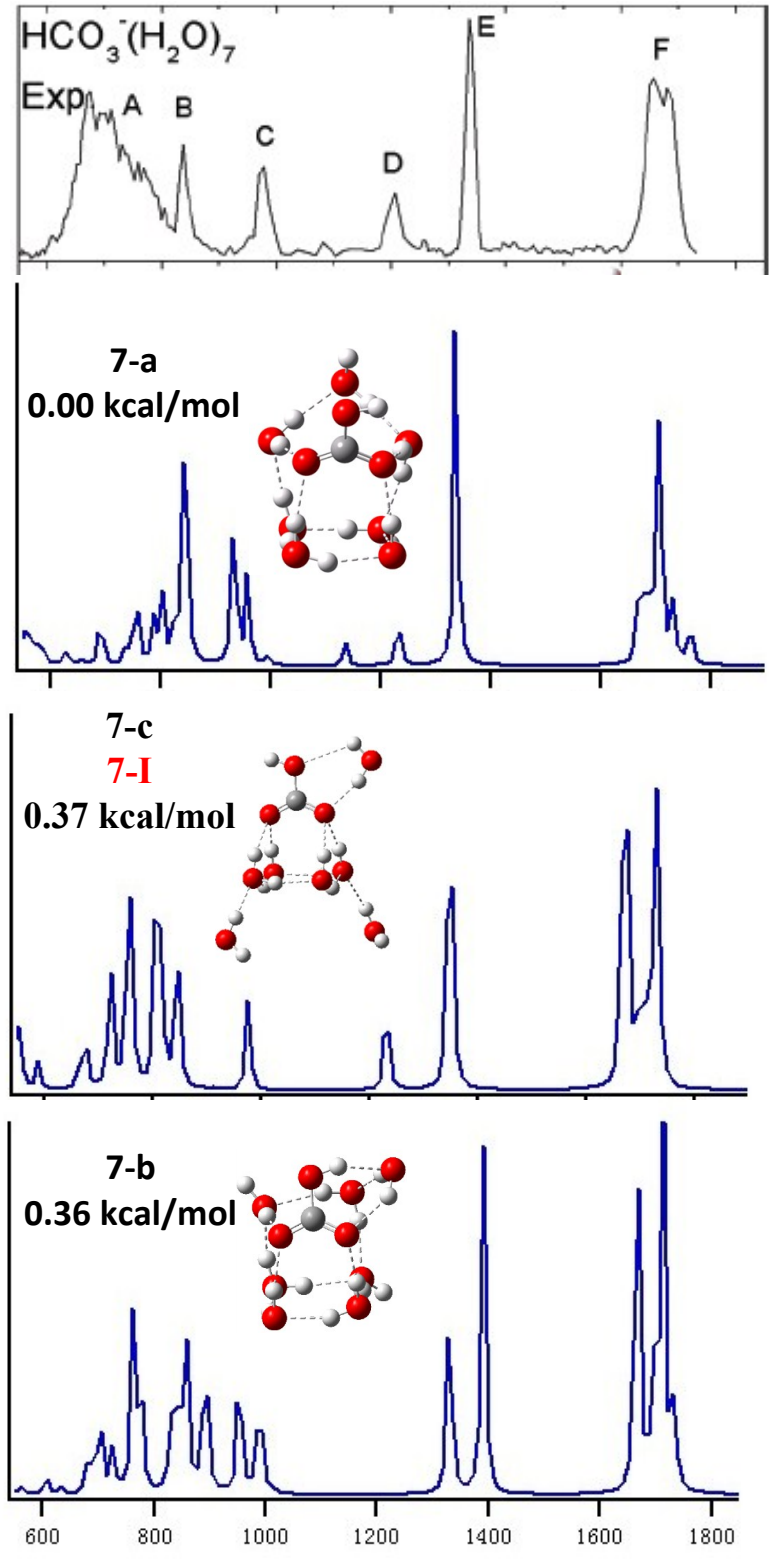



Fig. S20 Experimental (copied from Ref. 20) and theoretical infrared spectra of $HCO_3^-(H_2O)_7$ clusters.

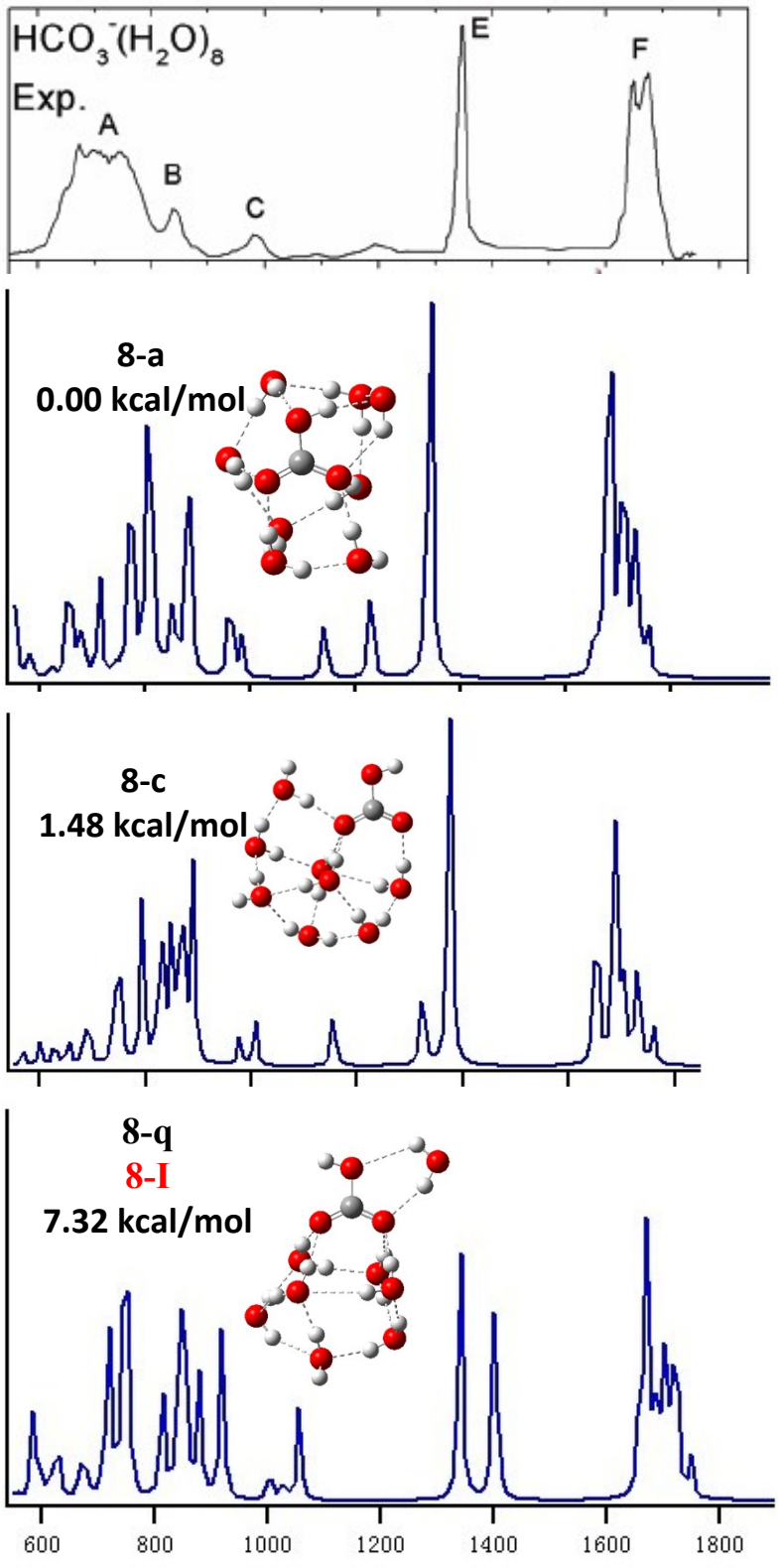



Fig. S21 Experimental (copied from Ref. 20) and theoretical infrared spectra of $HCO_3^-(H_2O)_8$ clusters.

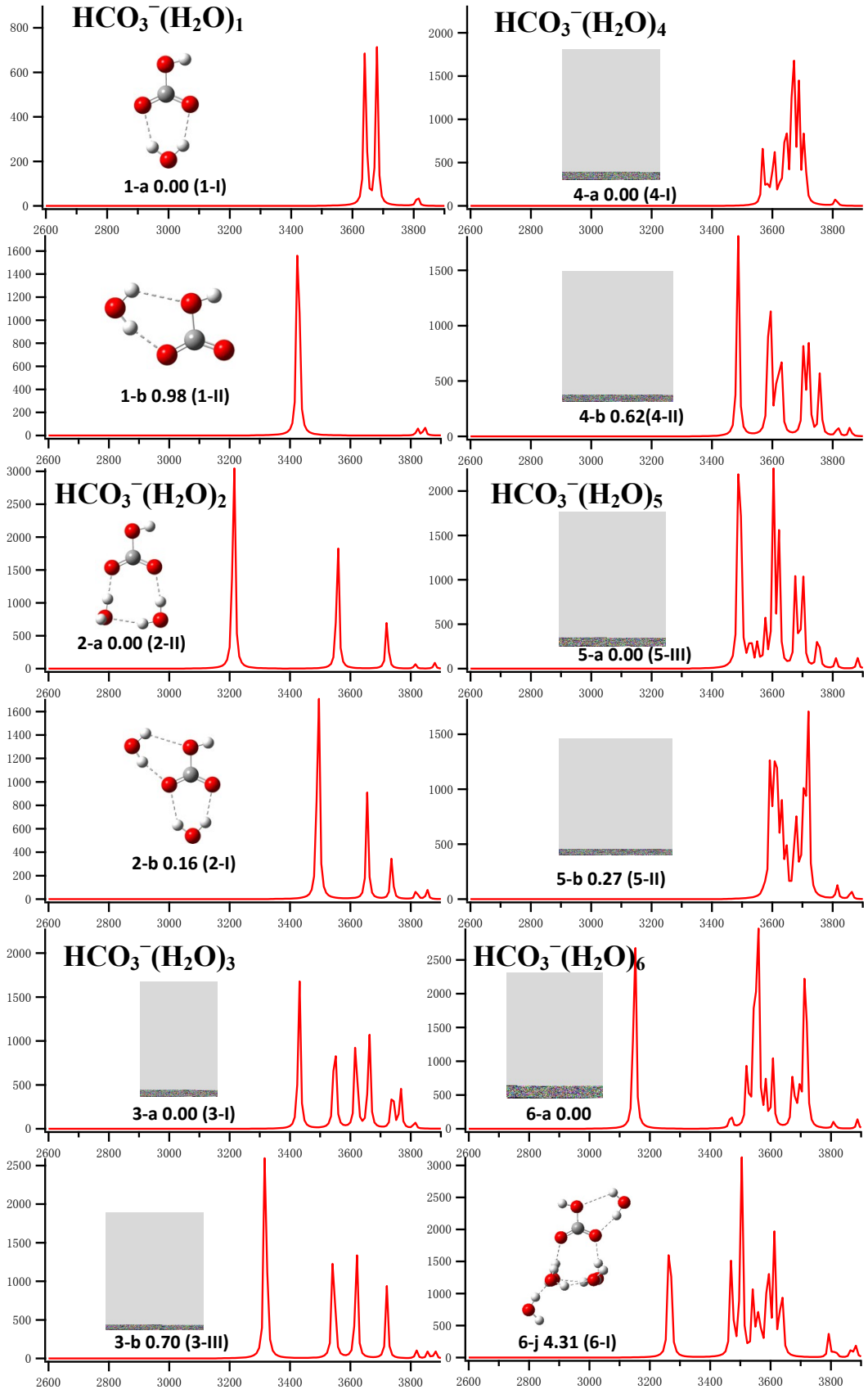



Fig. S22 Simulated IR spectra (O-H stretching mode: 2600-3900 $cm^{-1}$) of $HCO_3^-(H_2O)_n$, n=1-6 clusters at B3LYP/6-311++G(3df, 3pd).

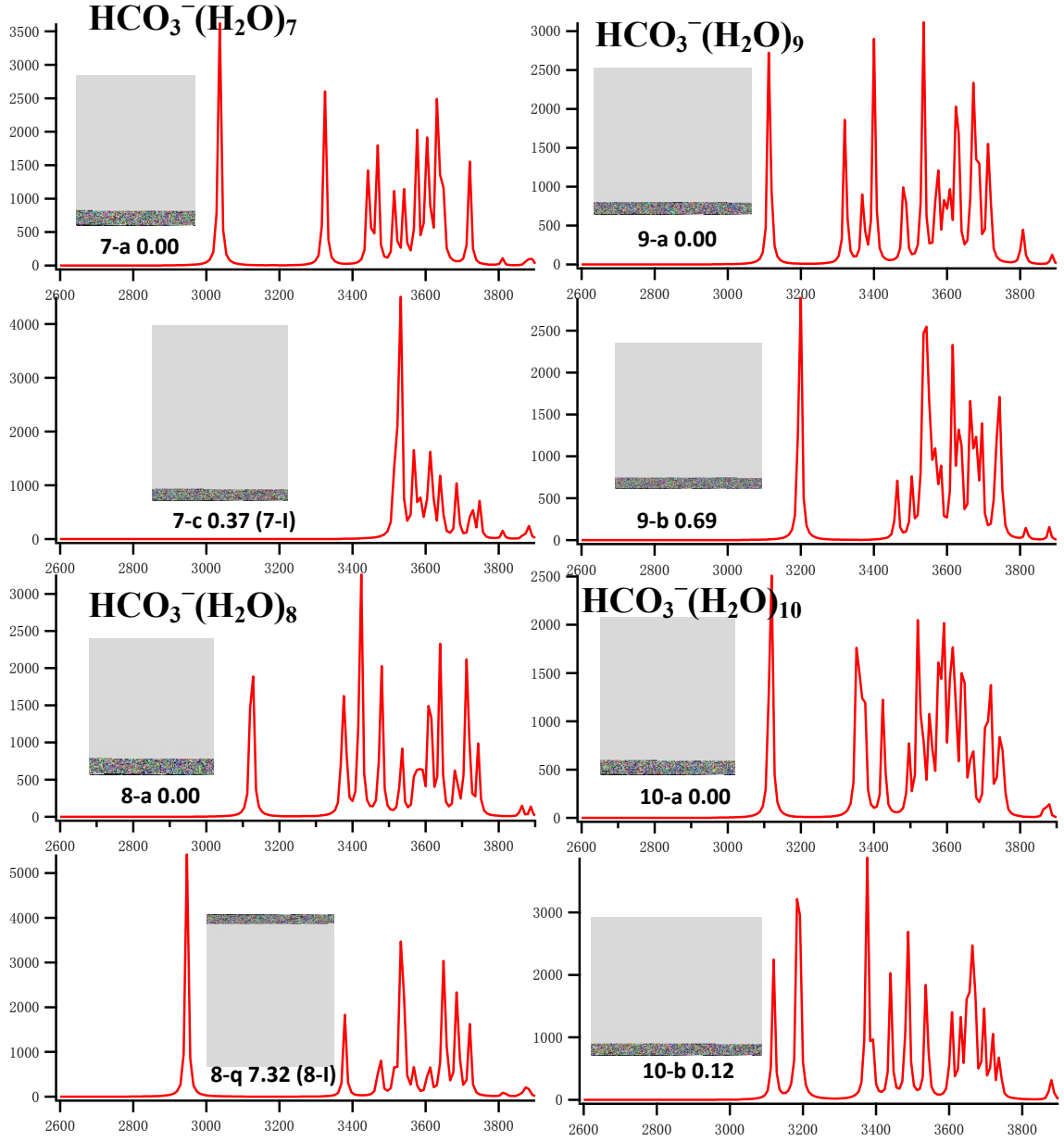



Fig. S23 Simulated IR spectra (O-H stretching mode: 2600-3900 $cm^{-1}$) of $HCO_3^-(H_2O)_n$, n=7-10 clusters at B3LYP/6-311++G(3df, 3pd).

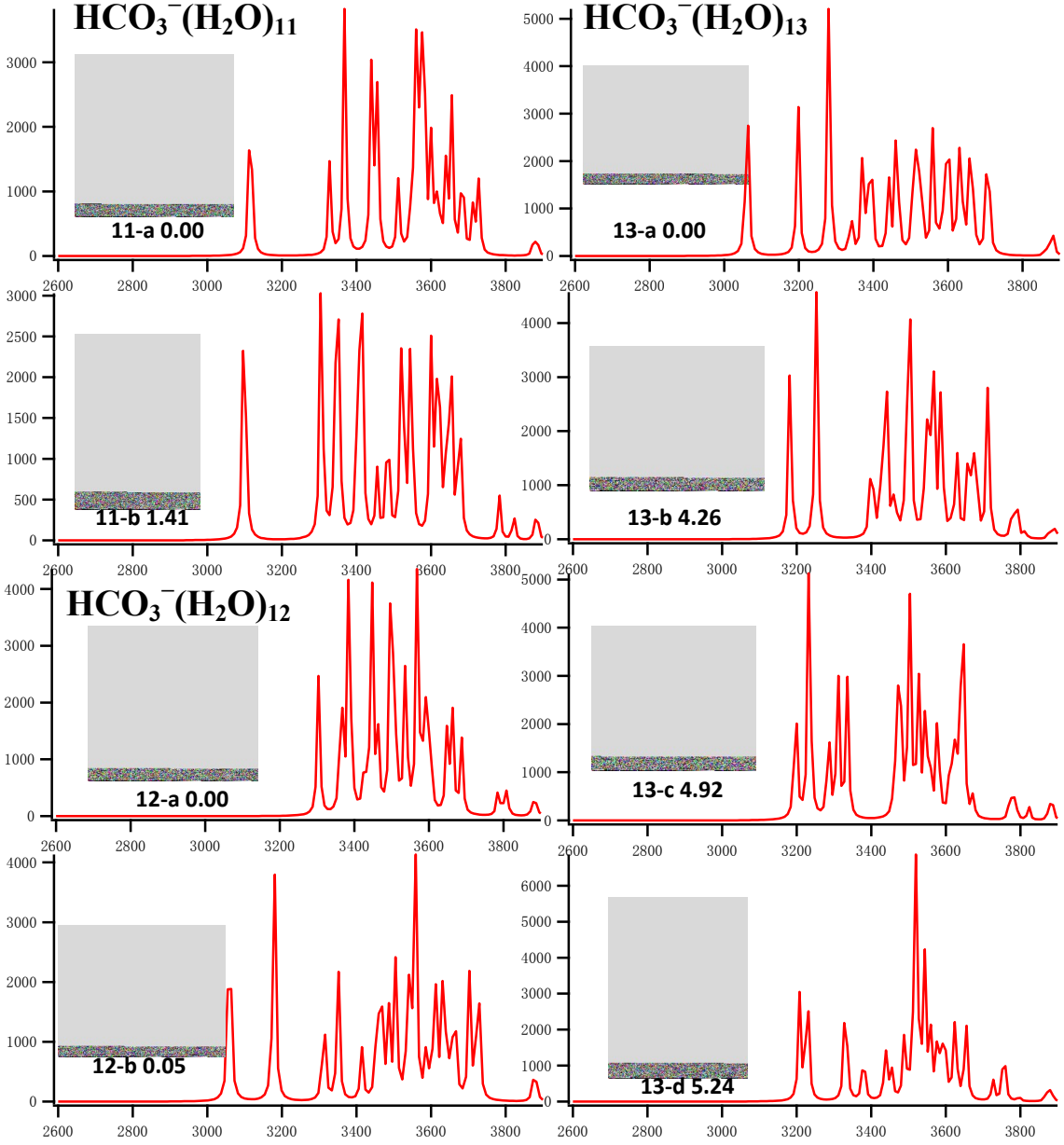



Fig. S24 Simulated IR spectra (O-H stretching mode: 2600-3900 $cm^{-1}$) of $HCO_3^-(H_2O)_n$, n=11-13 clusters at B3LYP/6-311++G(3df, 3pd).

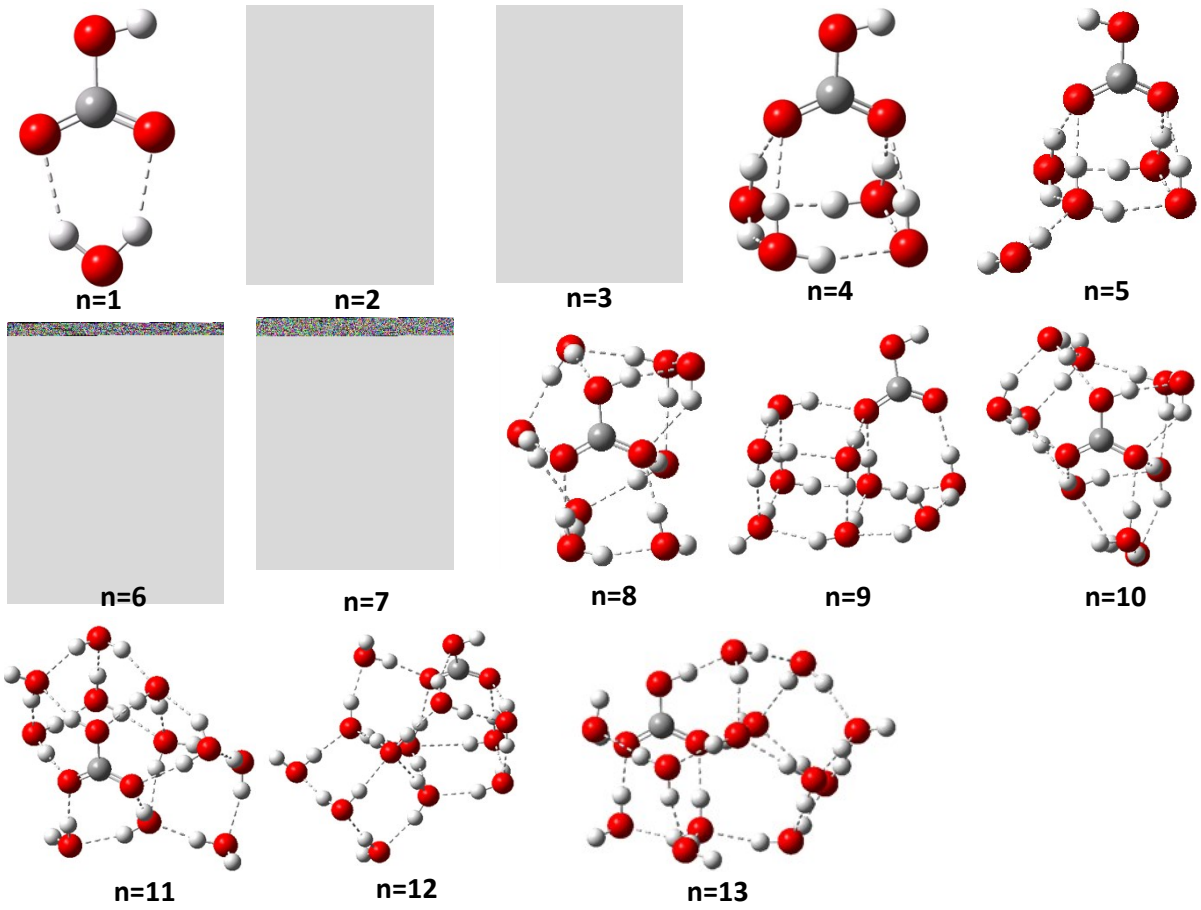



Fig. S25 The most probable structures of $HCO_3^-(H_2O)_n$, n=1-13 clusters determined by comparison of NIPE spectra, BH structural search and available IR spectra.

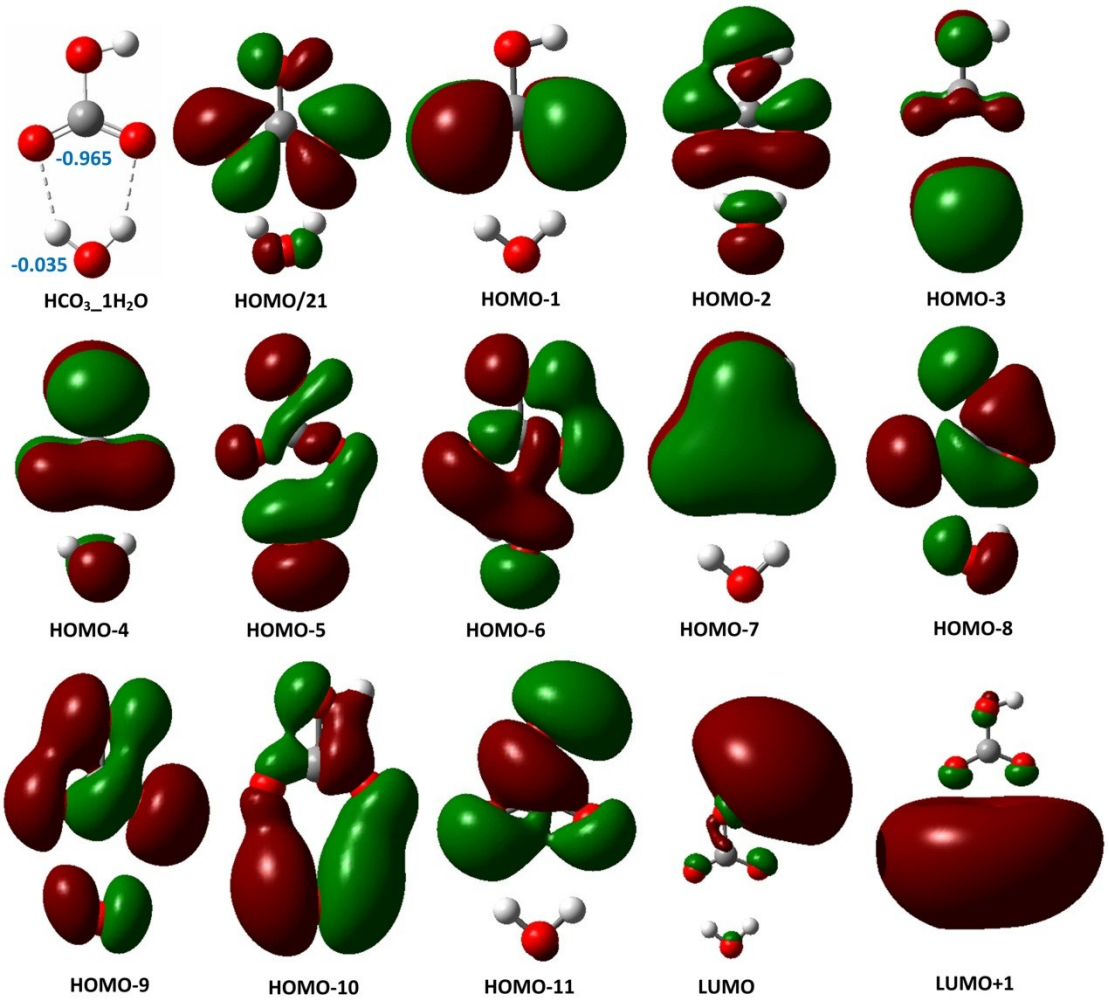



Fig. S26 Molecular orbitals of the minimum energy isomer of $HCO_3^-(H_2O)_1$.

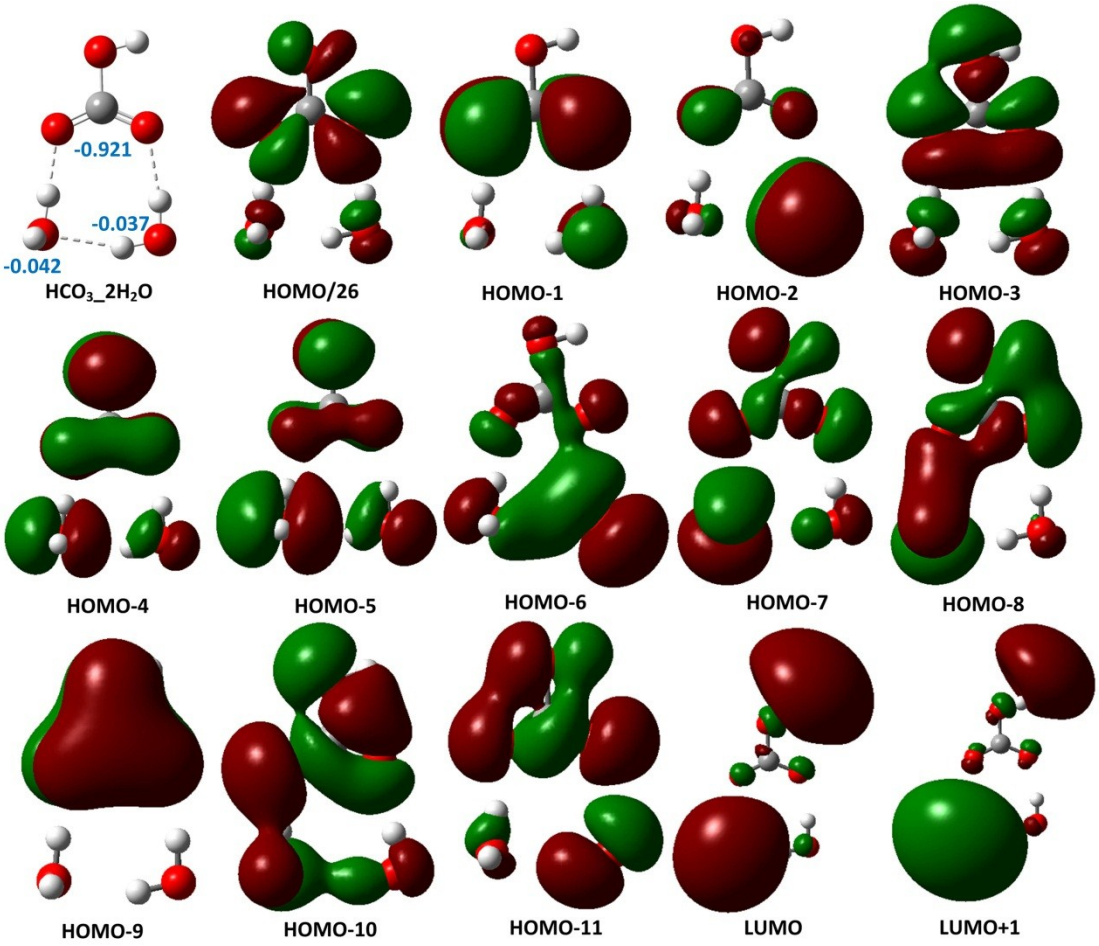



Fig. S27 Molecular orbitals of the minimum energy isomer of $HCO_3^-(H_2O)_2$.

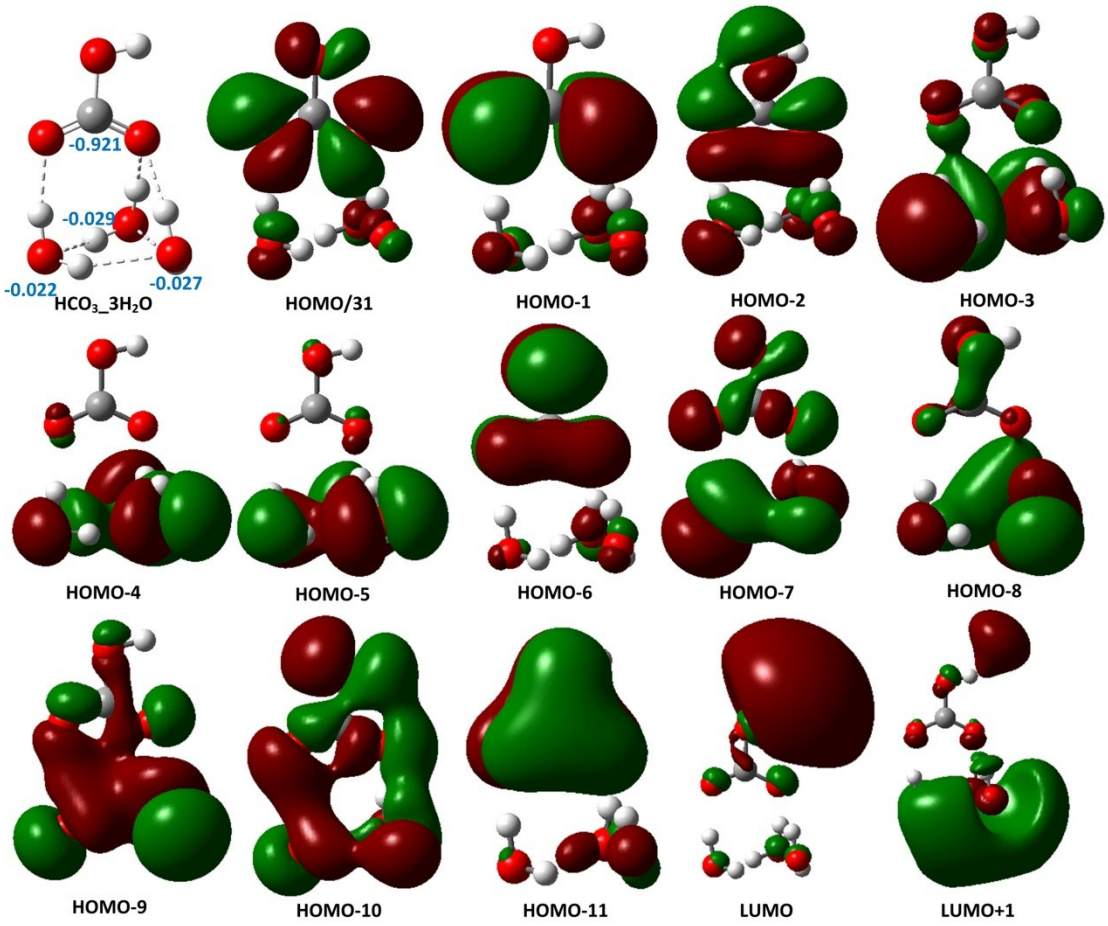



Fig. S28 Molecular orbitals of the minimum energy isomer of $HCO_3^-(H_2O)_3$.

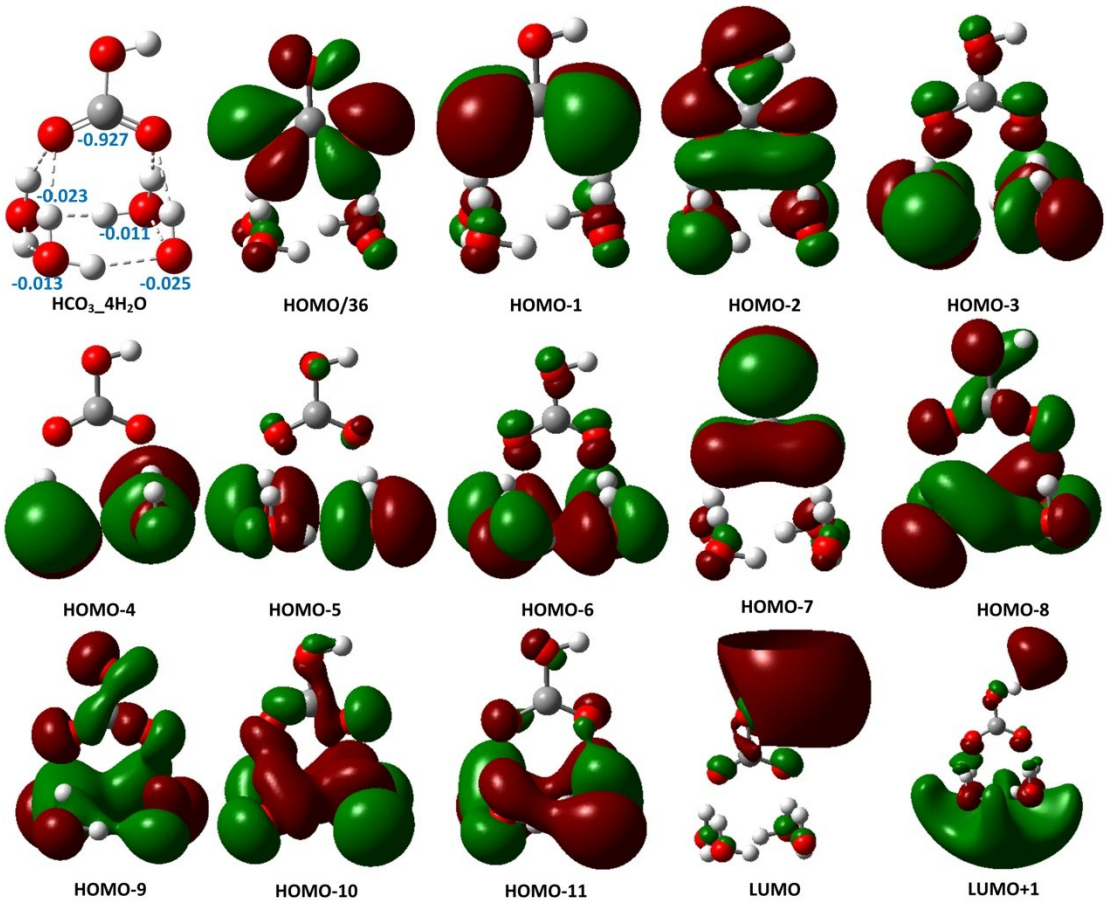



Fig. S29 Molecular orbitals of the minimum energy isomer of $HCO_3^-(H_2O)_4$.

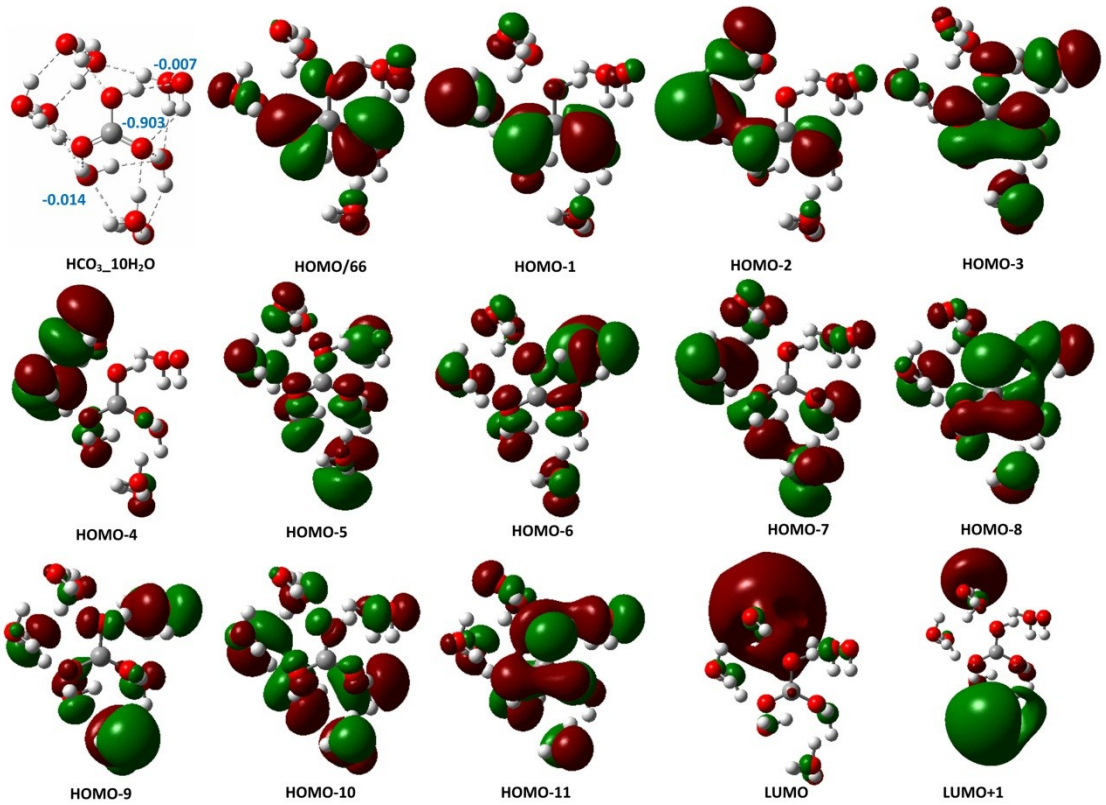



Fig. S30 Molecular orbitals of the minimum energy isomer of $HCO_3^-(H_2O)_{10}$.

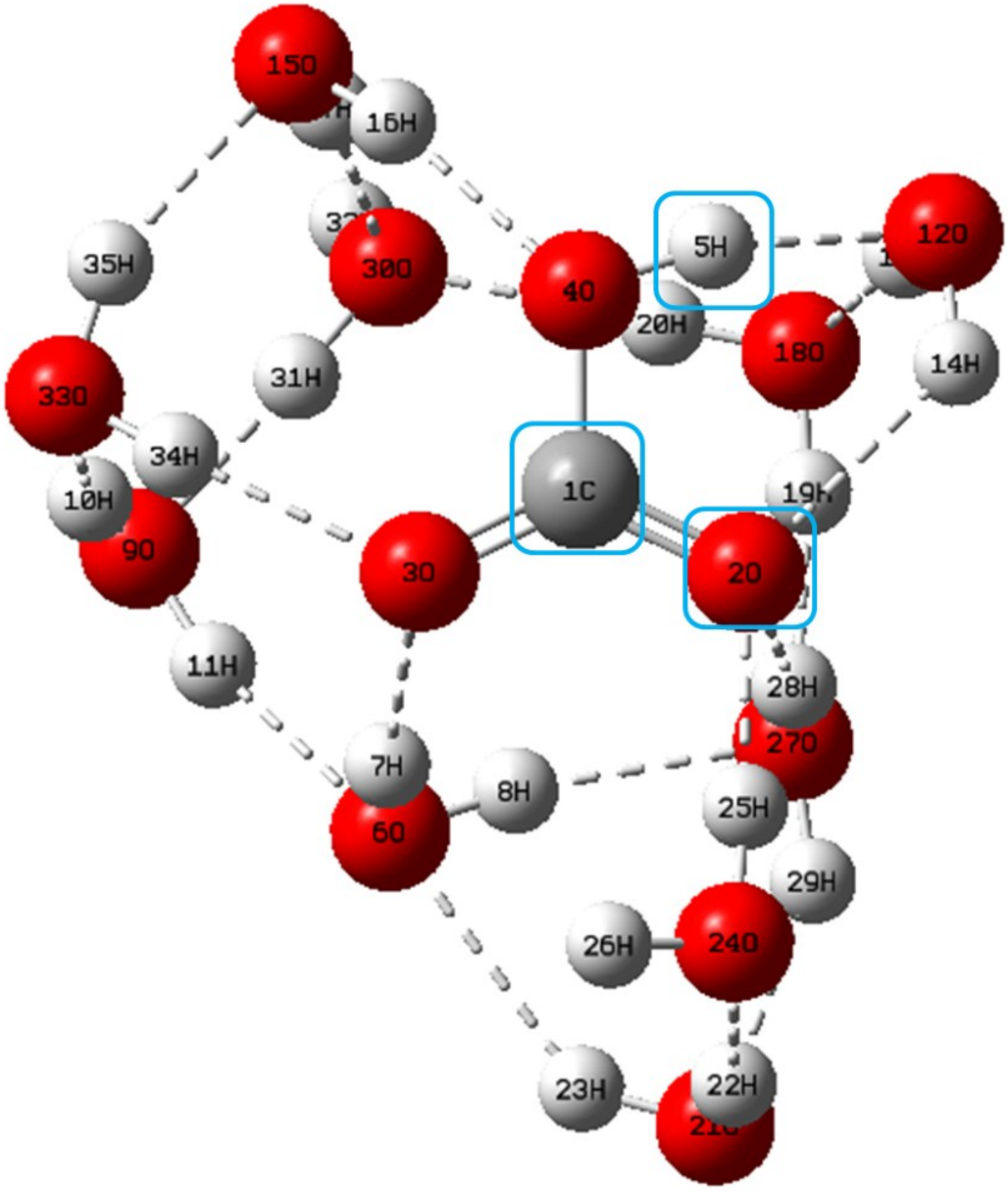



Fig. S31 Symbols and labels of each atom of $HCO_3^-(H_2O)_{10}$.


Figure S32. Top five low-lying isomers of $HCO_3^-(H_2O)_n$ (n = 9-13) at B3LYP/6-311++G(3df, 3pd) level of theory. Relative energies (in kcal/mol) are indicated.