Supporting Information

Determination of CO Adsorption Sites on Gold Clusters Au_n^- (n = 21-25): A Size Region That Bridges the Pyramidal and Core–Shell Structures

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Table S1. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{21}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
I	0	0	3.452	0.753
II	0.024	0.043	3.65	0.552
III	0.064	0.061	3.459	0.637
IV	0.174	0.115	3.744	0.373
V	0.181	0.114	3.578	0.44
VI	0.203	0.163	3.676	0.415
VII	0.207	0.158	3.621	0.389
VIII	0.21	0.139	3.768	0.217
IX	0.221	0.167	3.599	0.243
X	0.221	0.229	3.61	0.613
XI	0.221	0.168	3.636	0.444
XII	0.225	0.167	3.657	0.353
XIII	0.23	0.24	3.593	0.664
XIV	0.257	0.198	3.826	0.275
XV	0.257	0.269	3.801	0.297
XVI	0.261	0.264	3.496	0.634
XVII	0.269	0.293	3.635	0.734
XVIII	0.28	0.304	3.897	0.502
XIX	0.281	0.232	3.578	0.345
XX	0.282	0.274	3.359	0.838
XXI	0.289	0.236	3.622	0.304
XXII	0.291	0.293	3.312	0.957
XXIII	0.292	0.224	3.814	0.107
XXIV	0.292	0.305	3.67	0.426
XXV	0.295	0.238	3.684	0.257
XXVI	0.301	0.255	3.638	0.318
XXVII	0.313	0.24	3.831	0.082
XXVIII	0.319	0.279	3.874	0.139
XXIX	0.328	0.27	3.856	0.155
XXX	0.328	0.291	3.736	0.245

Table S2. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{21}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	**ΔE_a**	**ΔE_b**	**VDE**	**Gap**
XXXI	0.329	0.282	3.731	0.278
XXXII	0.333	0.315	3.348	0.879
XXXIII	0.333	0.286	3.699	0.335
XXXIV	0.341	0.296	3.607	0.405
XXXV	0.356	0.307	3.872	0.156
XXXVI	0.36	0.294	3.768	0.398
XXXVII	0.36	0.36	3.141	1.144
XXXVIII	0.361	0.303	3.67	0.292
XXXIX	0.362	0.312	3.823	0.223
XL	0.38	0.319	3.876	0.22
XLI	0.381	0.387	3.692	0.371
XLII	0.387	0.328	3.772	0.151
XLIII	0.391	0.349	3.797	0.155

Table S3. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{22}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
I	0	0	3.218	0.592
II	0.096	0.128	3.154	0.855
III	0.102	0.095	3.329	0.428
IV	0.13	0.124	3.587	0.123
V	0.154	0.152	3.442	0.392
VI	0.168	0.181	3.431	0.462
VII	0.169	0.156	3.305	0.494
VIII	0.175	0.182	3.206	0.637
IX	0.18	0.169	3.244	0.586
X	0.183	0.172	3.526	0.204
XI	0.183	0.173	3.369	0.381
XII	0.184	0.164	3.292	0.449
XIII	0.196	0.195	3.235	0.718
XIV	0.199	0.216	3.376	0.566
XV	0.208	0.246	3.433	0.531
XVI	0.214	0.204	3.365	0.418
XVII	0.218	0.212	3.315	0.213
XVIII	0.219	0.22	3.381	0.402
XIX	0.22	0.211	3.094	0.35
XX	0.236	0.236	3.415	0.505
XXI	0.238	0.231	3.21	0.647
XXII	0.243	0.246	3.431	0.297
XXIII	0.254	0.246	3.648	0.049
XXIV	0.256	0.245	3.323	0.515
XXV	0.257	0.251	3.393	0.395
XXVI	0.261	0.291	3.373	0.607
XXVII	0.264	0.263	3.511	0.351

Table S4. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{22}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
XXVIII	0.269	0.235	3.615	0.092
XXIX	0.273	0.28	3.327	0.538
XXX	0.275	0.289	2.988	0.683
XXXI	0.277	0.287	3.495	0.376
XXXII	0.281	0.277	3.401	0.402
XXXIII	0.291	0.279	3.094	0.791
XXXIV	0.293	0.308	3.233	0.745
XXXV	0.296	0.261	3.085	0.767
XXXVI	0.298	0.291	3.519	0.262
XXXVII	0.308	0.304	3.507	0.316
XXXVIII	0.311	0.323	3.445	0.481
XXXIX	0.313	0.308	3.528	0.178
XL	0.318	0.329	3.198	0.8
XLI	0.319	0.325	3.533	0.26
XLII	0.33	0.33	3.553	0.208
XLIII	0.332	0.327	3.283	0.229
XLIV	0.333	0.289	3.516	0.193
XLV	0.334	0.328	3.495	0.224
XLVI	0.335	0.336	3.591	0.189
XLVII	0.338	0.357	3.474	0.405
XLVIII	0.355	0.354	3.256	0.538
XLIX	0.374	0.388	3.562	0.154
L	0.401	0.398	3.759	0.109
LI	0.412	0.423	3.08	1.074

Table S5. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{23}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
I	0	0	3.723	0.317
II	0.033	0.054	3.717	0.231
III	0.036	0.028	3.631	0.251
IV	0.053	0.073	3.84	0.233
V	0.055	0.081	3.896	0.109
VI	0.069	0.091	3.738	0.294
VII	0.068	0.079	3.82	0.121
VIII	0.083	0.087	3.808	0.165
IX	0.094	0.093	3.728	0.329
X	0.095	0.103	3.634	0.279
XI	0.097	0.121	3.511	0.36
XII	0.101	0.128	3.851	0.276
XIII	0.105	0.12	3.694	0.346
XIV	0.107	0.127	3.688	0.179
XV	0.108	0.131	3.781	0.329
XVI	0.11	0.118	3.722	0.343
XVII	0.113	0.117	3.707	0.18
XVIII	0.114	0.14	3.765	0.218
XIX	0.114	0.147	3.827	0.151
XX	0.123	0.135	3.576	0.384
XXI	0.128	0.14	3.724	0.27
XXII	0.13	0.125	3.571	0.373

Table S6. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{23}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
XXIII	0.141	0.182	3.943	0.105
XXIV	0.153	0.162	3.808	0.198
XXV	0.153	0.21	3.982	0.136
XXVI	0.154	0.18	3.82	0.177
XXVII	0.157	0.175	3.695	0.393
XXVIII	0.161	0.186	3.902	0.199
XXIX	0.161	0.189	3.74	0.212
XXX	0.162	0.175	3.753	0.227
XXXI	0.164	0.187	3.818	0.126
XXXII	0.168	0.182	3.822	0.285
XXXIII	0.193	0.228	3.892	0.282
XXXIV	0.199	0.211	3.817	0.044
XXXV	0.2	0.195	3.66	0.288
XXXVI	0.208	0.232	3.762	0.225
XXXVII	0.232	0.271	3.874	0.132
XXXVIII	0.233	0.26	3.776	0.419

Table S7. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{24}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
I	0	0	3.7	0.072
II	0.015	0.003	3.318	0.584
III	0.073	0.062	3.195	0.666
IV	0.078	0.09	3.285	0.721
V	0.091	0.099	3.333	0.597
VI	0.095	0.094	3.348	0.271
VII	0.101	0.092	3.386	0.403
VIII	0.105	0.109	3.389	0.417
IX	0.111	0.139	3.313	0.699
X	0.113	0.108	3.358	0.439
XI	0.124	0.141	3.706	0.178
XII	0.135	0.151	3.338	0.65
XIII	0.138	0.152	3.247	0.572
XIV	0.149	0.161	3.66	0.207
XV	0.161	0.154	3.449	0.153
XVI	0.163	0.2	3.361	0.545
XVII	0.164	0.184	3.359	0.568
XVIII	0.166	0.198	3.175	0.729
XIX	0.168	0.17	3.629	0.234
XX	0.171	0.177	3.429	0.505
XXI	0.175	0.178	3.453	0.326
XXII	0.177	0.19	3.366	0.613
XXIII	0.178	0.188	3.444	0.489
XXIV	0.186	0.207	3.497	0.334
XXV	0.188	0.201	3.646	0.301
XXVI	0.191	0.227	3.594	0.369
XXVII	0.197	0.189	3.567	0.232

Table S8. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{24}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
XXVIII	0.199	0.198	3.472	0.283
XXIX	0.2	0.212	3.409	0.374
XXX	0.207	0.203	3.47	0.364
XXXI	0.211	0.203	3.348	0.486
XXXII	0.211	0.198	3.357	0.356
XXXIII	0.218	0.234	3.282	0.481
XXXIV	0.22	0.226	3.618	0.145
XXXV	0.233	0.244	3.429	0.404
XXXVI	0.235	0.265	3.245	0.83
XXXVII	0.237	0.236	3.651	0.162
XXXVIII	0.238	0.241	3.352	0.542
XXXIX	0.239	0.275	3.422	0.602
XL	0.241	0.246	3.745	0.133
XLI	0.258	0.263	3.392	0.509
XLII	0.267	0.307	3.265	0.65
XLIII	0.273	0.294	3.14	0.765
XLIV	0.274	0.286	3.428	0.32
XLV	0.279	0.301	3.709	0.228
XLVI	0.29	0.308	3.441	0.494

Table S9. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{25}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
I	0	0	3.76	0.177
II	0.013	0.029	3.875	0.177
III	0.068	0.081	3.936	0.063
IV	0.126	0.163	3.911	0.086
V	0.141	0.133	3.772	0.176
VI	0.165	0.174	3.89	0.081
VII	0.182	0.198	3.924	0.123
VIII	0.186	0.252	3.898	0.19
IX	0.19	0.197	3.847	0.079
X	0.213	0.215	3.831	0.047
XI	0.22	0.24	3.918	0.127
XII	0.236	0.227	3.849	0.143
XIII	0.253	0.278	3.798	0.213
XIV	0.256	0.308	3.85	0.228
XV	0.279	0.286	3.777	0.169
XVI	0.279	0.288	3.722	0.255
XVII	0.283	0.307	3.767	0.371
XVIII	0.284	0.301	3.878	0.14
XIX	0.308	0.322	3.767	0.173
XX	0.308	0.335	3.811	0.211
XXI	0.31	0.337	3.858	0.125
XXII	0.311	0.331	3.769	0.274
XXIII	0.316	0.319	3.659	0.257
XXIV	0.317	0.335	3.877	0.166
XXV	0.322	0.353	3.906	0.15
XXVI	0.323	0.315	3.763	0.106
XXVII	0.33	0.382	3.626	0.159

Table S10. Experimental first VDE (eV) labeled X in plots, the energy gap (eV) between peaks labeled X and A or peaks labeled X' and A' from the 193nm experimental spectra for $Au_{25}CO^-$, relative energies (eV) computed at PBE0/ CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP(with SO effects for Au) (ΔE_b) levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), theoretical first VDE (eV) and energy gap (eV)

Isomer	ΔE_a	ΔE_b	**VDE**	**Gap**
XXVIII	0.337	0.34	3.671	0.254
XXIX	0.338	0.359	3.805	0.255
XXX	0.339	0.34	3.728	0.219
XXXI	0.341	0.372	3.73	0.37
XXXII	0.342	0.368	3.813	0.174
XXXIII	0.353	0.378	3.768	0.231
XXXIV	0.356	0.363	3.83	0.106
XXXV	0.358	0.393	3.846	0.315
XXXVI	0.36	0.386	3.7	0.258
XXXVII	0.366	0.387	3.821	0.102
XXXVIII	0.372	0.396	3.919	0.057
XXXIX	0.375	0.388	3.776	0.231
XL	0.378	0.369	3.685	0.222
XLI	0.383	0.398	3.718	0.341
XLII	0.384	0.398	3.905	0.137
XLIII	0.386	0.416	3.71	0.27
XLIV	0.389	0.406	3.644	0.348
XLV	0.389	0.422	3.8	0.142
XLVI	0.398	0.414	3.755	0.176
XLVII	0.403	0.454	3.853	0.235
XLVIII	0.404	0.415	3.754	0.226
XLIX	0.405	0.411	3.828	0.089
L	0.406	0.431	3.74	0.267
LI	0.408	0.436	3.774	0.167
LII	0.415	0.438	3.605	0.34
LIII	0.422	0.434	3.666	0.21
LIV	0.442	0.494	3.822	0.274
LV	0.445	0.439	3.696	0.327
LVI	0.454	0.461	3.723	0.321
LVII	0.472	0.458	3.851	0.162
LVIII	0.525	0.553	3.439	0.791

Table S11. Assigned isomers of Au_nCO^- clusters and RMSD in the peak positions. In case where more than one isomer is assigned the RMSD in peak positions is calculated for the overlay of spectra of the major and minor isomers.

Anion Cluster	Major Isomer	Minor Isomer	RMSD (in eV)
$Au_{21}CO^-$	IV	II	0.018
$Au_{22}CO^-$	I	III, IV	0.022
$Au_{23}CO^-$	VII	-	0.021
$Au_{24}CO^-$	II	-	0.063
$Au_{25}CO^-$	I	II	0.064

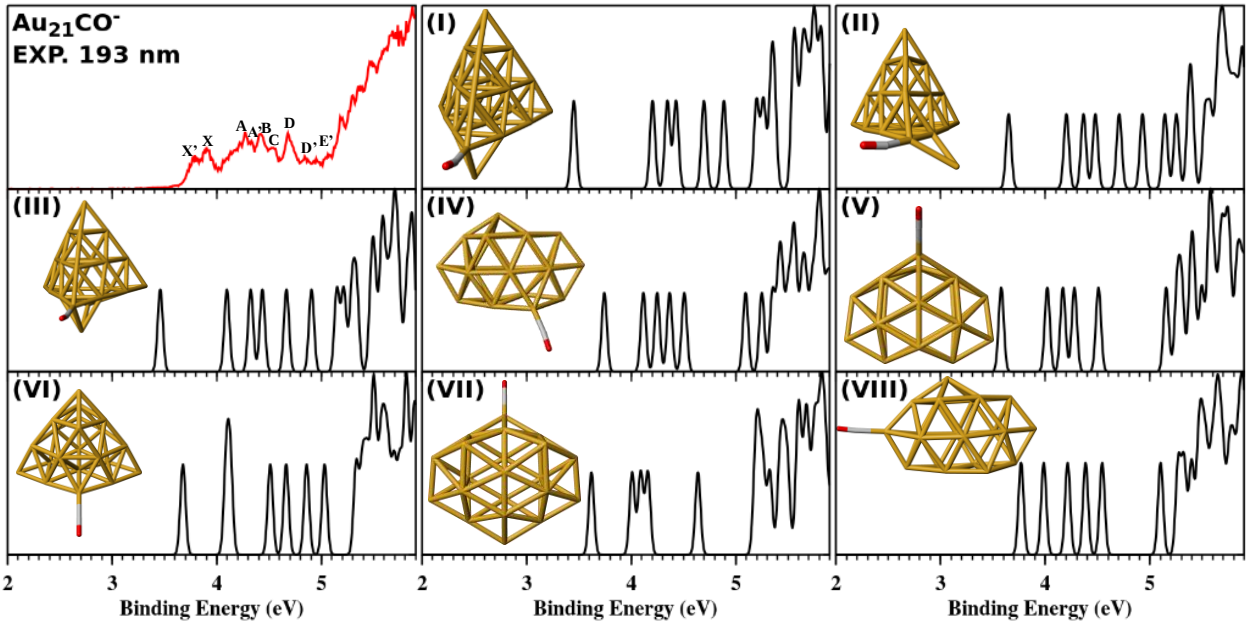

Figure S1. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^-$.

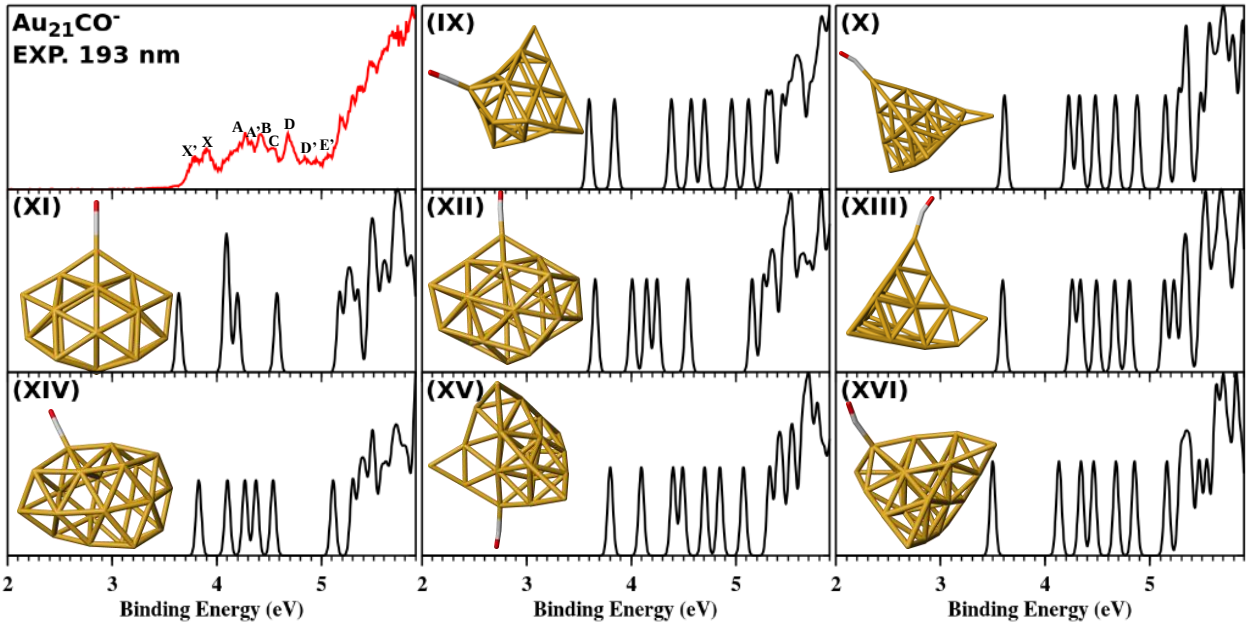

Figure S2. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^{-}$.

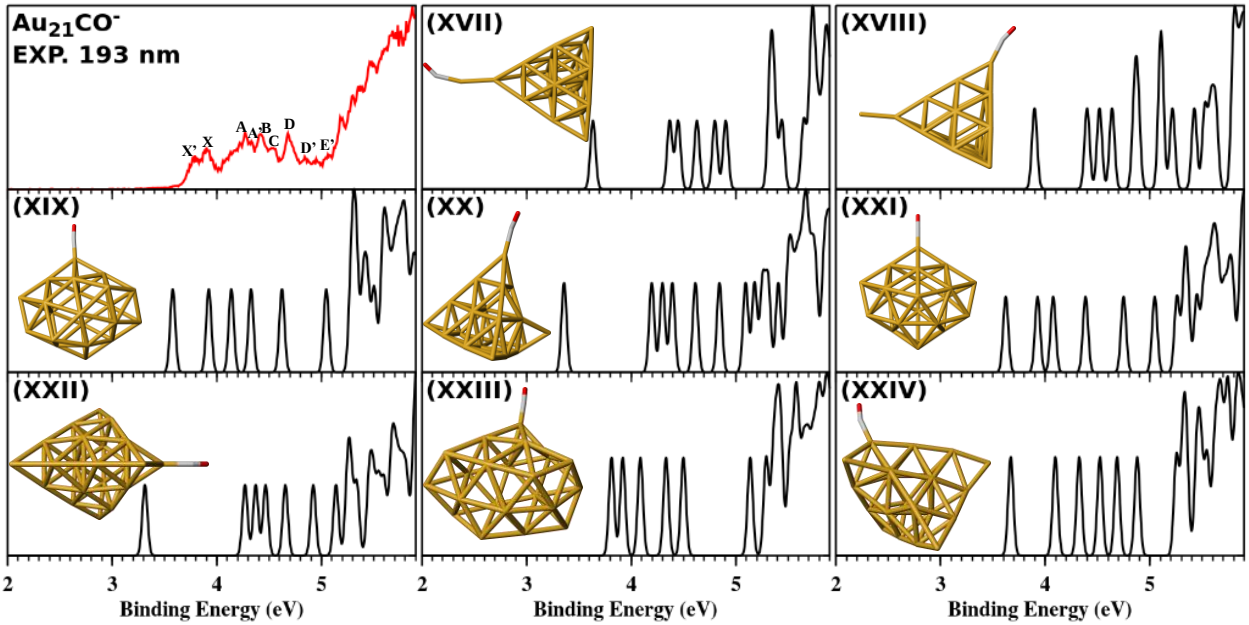

Figure S3. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^{-}$.

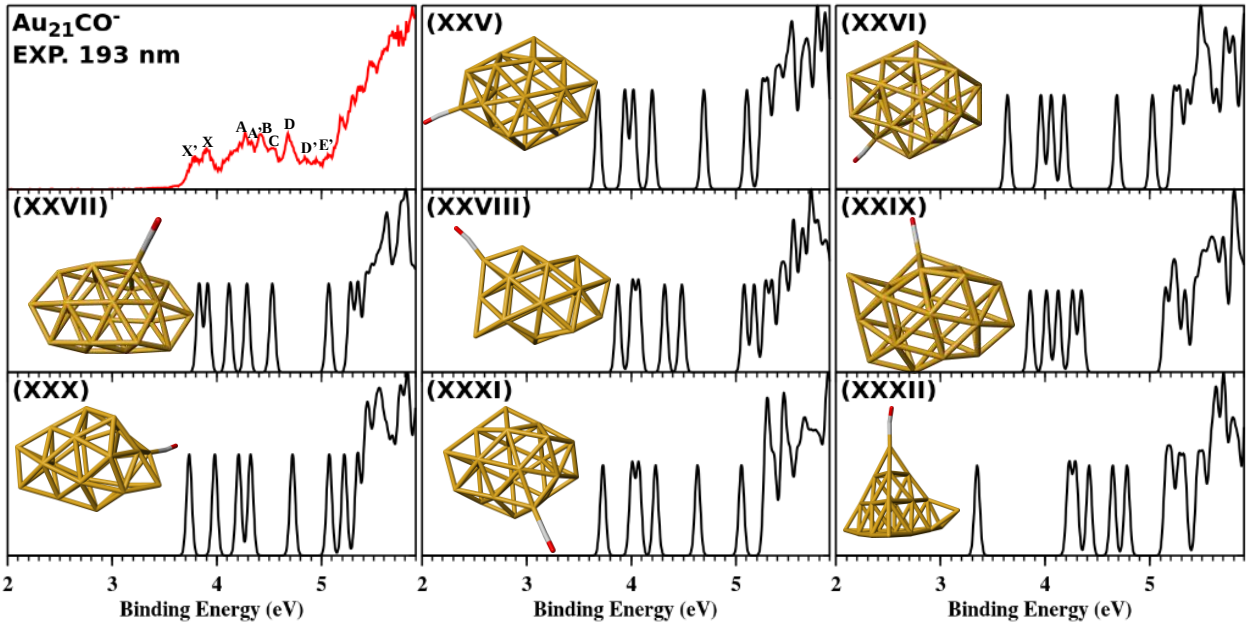

Figure S4. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^{-}$.

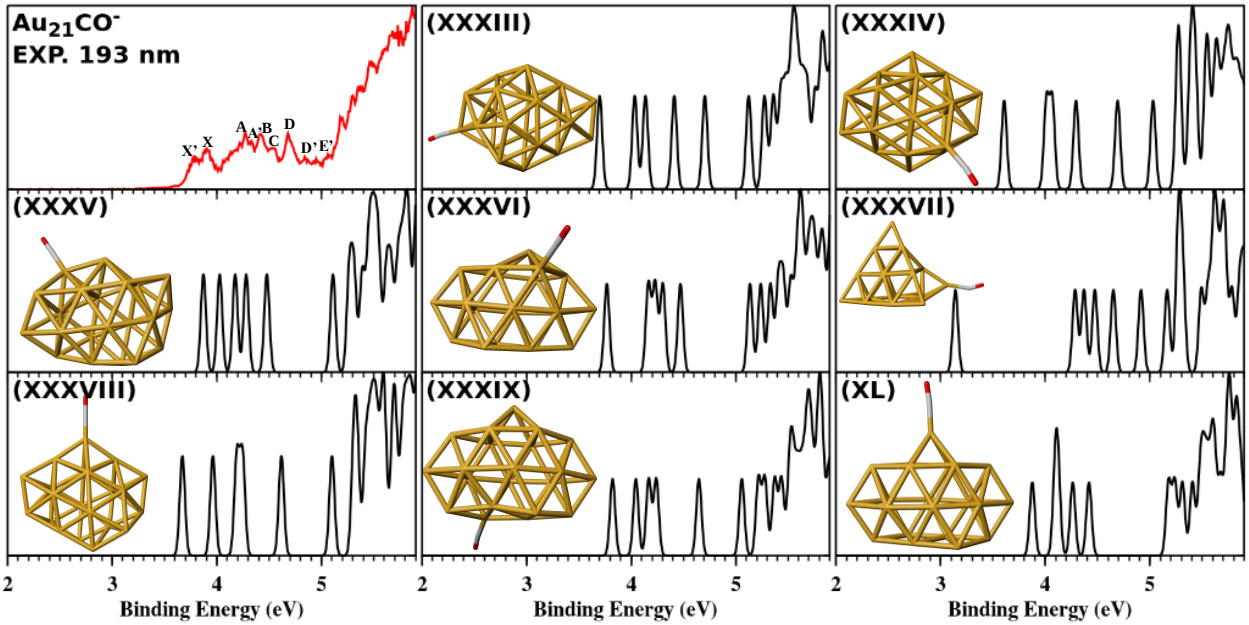

Figure S5. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^{-}$.

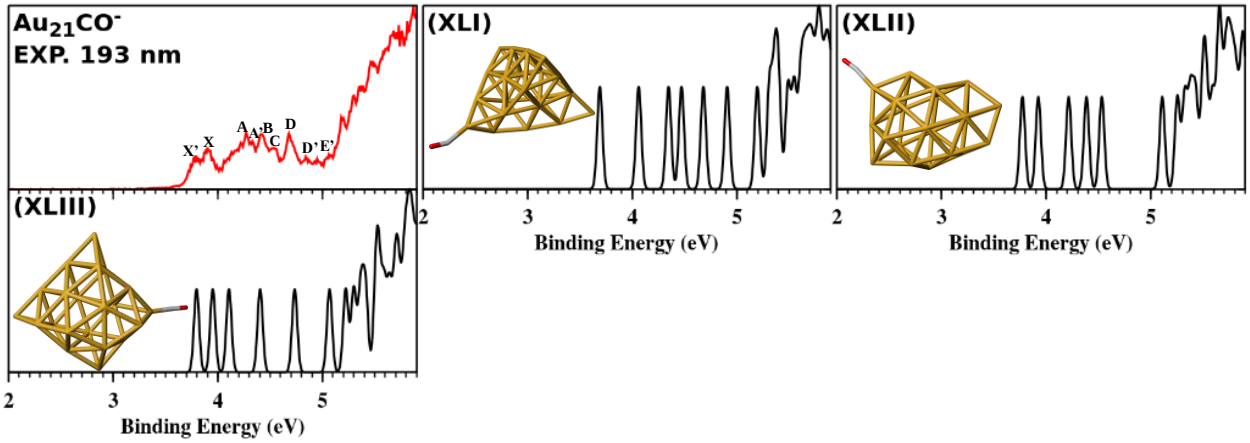

Figure S6. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{21}CO^-$.

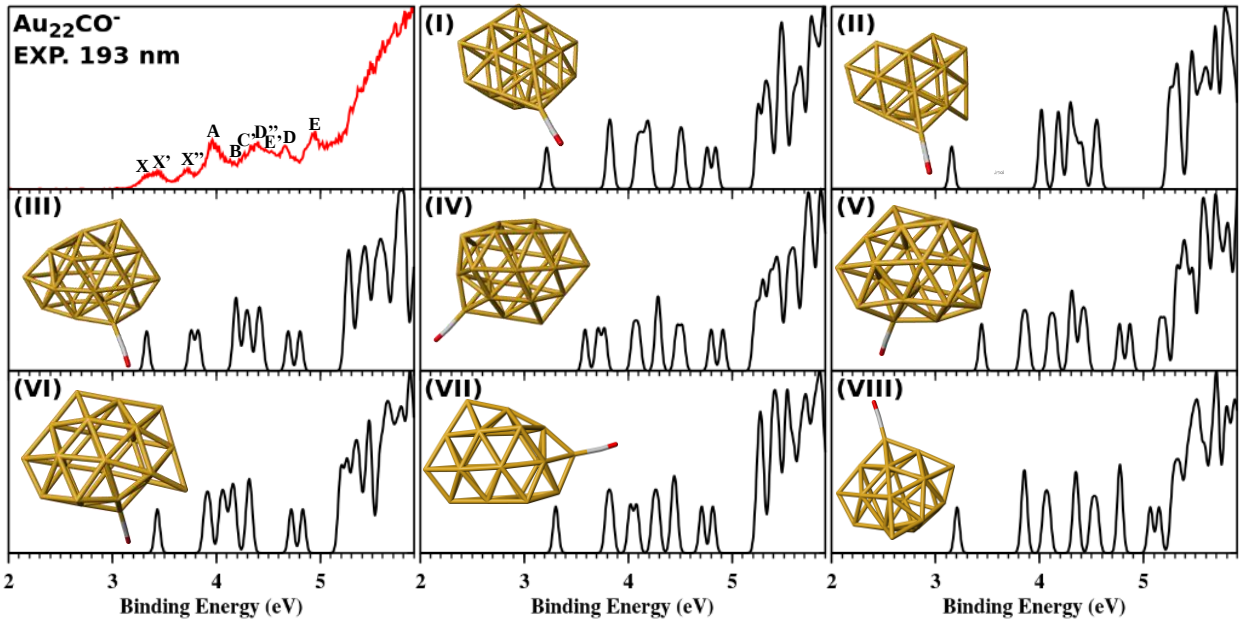

Figure S7. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^-$.

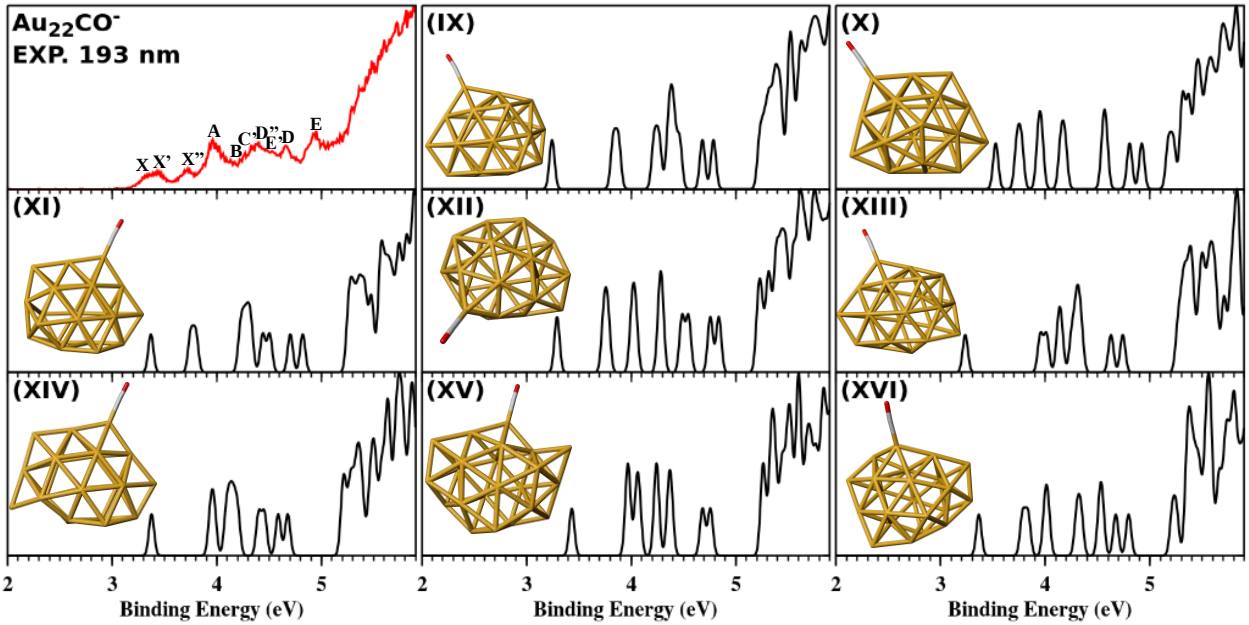

Figure S8. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

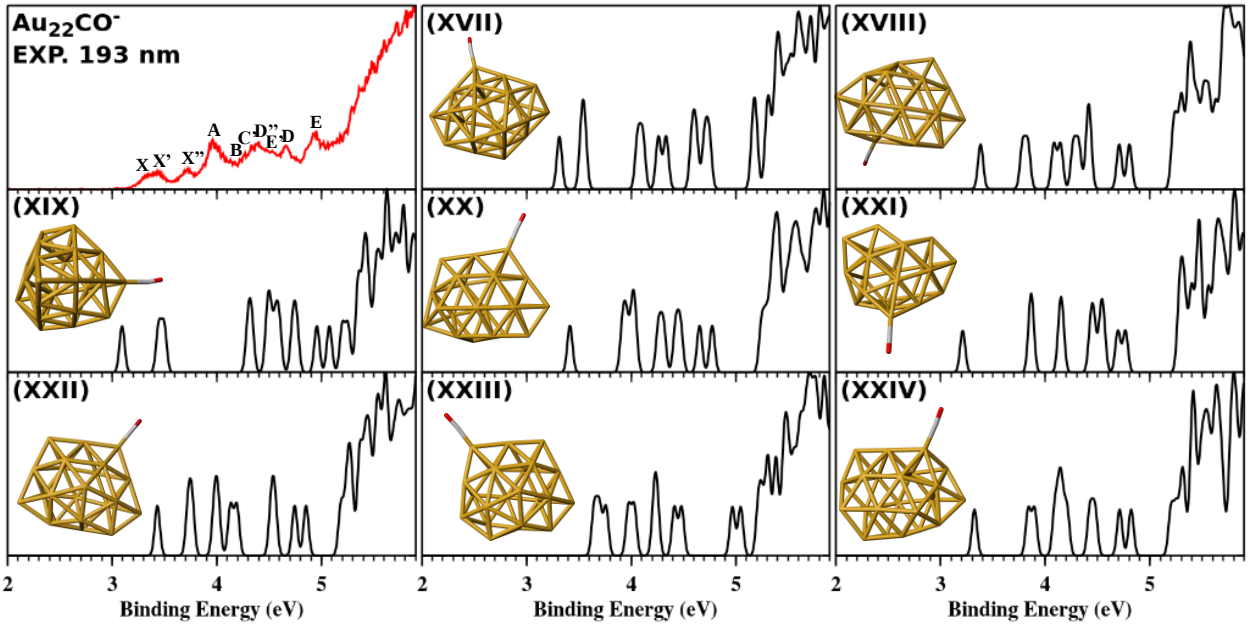

Figure S9. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

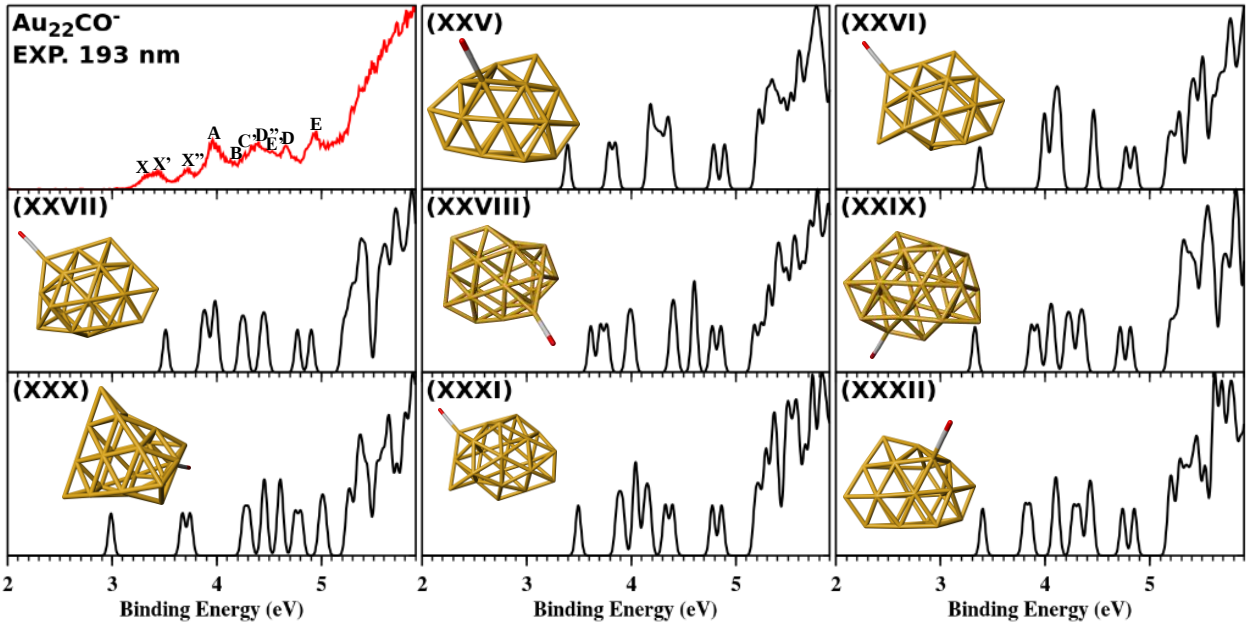

Figure S10. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

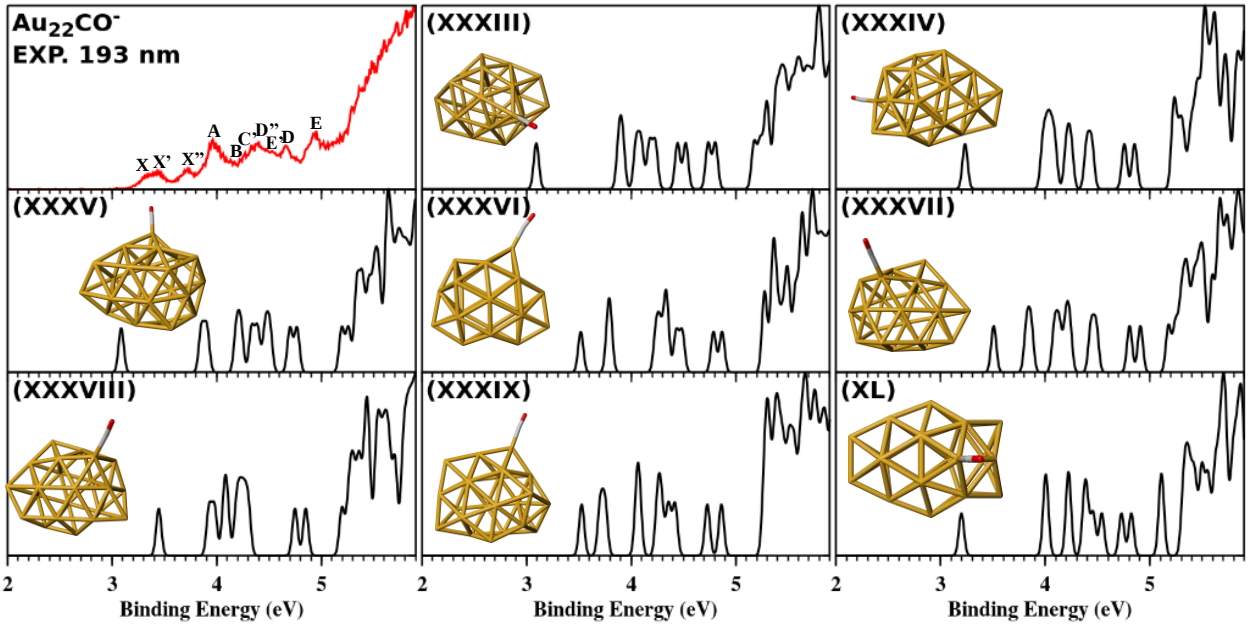

Figure S11. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

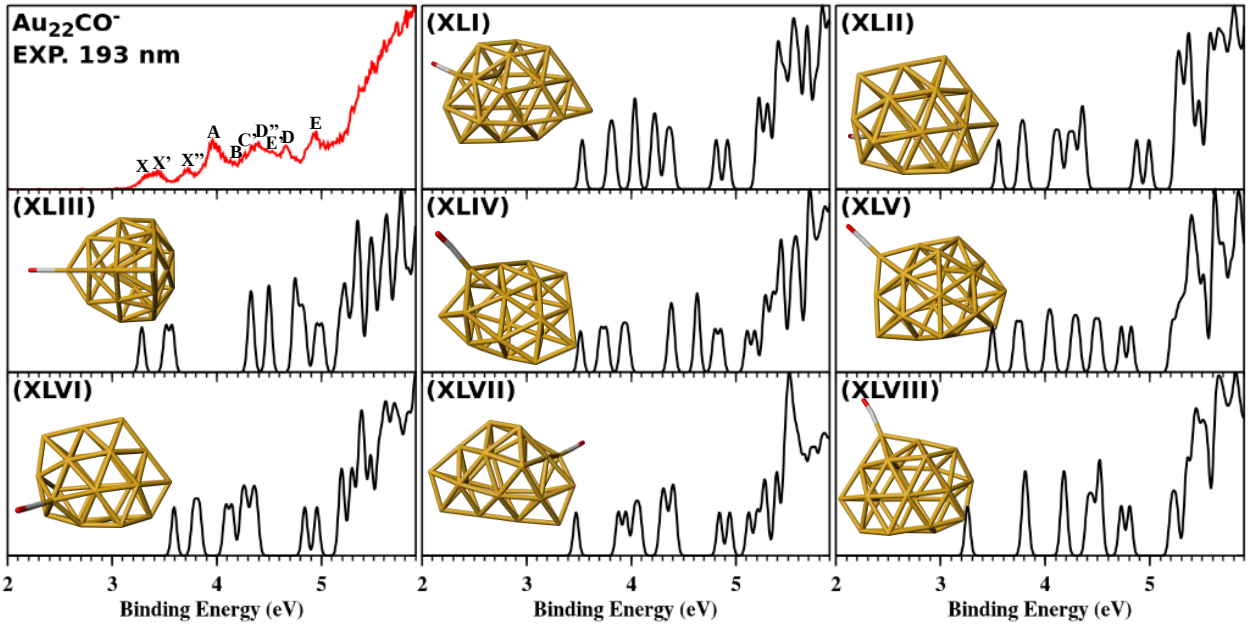

Figure S12. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

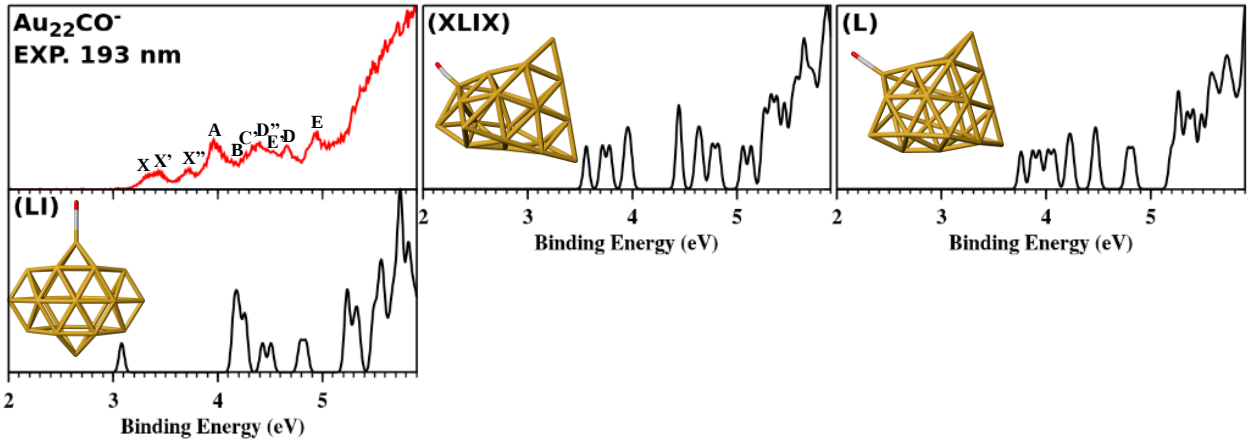

Figure S13. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{22}CO^{-}$.

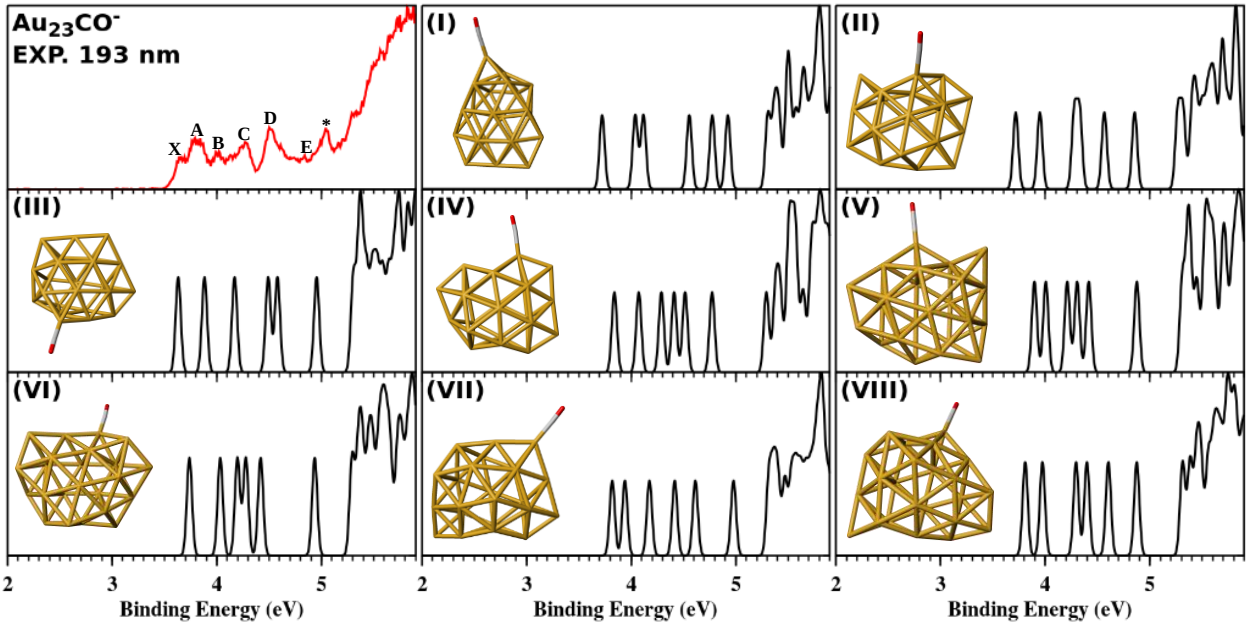

Figure S14. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{23}CO^{-}$.

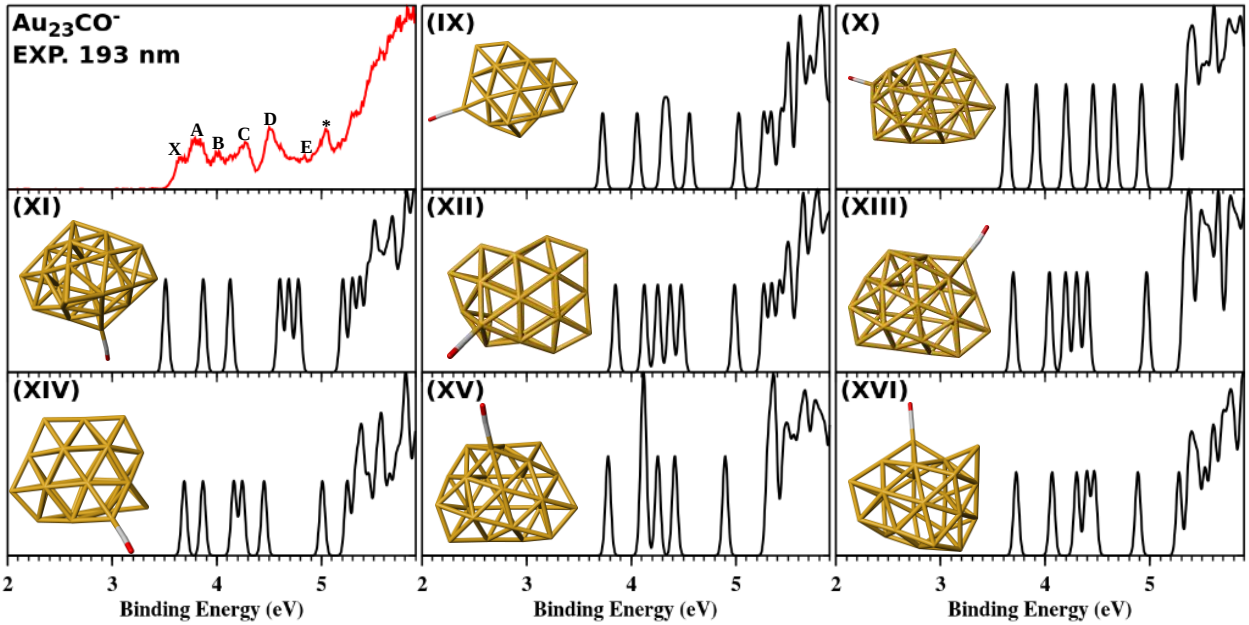

Figure S15. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{23}CO^{-}$.

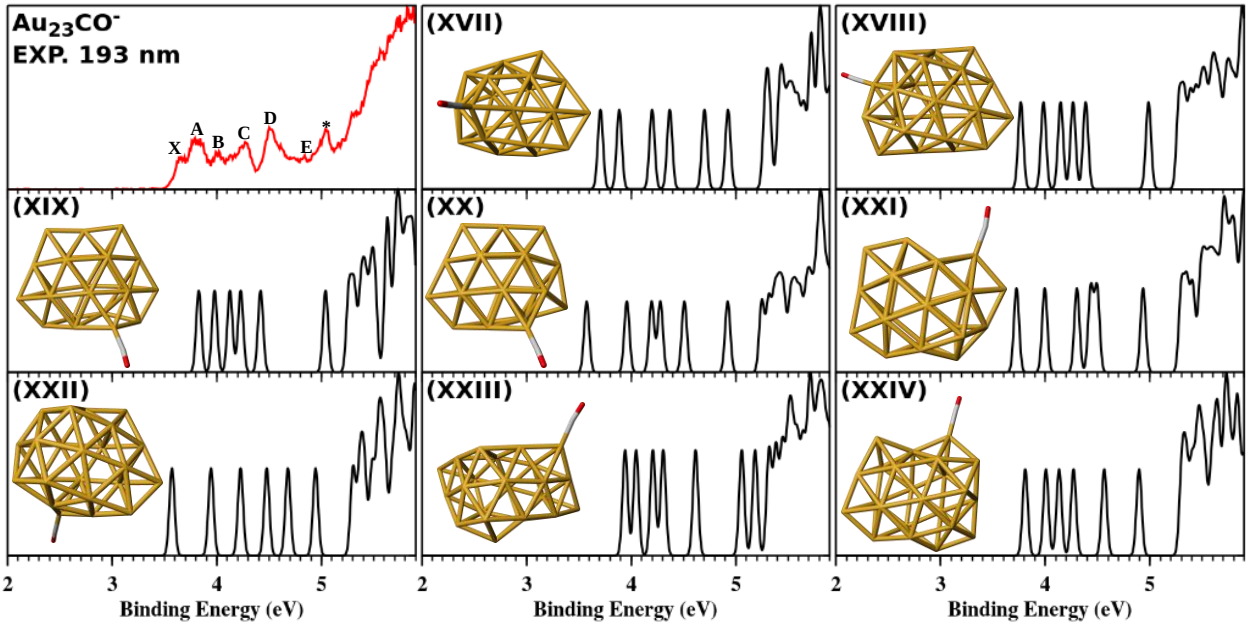

Figure S16. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{23}CO^{-}$.

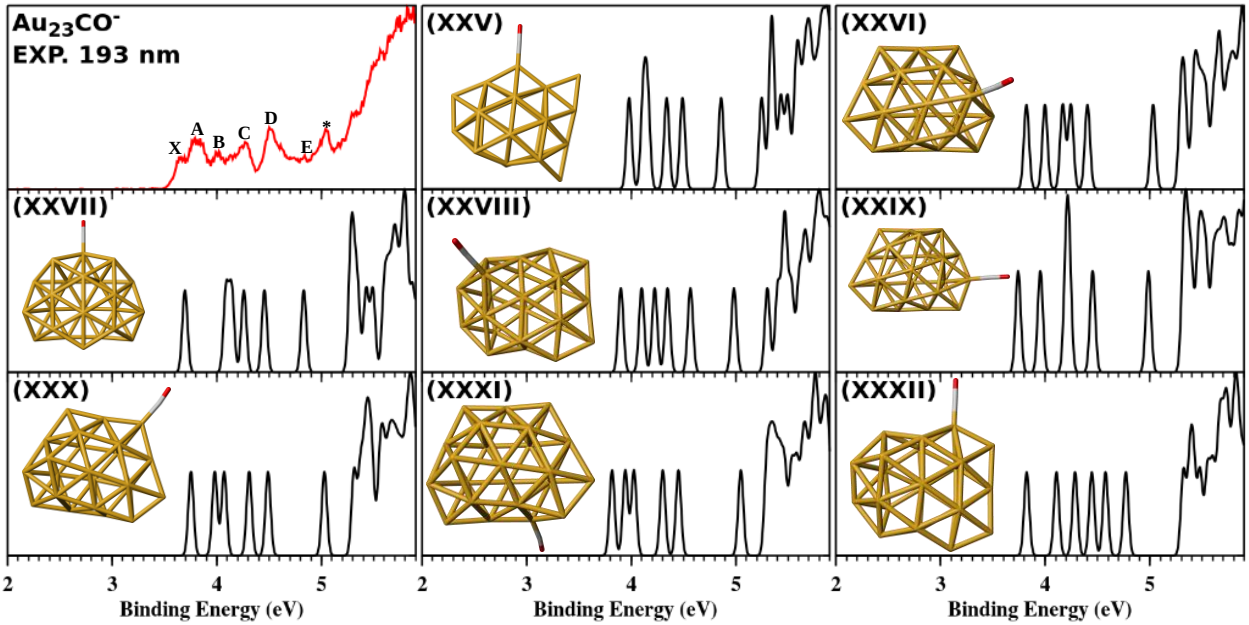

Figure S17. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{23}CO^{-}$.

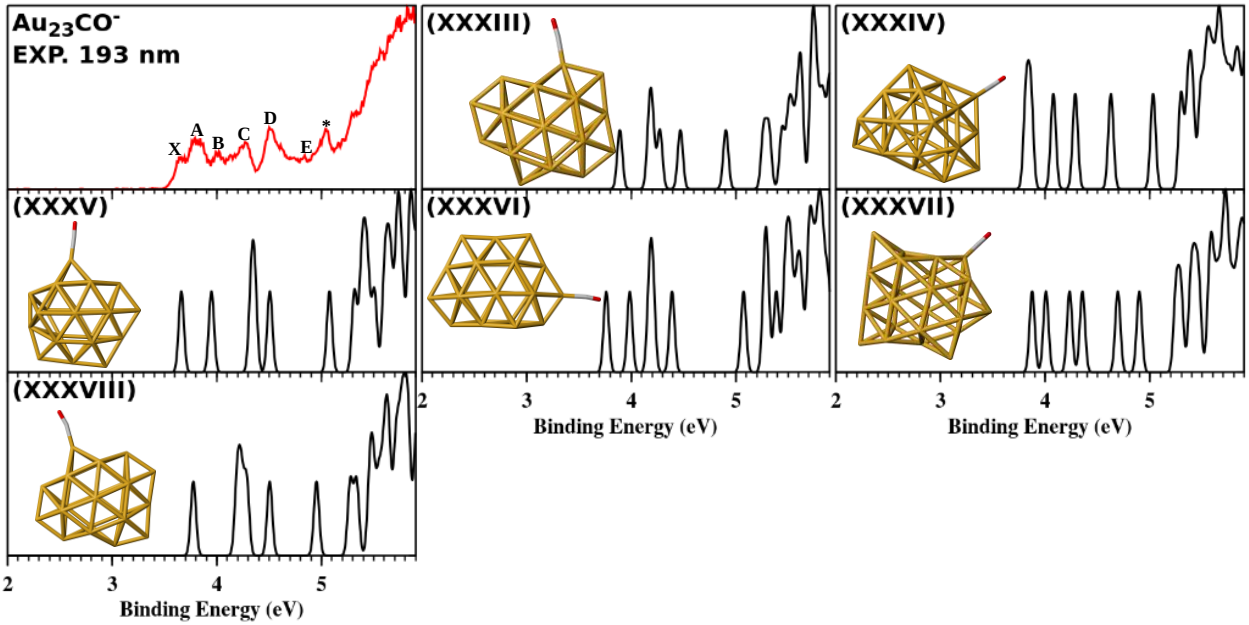

Figure S18. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{23}CO^-$.

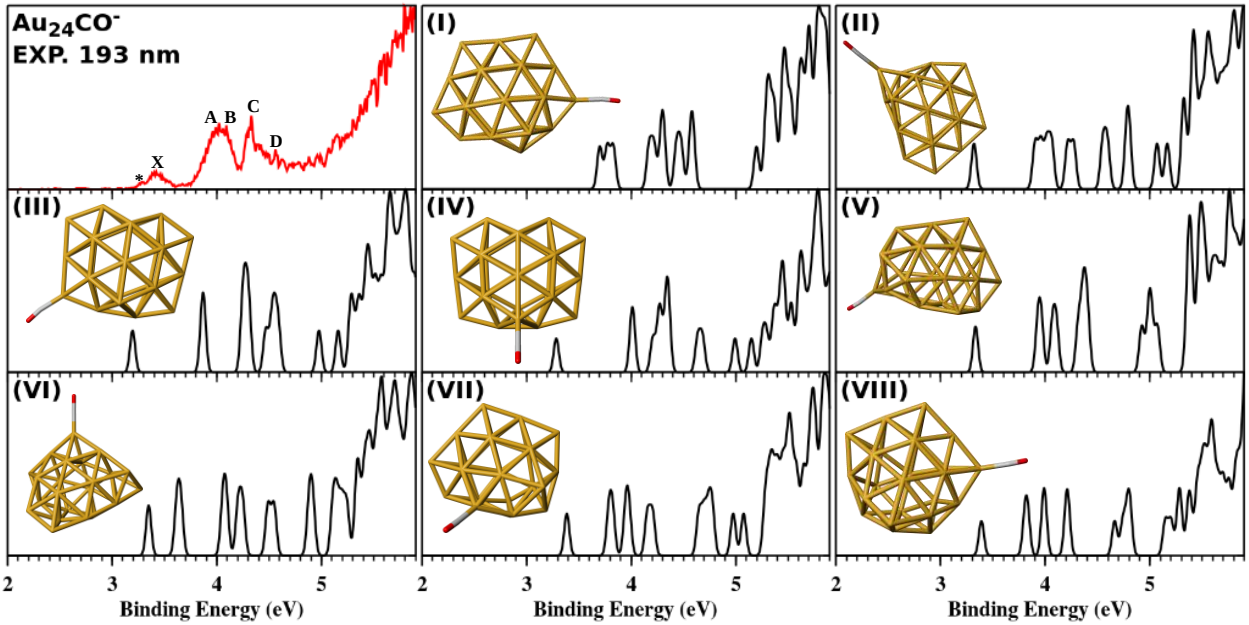

Figure S19. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^-$.

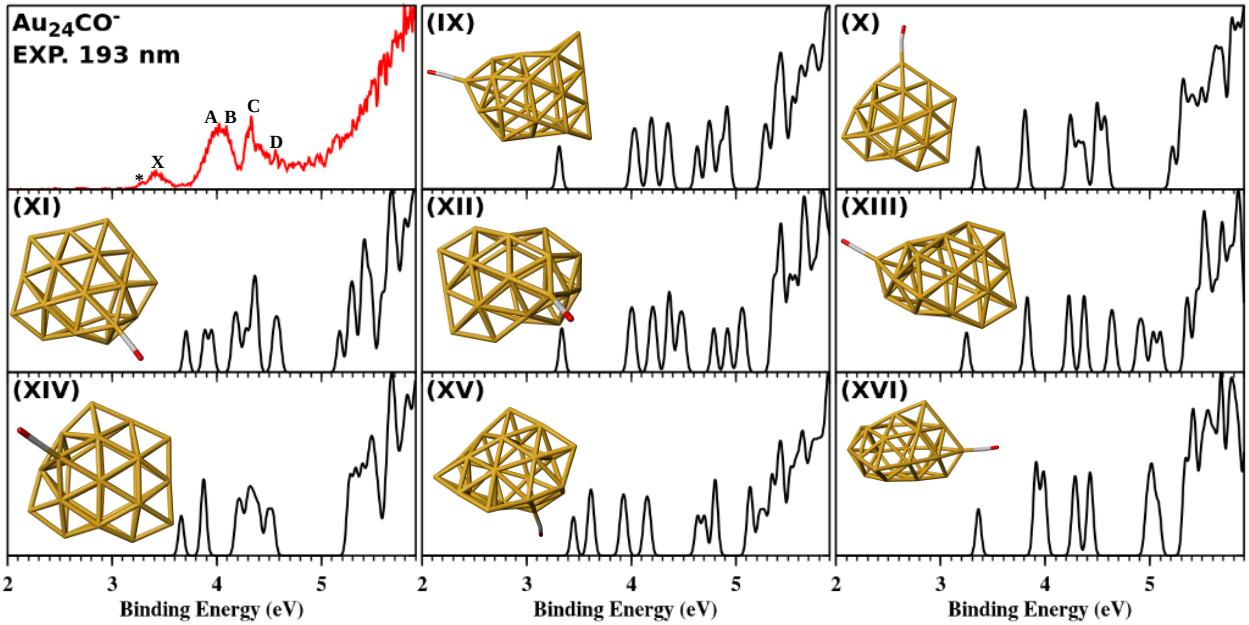

Figure S20. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^{-}$.

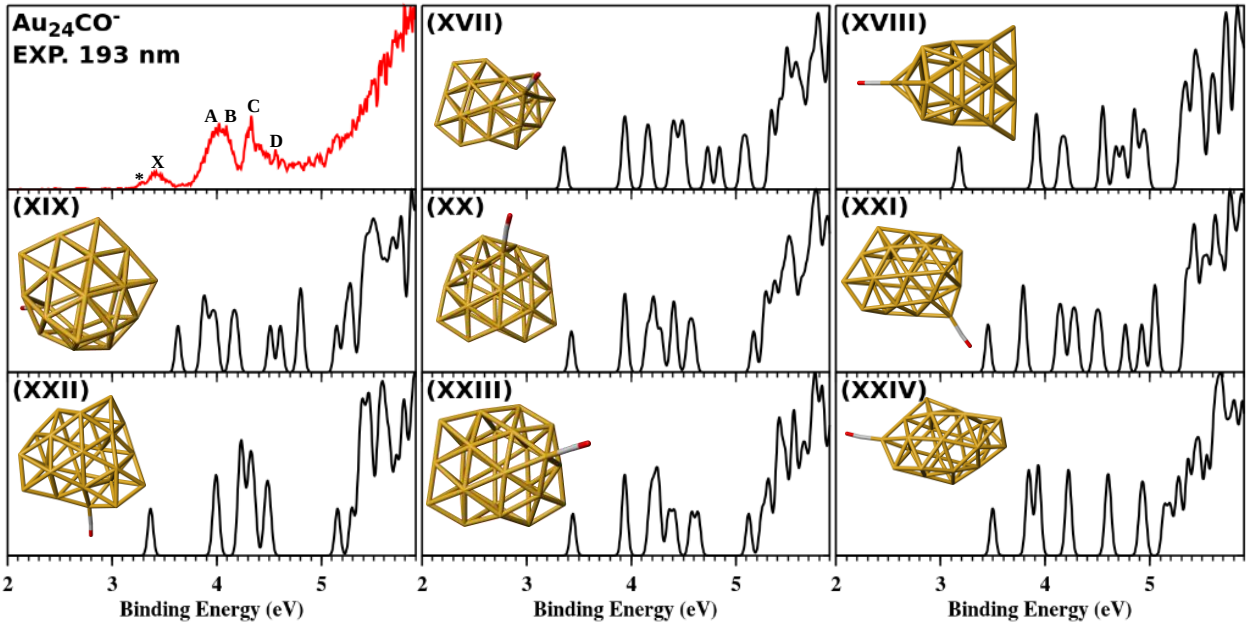

Figure S21. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^{-}$.

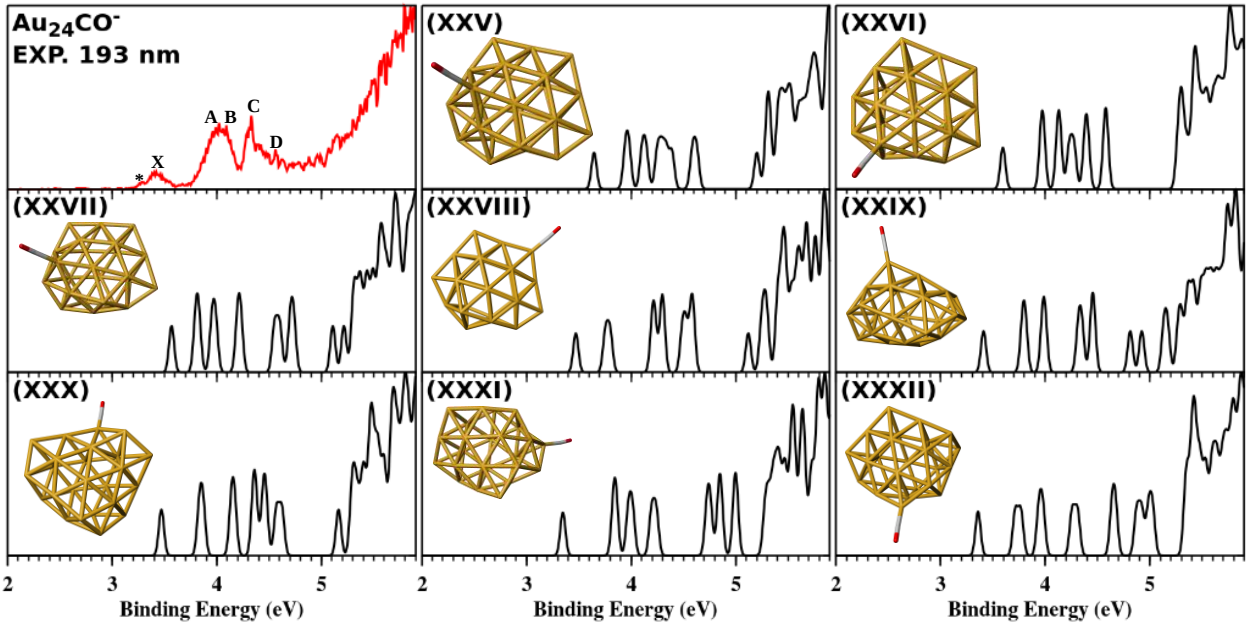

Figure S22. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^{-}$.

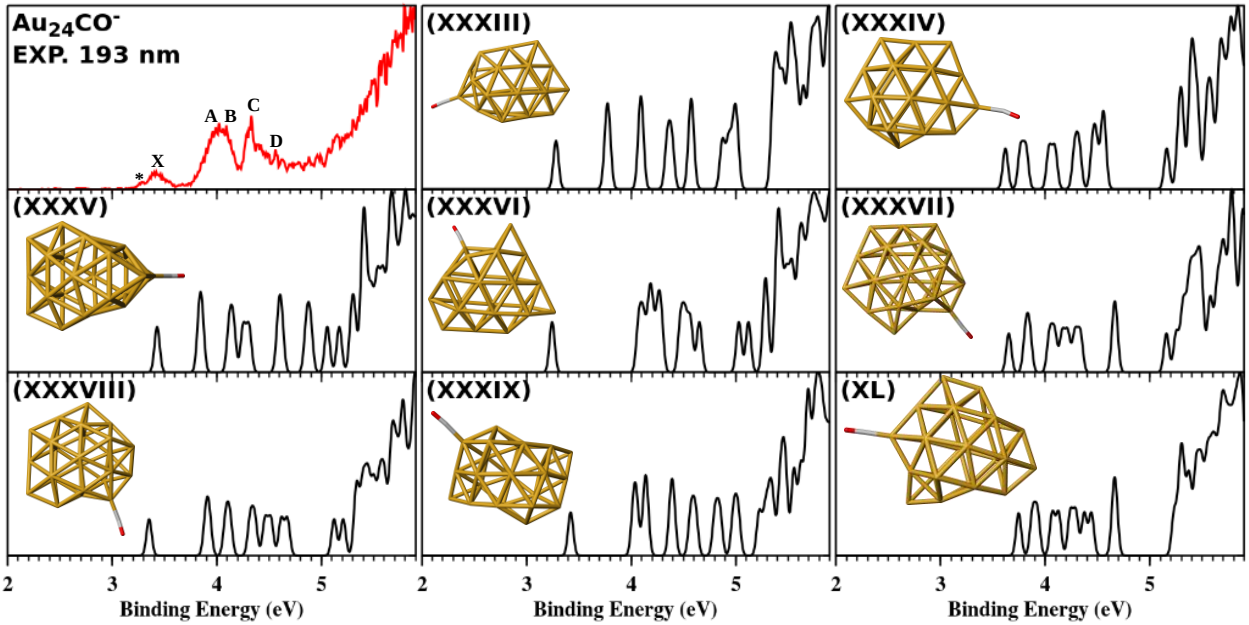

Figure S23. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^{-}$.

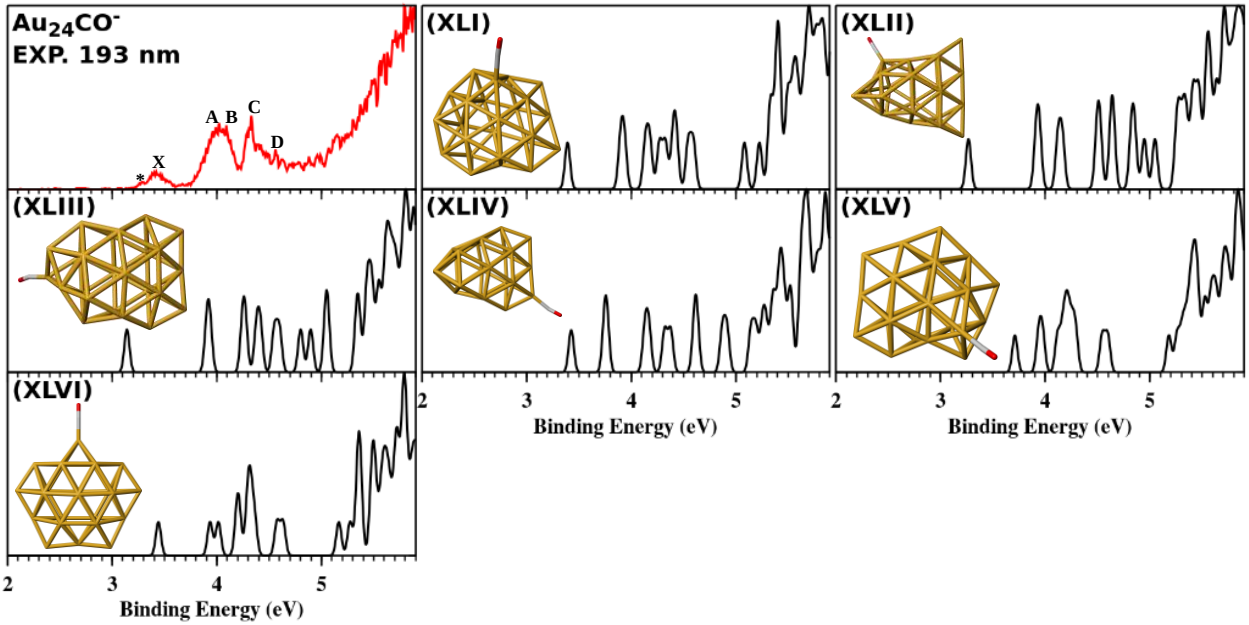

Figure S24. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{24}CO^-$.

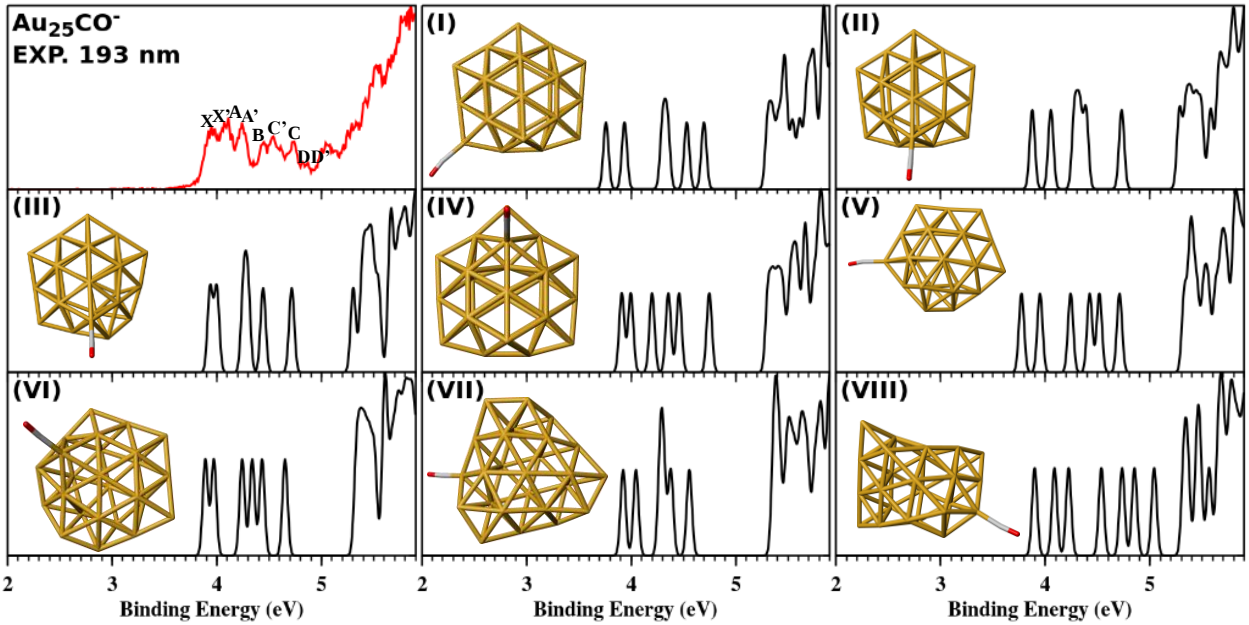

Figure S25. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^-$.

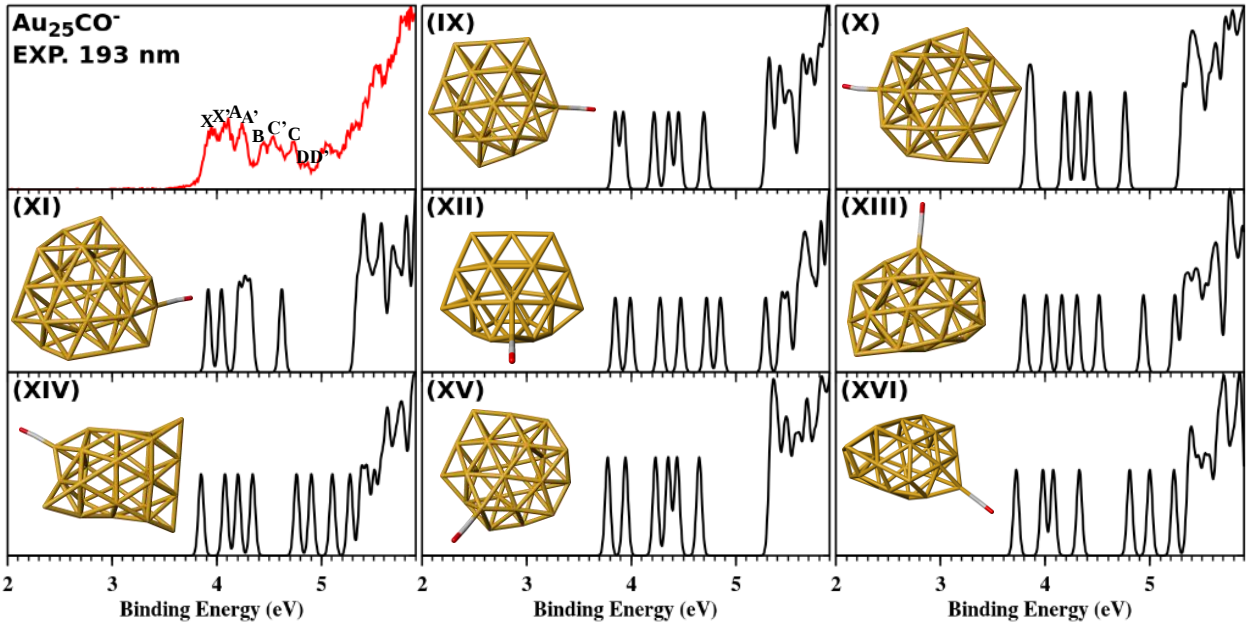

Figure S26. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

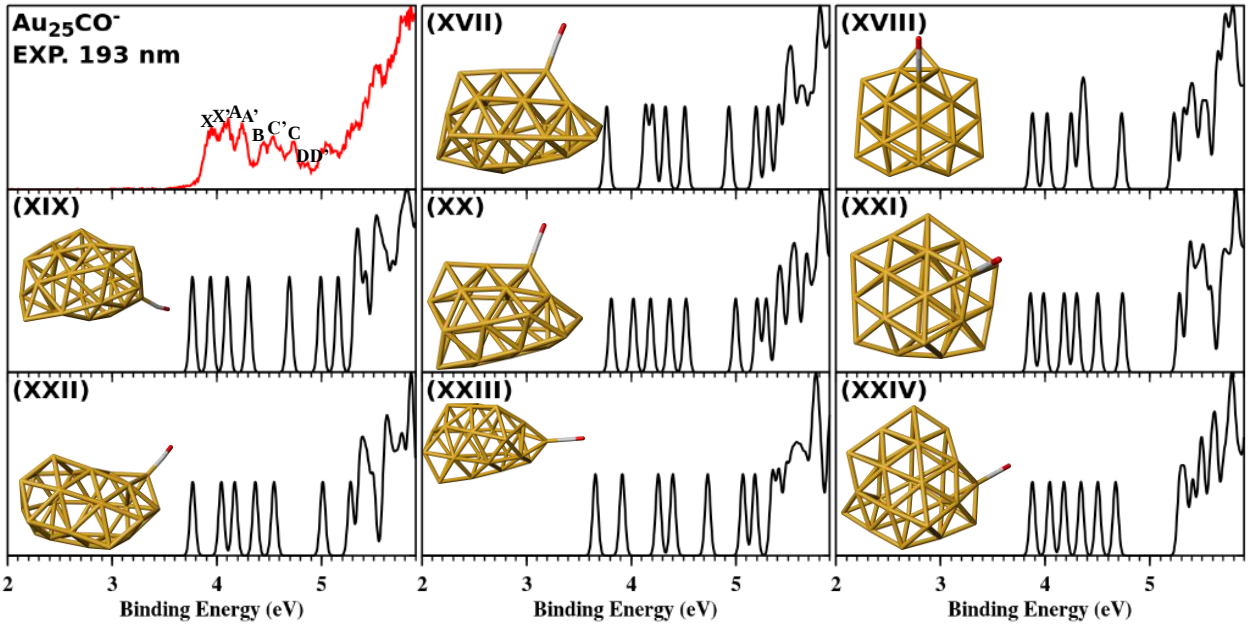

Figure S27. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

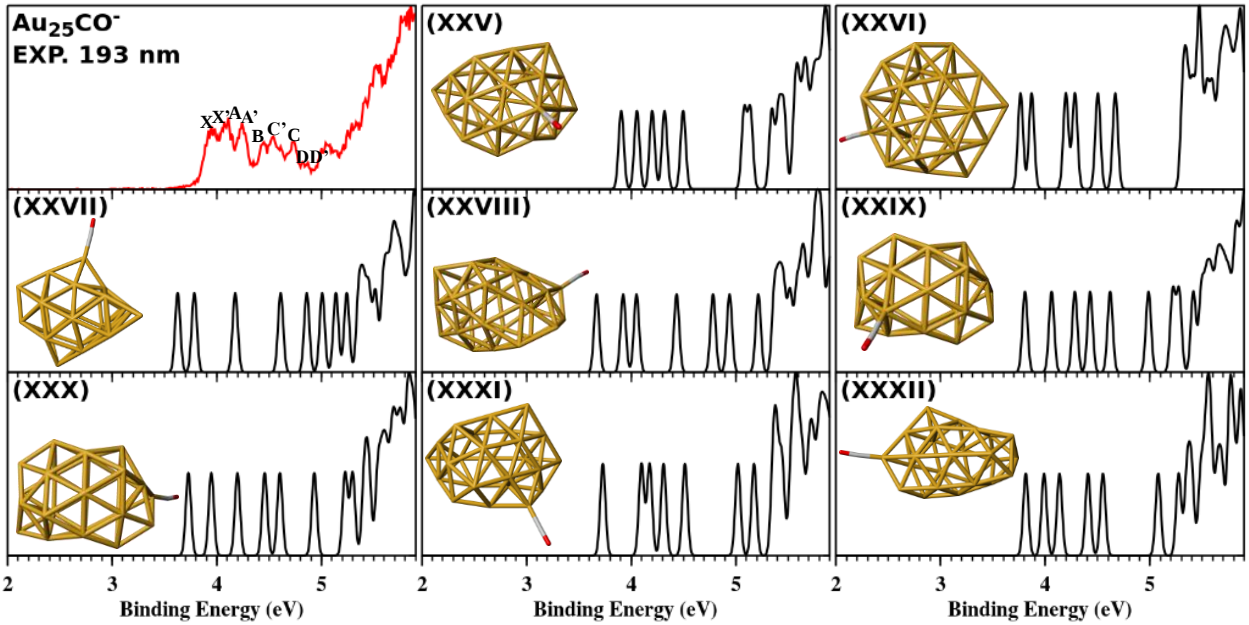

Figure S28. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

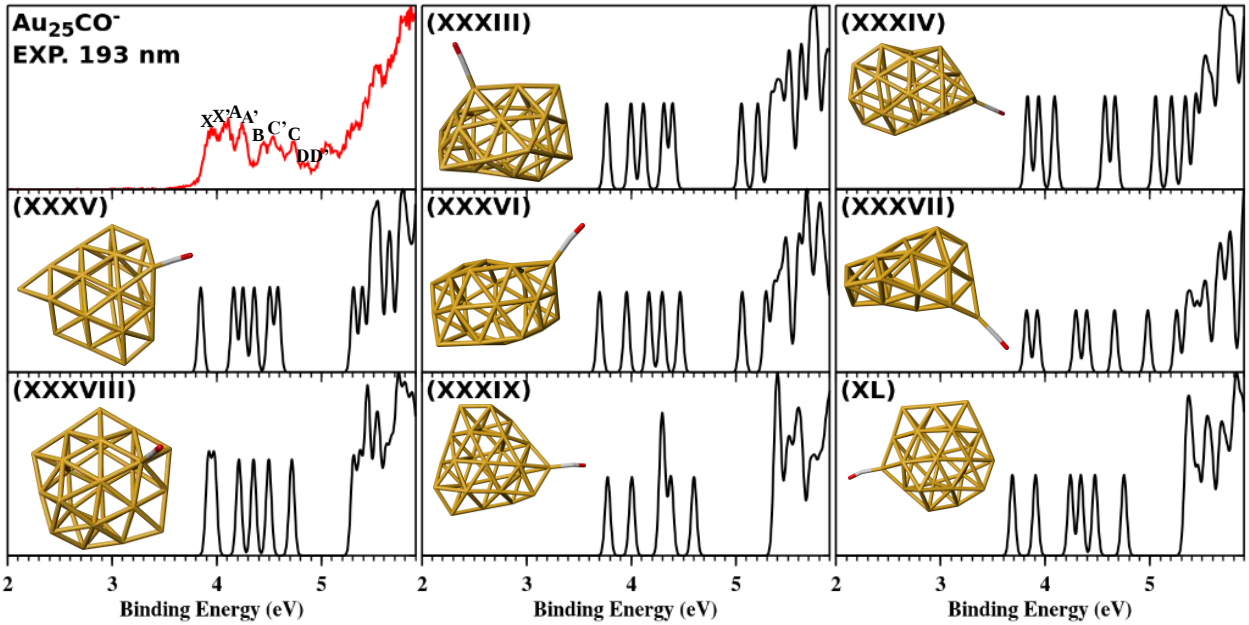

Figure S29. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

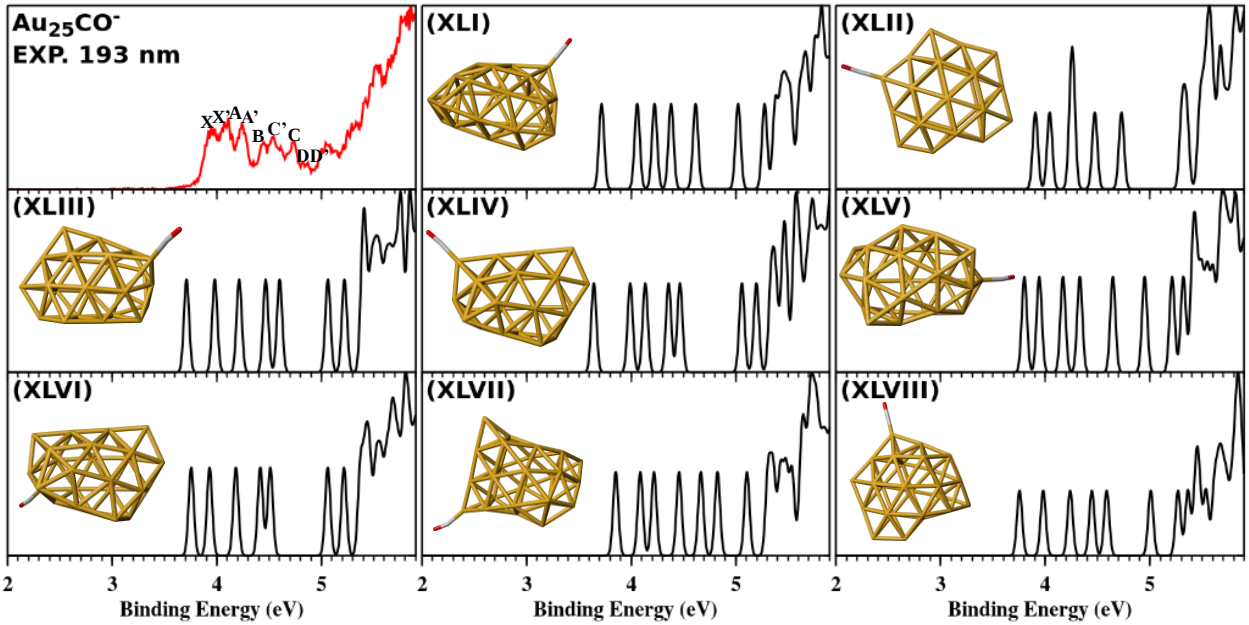

Figure S30. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

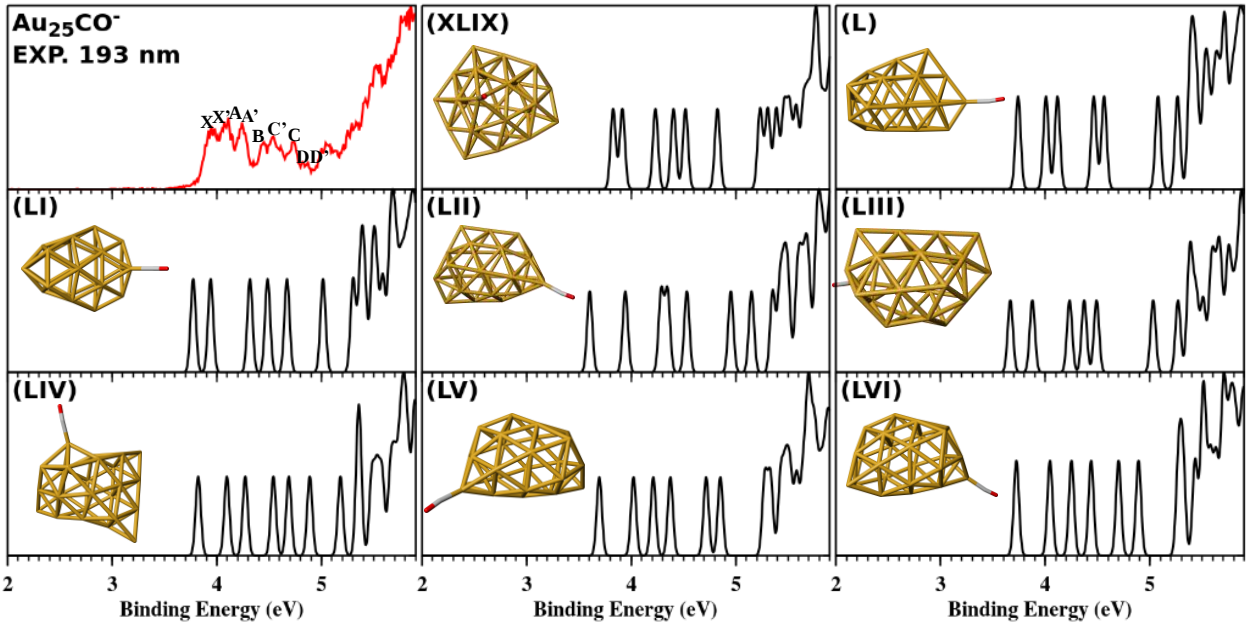

Figure S31. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

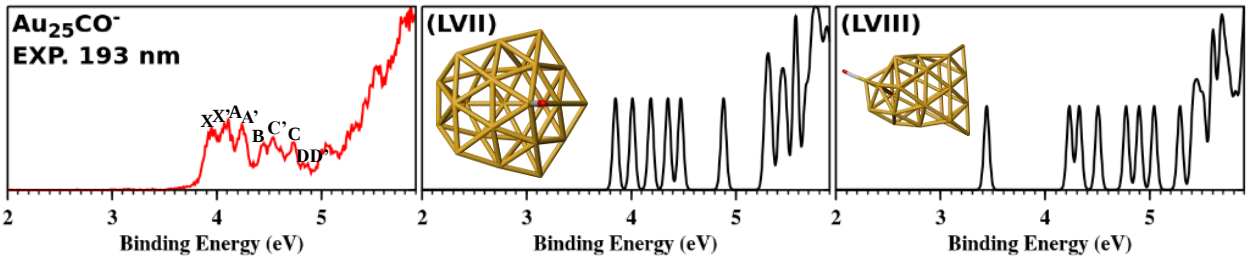

Figure S32. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of $Au_{25}CO^{-}$.

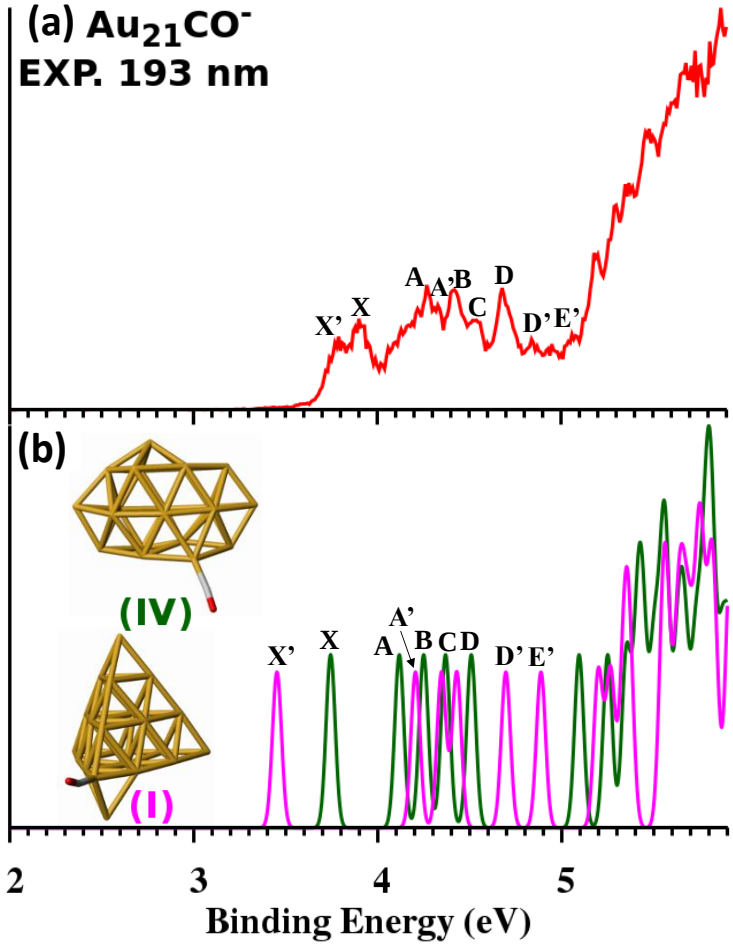

Figure S33. Comparison of the combined simulated spectrum (with isomer IV as major and isomer I as minor) with the 193 nm experimental spectra of $Au_{21}CO^{-}$.

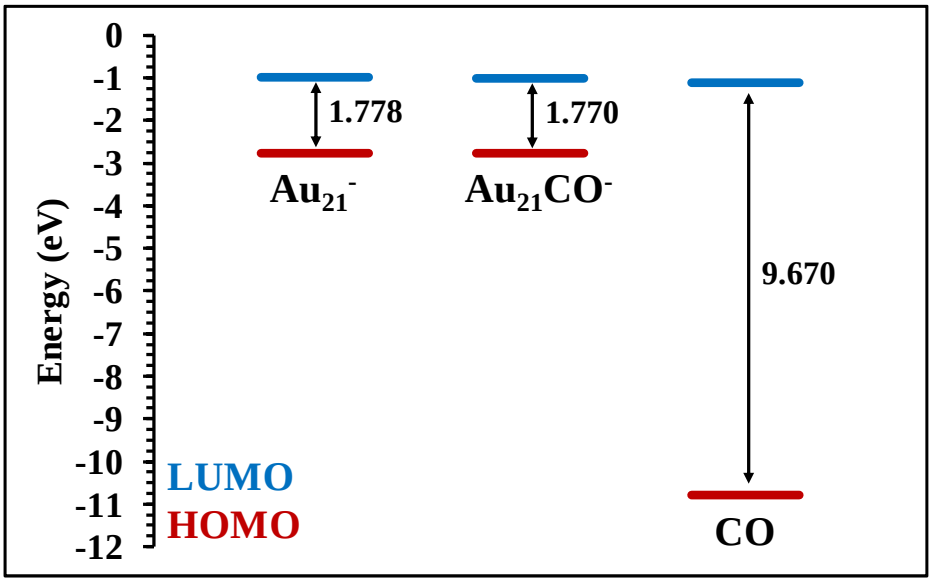

Figure S34. Comparison between the energies of the HOMO and LUMO levels of Au_{21}^-, $Au_{21}CO^-$ clusters and free CO molecule. The zero of the energy scale is the vacuum level.

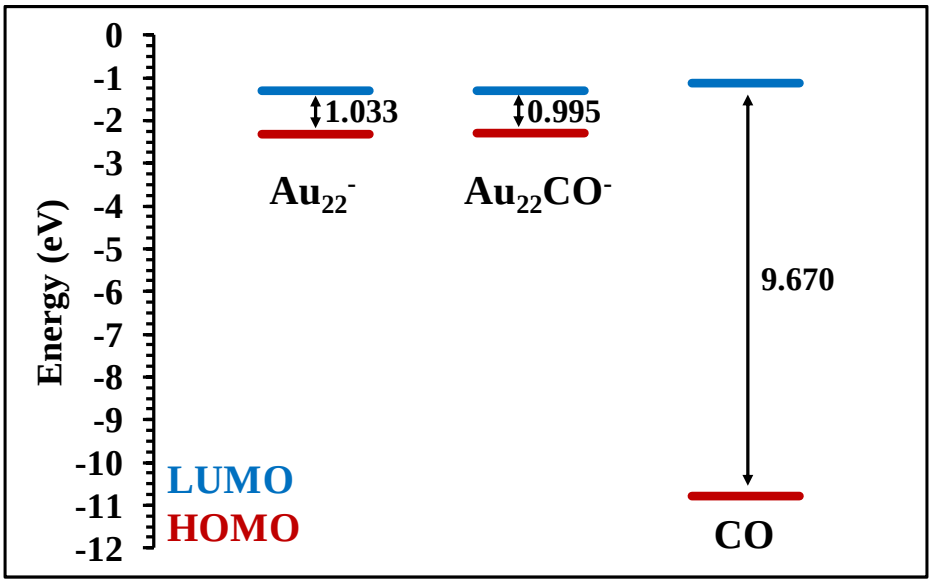

Figure S35. Comparison between the energies of the HOMO and LUMO levels of Au_{22}^-, $Au_{22}CO^-$ clusters and free CO molecule. The zero of the energy scale is the vacuum level.

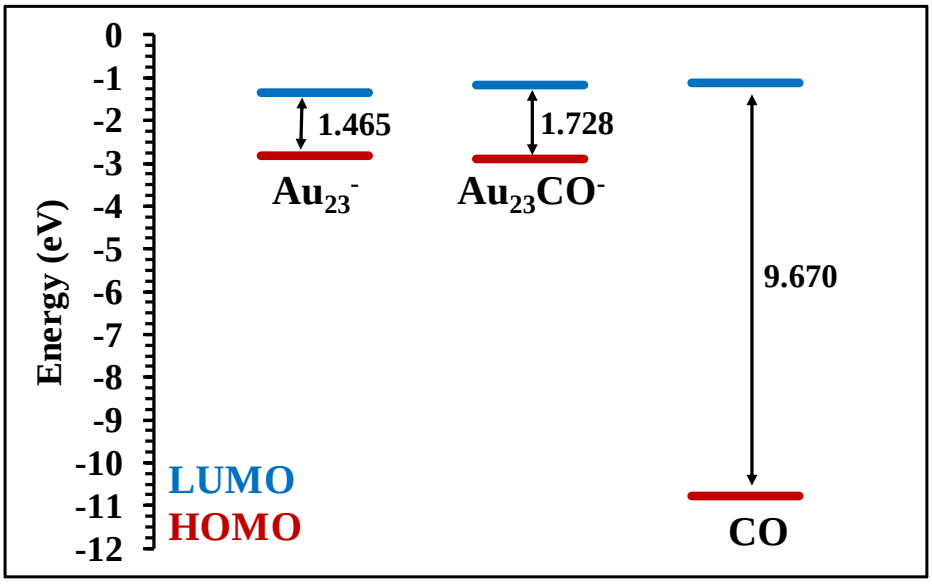

Figure S36. Comparison between the energies of the HOMO and LUMO levels of Au_{23}^-, $Au_{23}CO^-$ clusters and free CO molecule. The zero of the energy scale is the vacuum level.

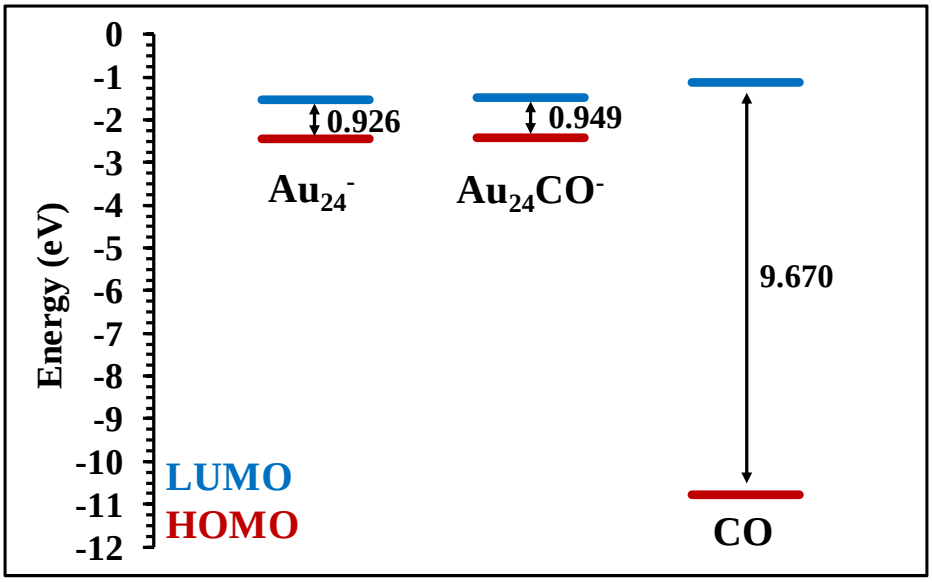

Figure S37. Comparison between the energies of the HOMO and LUMO levels of Au_{24}^-, $Au_{24}CO^-$ clusters and free CO molecule. The zero of the energy scale is the vacuum level.

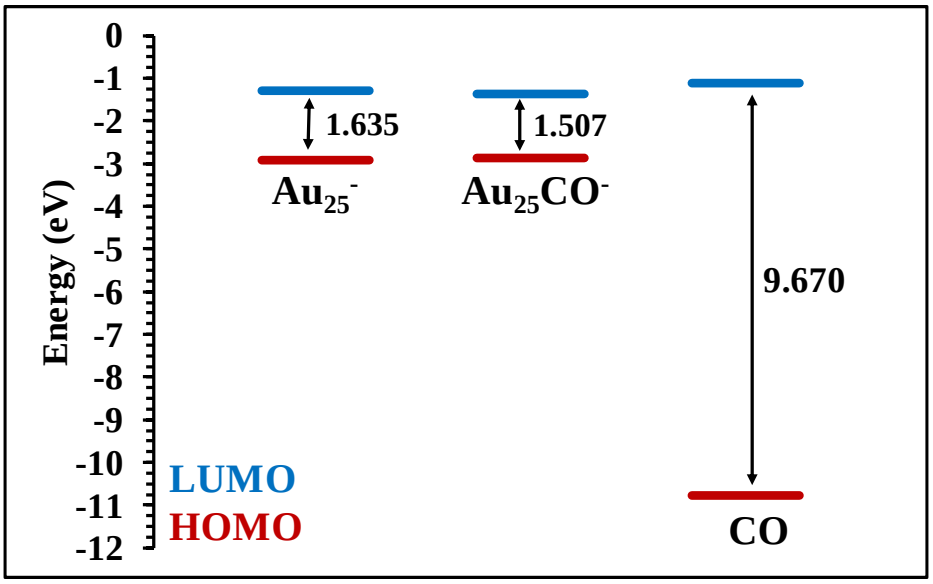

Figure S38. Comparison between the energies of the HOMO and LUMO levels of Au_{25}^-, $Au_{25}CO^-$ clusters and free CO molecule. The zero of the energy scale is the vacuum level.