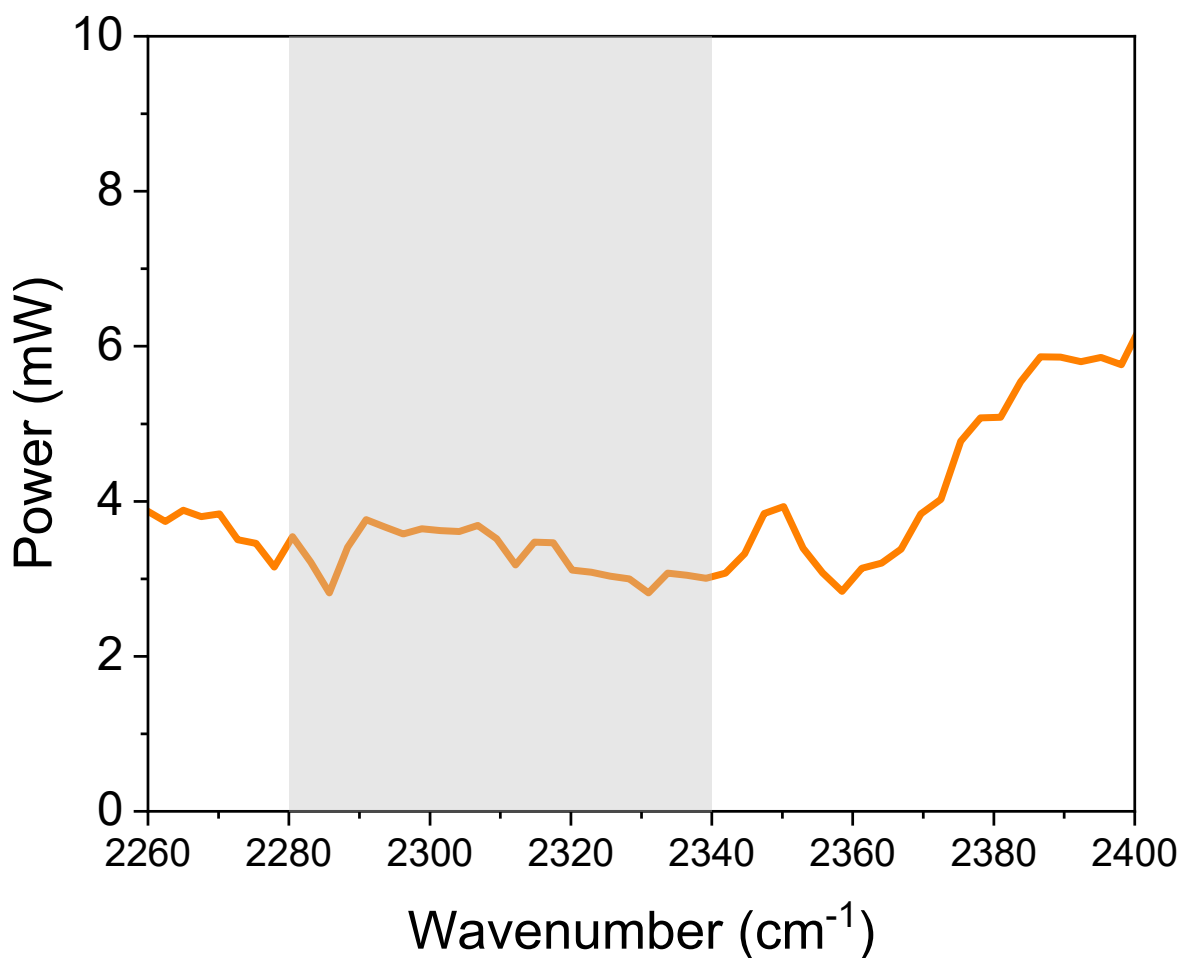## Supporting Information

Spectroscopic Investigation of Size-Dependent CO₂ Binding on Cationic Copper Clusters: Analysis of CO₂ Asymmetric Stretch

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5.

Figure S1: The power curve of the laser employed, with the shaded gray area denoting the frequency range where the CO₂ stretch vibration was detected.
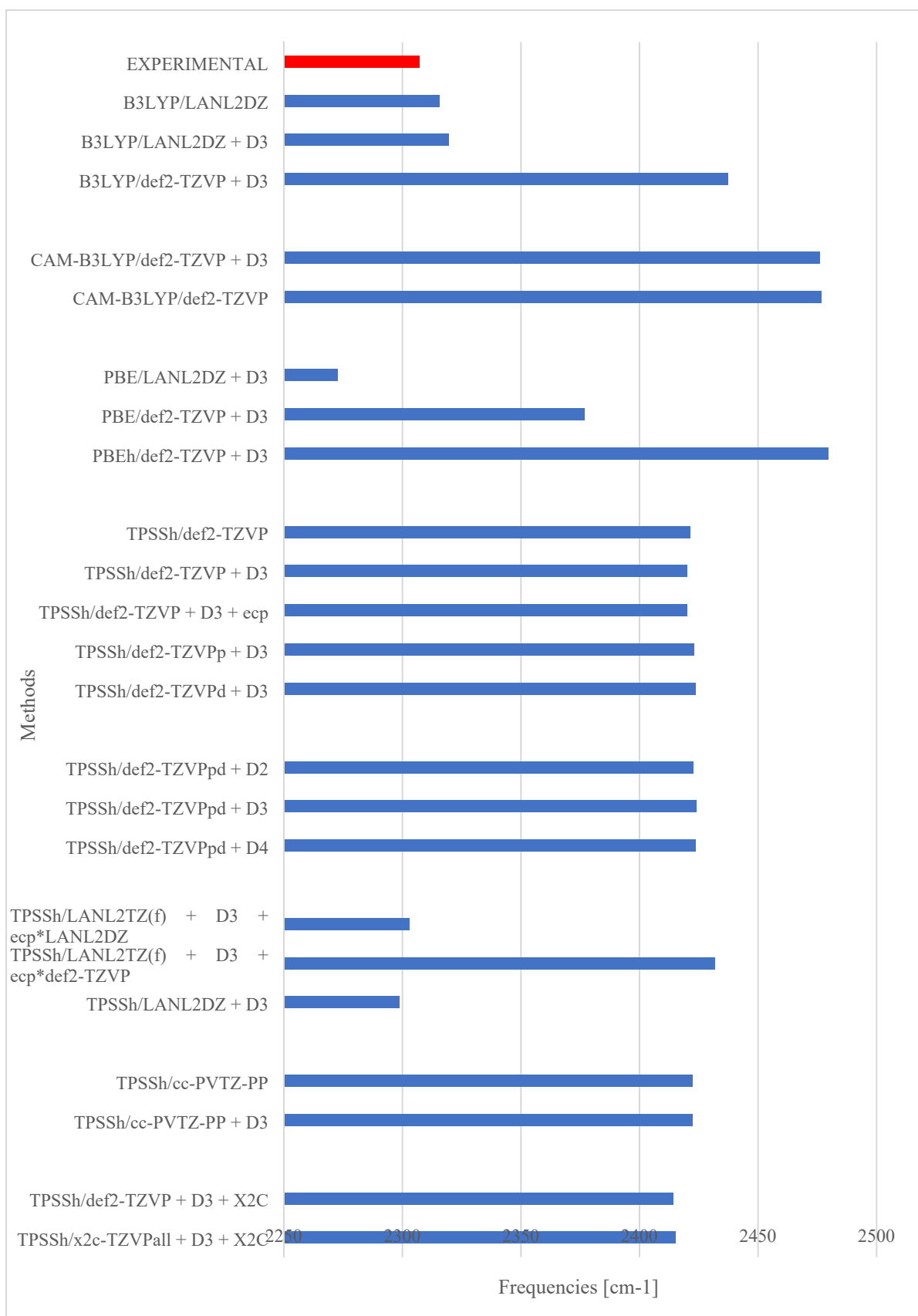
Figure S2: Benchmarking of different methods for harmonic frequency calculations on the asymmetrical stretching vibrational mode of the CO_2 in the $Cu_4[CO_2]^+$ adduct, with carbon mass corresponding to the natural abundance. Ecp*XXX the application of an effective core potential.

Method	TPSSh/LANL2DZ	TPSSh/def2-TZVP	TPSSh-D3/def2-TZVP	TPSSh/cc-pVTZ
Harmonic	2267	2400	2400	2406
TOSH	2218	2352	2351	2357
VCI[1]	2272	2408	2407	2413
VCI[2]	2226	2359	2359	2365
VCI[3]	2229	2362	2361	2367
VCI[4]	2220	2353	2352	2358
VCI[5]	2218	2352	2351	2357
VCI[6]	2218	2352	2351	2357

Table S1: Benchmarking of different methods for anharmonic calculations of the asymmetrical stretching vibrational mode of gas phase CO_2 molecule, with carbon mass set corresponding to natural abundance. The experimental value[1] is 2349 cm^{-1}.

TPSSh-D3/def2-TZVP

Method	$Cu[CO_2]^+$	$Cu_2[CO_2]^+$	$Cu_3[CO_2]^+$	$Cu_4[CO_2]^+$
Experimental	2316	2323	2318	2312
Harmonic	2429	2435	2431	2419
TOSH	2381	2385	2384	
VCI[1]	2434	2437	2437	
VCI[2]	2389	2392	2392	
VCI[3]	2391	2395	2394	
VCI[4]	2382	2386	2385	
VCI[5]	2381	2385	2384	
VCI[6]	2381	2385	2384	
Anharmonic scaling factor (n=1):	0.98			
Anharmonic scaling factor (n=2):	0.98			
Anharmonic scaling factor (n=3):	0.98			

TPSSh/LANL2DZ

Method	$Cu[CO_2]^+$	$Cu_2[CO_2]^+$	$Cu_3[CO_2]^+$	$Cu_4[CO_2]^+$
Experimental	2316	2323	2318	2312
Harmonic	2325	2311	2307	2300
TOSH	2277	2262	2257	
VCI[1]	2326	2314	2309	
VCI[2]	2284	2270	2265	
VCI[3]	2287	2272	2268	
VCI[4]	2278	2263	2259	
VCI[5]	2277	2262	2258	
VCI[6]	2277	2262	2257	
Anharmonic scaling factor (n=1):	0.98			
Anharmonic scaling factor (n=2):	0.98			
Anharmonic scaling factor (n=3):	0.98			

Table S2: Benchmarking of TPSSh-D3/def2-TZVP and TPSSh/LANL2DZ methods for anharmonic calculations of the asymmetrical stretching vibrational mode of $Cu_n[CO_2]^+$ complexes with n = 1-4, with carbon mass corresponding to natural abundance.
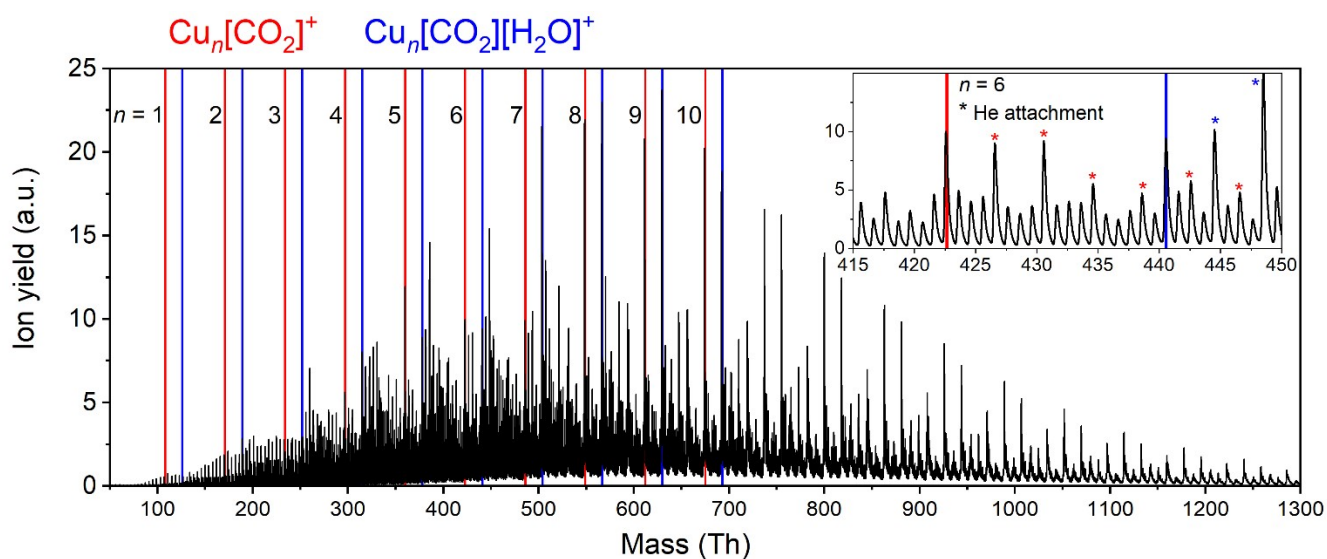
Figure S3: Mass spectrum where the experimental setup was optimised to create larger Cu_n clusters. The red and blue vertical lines highlight the positions of the $Cu_n[CO_2]^+$ and $Cu_n[CO_2][H_2O]^+$, respectively, for $n = 1 - 10$. In the inset the He attachment on the $Cu_6[CO_2]^+$ and $Cu_6[CO_2][H_2O]^+$ cluster is shown with red and blue asterisks accordingly.
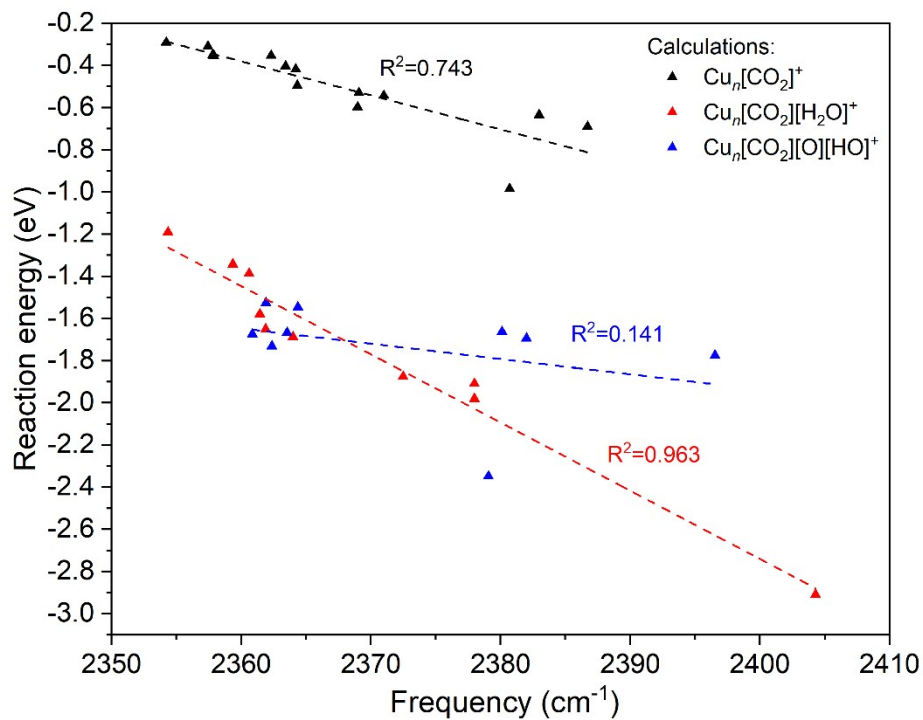
Figure S4: Correlation between binding energies and position of the asymmetric stretching vibrational mode of the bound CO_2 for all calculated $Cu_n[CO_2]^+$, $Cu_n[CO_2][H_2O]^+$ and $Cu_n[CO_2][H][OH]^+$ structures. The linear fit is shown with a dashed line and R^2 is calculated for each system. With carbon mass corresponding to natural abundance.
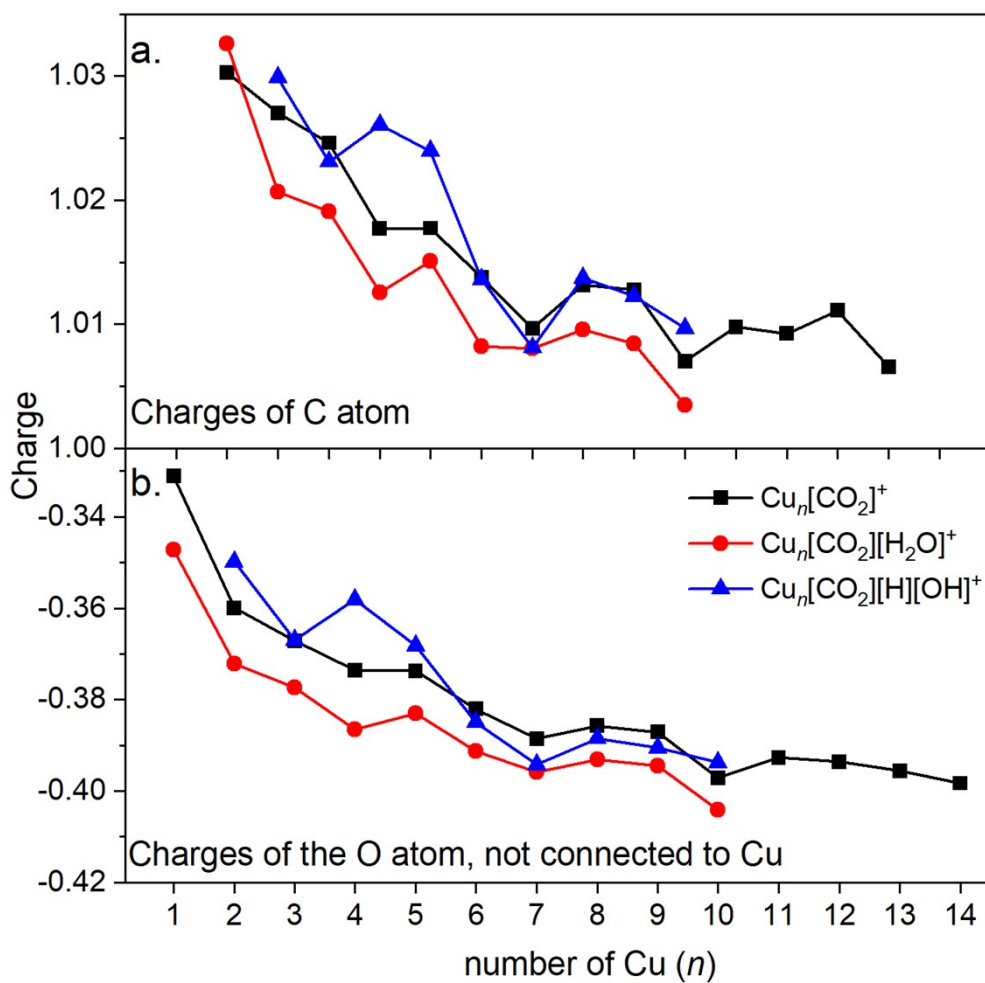
Figure S5: a. Charges of the C atom in the CO_2 as a function of different cluster-complex sizes. b. Charges of the O atom (which is NOT connected to the cluster) in the CO_2 as a function of different cluster-complex sizes.
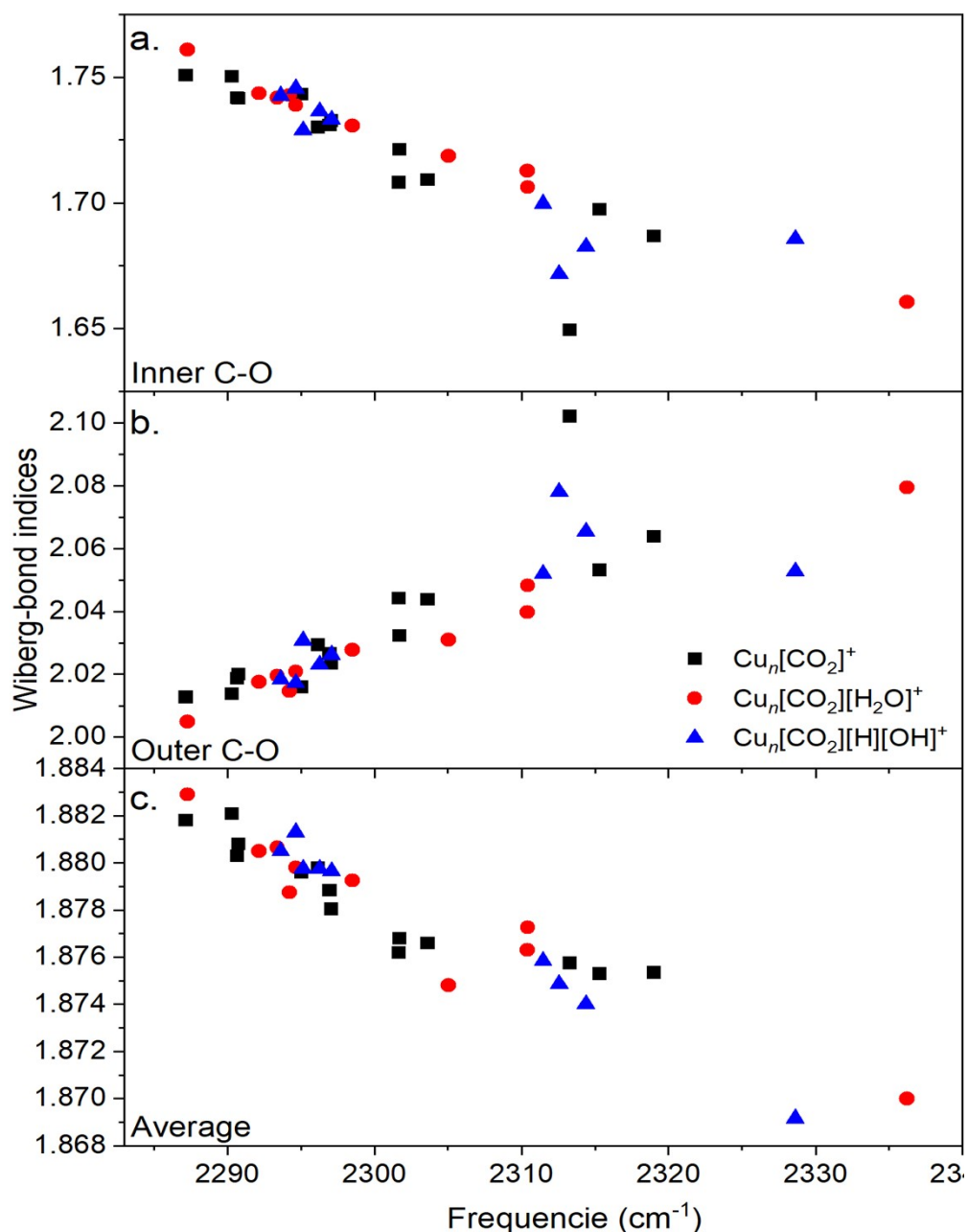
Figure S6: Wiberg bond indices of a. the C-O bond (where oxygen is connected to the cluster, i.e. inner oxygen); b. the C-O bond (where oxygen is not connected to the cluster, i.e. outer oxygen); c. both C-O bonds (inner and outer) with respect to the CO_2 asymmetric stretch vibrational frequency.

1.   T. Shimanouchi, *Tables of molecular vibrational frequencies*, National Bureau of Standards Washington, DC, 1972.