Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for "A theoretical study of the structures and optical spectra of helical copper-silver clusters"

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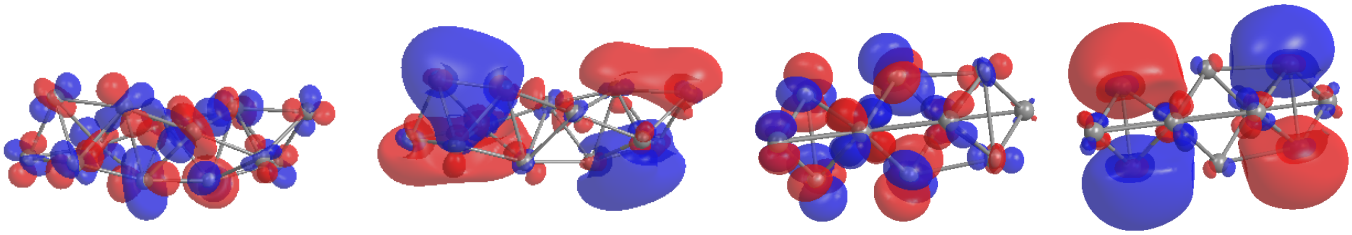

Figure S1: The interband transition-dominated excitations from the high energy regions of Ag_{13}^{+} optical response spectra. From left to right: the hole and particles states of the Bernal spiral, and the hole and particle states of the nanorod. The hole states in both cases are considerably less collective than for the lower energy excitations, and display predominantly d-like atomic orbitals, localised upon atoms.

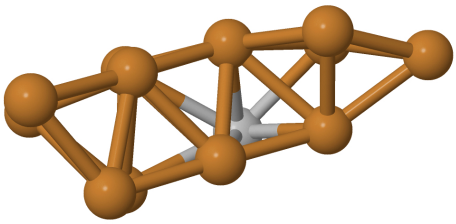

Figure S2: Resultant local minimum after reminimisation of $Cu_{12}Ag_{1}^{+}$, with the silver atom doped into site 6 of the spiral, at the NWCHEM-TZVPP level of theory. The cluster rearranges from the Bernal spiral to an unsymmetrical structure with some fcc-character, which is distorted by the presence of the silver atom.

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Peak Position	Oscillator Strength
2.99	0.087
3.00	0.093
3.28	0.086
3.29	0.083
3.63	0.231
3.79	0.080
3.79	0.080
3.98	0.178
3.96	0.182
4.23	**0.929**
4.41	**1.400**
4.42	**1.399**
4.63	**0.594**

Table S1: Positions of all transitions in the spectrum of Ag_{13}^{+} (icosahedron) with oscillator strengths above 0.05. Transitions with oscillator strengths above 0.5 are indicated by bold font.

Peak Position	Oscillator Strength
2.88	0.099
3.37	**0.535**
3.50	0.105
3.71	0.111
3.78	**2.764**
3.90	0.123
4.09	0.051
4.11	0.137
4.26	0.250
4.35	**1.420**
4.42	0.057
4.46	0.144
4.64	0.083
4.65	0.056
4.79	**0.503**
4.80	0.156
4.82	0.152
4.87	**0.890**
4.88	0.131
4.90	0.146
4.92	0.253
4.96	0.074
4.97	0.241
5.05	0.062
5.10	0.061
5.19	0.072

Table S2: Positions of all transitions in the spectrum of Ag_{13}^{+} (rod) with oscillator strengths above 0.05. Transitions with oscillator strengths above 0.5 are indicated by bold font.

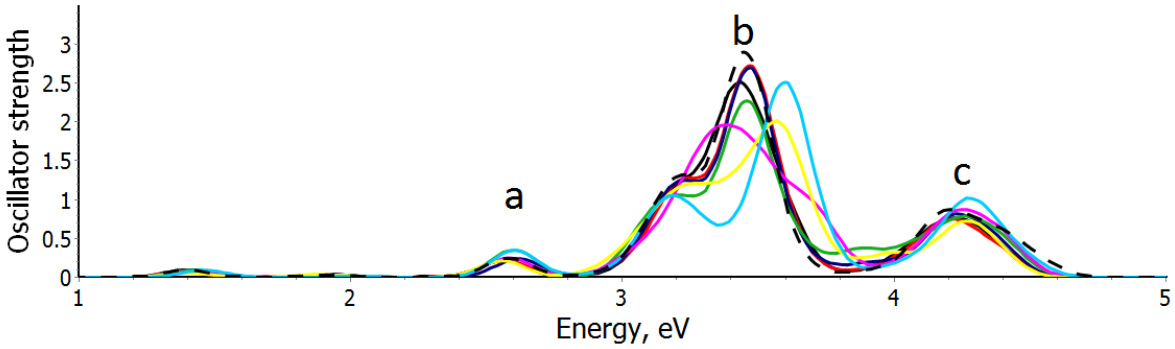


Figure S3: Overlaid view of the $Ag_{12}Cu_1^+$ def2-TZVPP spectra, showing a significant deviation only for the centrally doped sites, and little significant variation of oscillator strengths. Site 1 is black, site 2 is red, site 3 is dark blue, site 4 is green, site 5 is pink, site 6 is yellow and site 7 is cyan. Major peak regions are labelled a, b and c.

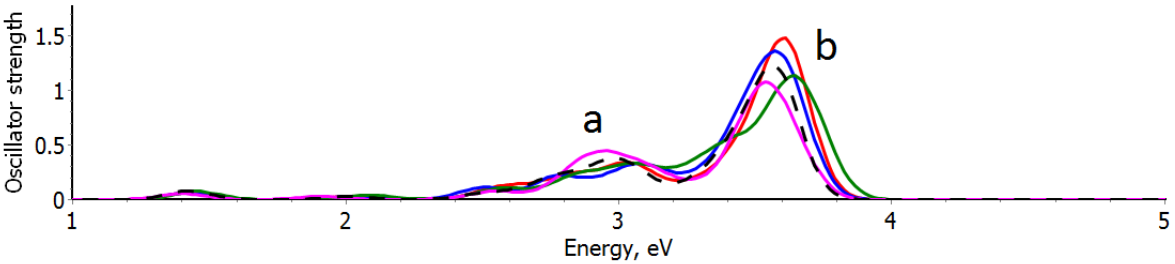
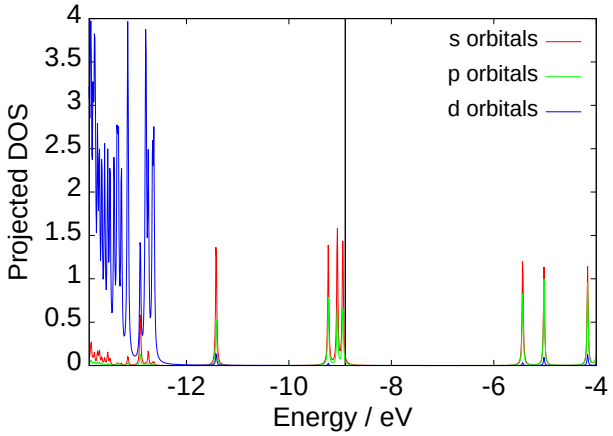
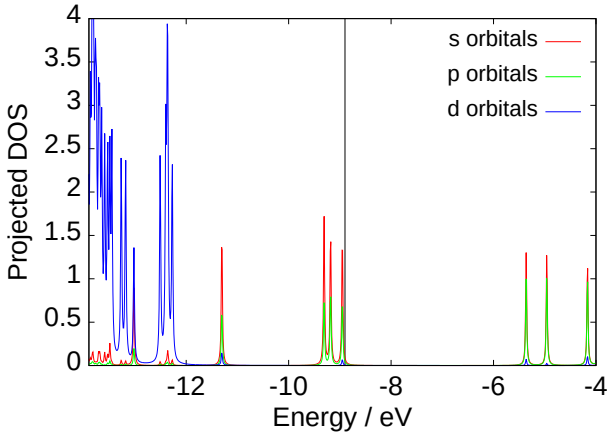


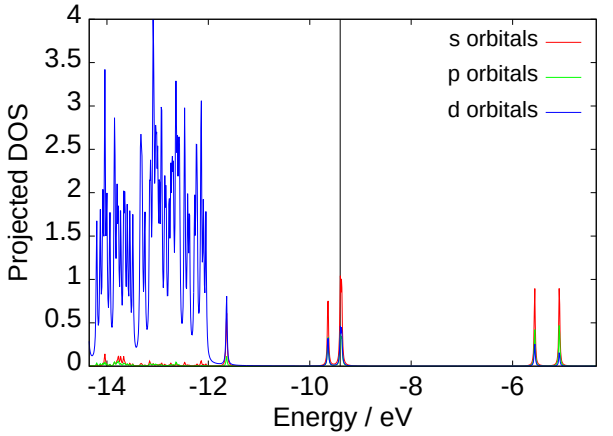
Figure S4: Overlaid view of the $Cu_{12}Ag_1^+$ def2-TZVPP spectra of dopant sites 1 (red), 3 (blue), 5 (green) and 7 (pink). The dashed line corresponds the pure Cu_{13}^+ helix for comparison.



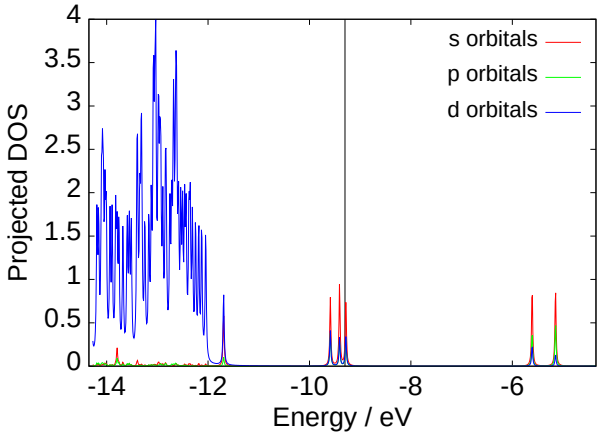
(a) $Ag_{12}Cu_1^+$ Site 1



(b) $Ag_{12}Cu_1^+$ Site 1



(c) $Cu_{12}Ag_1^+$ Site 1



(d) $Cu_{12}Ag_1^+$ Site 7

Figure S5: Projected DOS plots for $Ag_{12}Cu_1^+$ and $Cu_{12}Ag_1^+$, with dopants in positions 1 and 7. It is notable that there is significantly greater d-band density in the calculated range for the copper-rich clusters, and that the d band extends to higher energies than in the silver-rich clusters. In addition, the Fermi energies for $Ag_{12}Cu_1^+$ are -8.9 and -8.9 eV, whereas for $Cu_{12}Ag_1^+$, they are -9.4 and -9.4 eV, giving a reduced gap between HOMO and d-band for copper-rich helices. Finally it should be noted that the DOS profiles are not significantly changed with varying dopant position for either cluster.

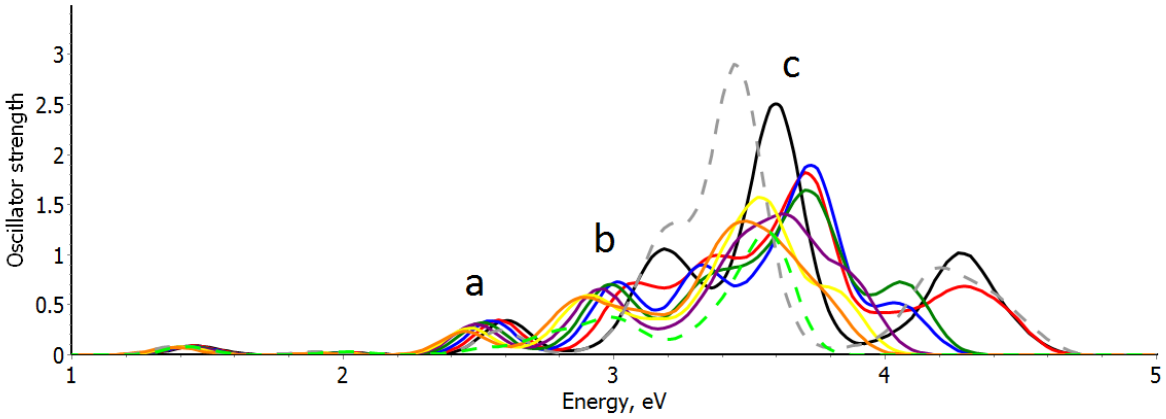


Figure S6: Overlaid view of the TDDFT spectra of $Ag_{(13-x)}Cu_x^+$ (x = 0-7 and 13), calculated with the def2-TZVPP basis and the LC-ωPBE xc-functional. Colours correspond to x = 1 (black), x = 2 (red), x = 3 (dark blue), x = 4 (green), x = 5 (purple), x = 6 (yellow), x = 7 (orange), Both pure spirals Ag_{13}^+ (grey dashed) and Cu_{13}^+ (green dashed) are included for comparison.

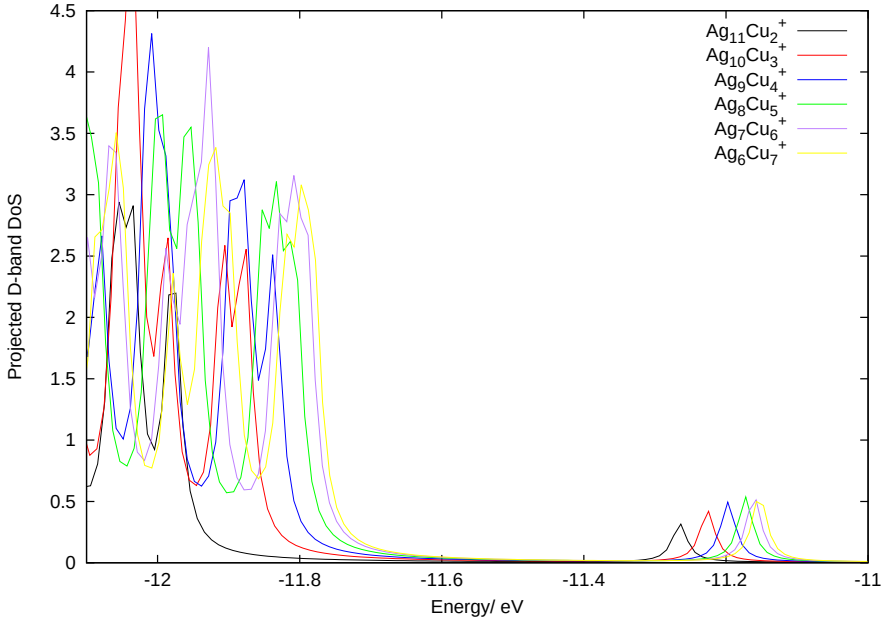


Figure S7: Projected d band densities of states for each dopant level of $Ag_{(13-x)}Cu_x^+$ x = 2-7, showing a systematic increase in d band edge energy on increased copper doping level. This trend is consistent both for the major d-band region below -11.7 eV, and for the much smaller region around -11.2 eV which also corresponds to d electrons.