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

Supplemental information for:
First-principles analysis of the efficiency of photovoltaic layers for CuAu-like chalcogenides and silicon

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1 Band gap discrepancy

For some compounds, the calculated band gap of the chalcopyrite (CH) phase does not correspond well to the experimental value. One possible reason for these discrepancies is the sensitivity of the band gap of chalcogenides to the anion displacement u. Jaffe and Zunger [1] used standard DFT to demonstrate the influence of u on the calculated band gap, finding that an increased u leads to higher band gaps for CH-CuInSe$_2$ and CH-CuAlS$_2$. Similar results were found by Vidal et al. [2] using HSE06 to calculate the band gap of CH-CuInS$_2$. In Table 1, we present the u parameter calculated using PBE versus a set of experimental results. We can see that although u corresponds well to experiment for some compounds, there are significant differences for others. For example, the calculated u of both CH-CuInS$_2$ and CH-CuInSe$_2$ are below the experimental range. Considering the influence of u on the band gap, it is not unreasonable to assert that the underestimation of the band gap may be related to the low values found for u.

2 Optical properties

For the calculation of the SLME, we require the dielectric tensor of the studied material. For all of the structures considered in this paper, the dielectric tensor is found to be diagonal and has two independent components:

$$\varepsilon_{\alpha\beta}(E) = \begin{pmatrix} \varepsilon_{xx}(E) & 0 & 0 \\ 0 & \varepsilon_{xx}(E) & 0 \\ 0 & 0 & \varepsilon_{zz}(E) \end{pmatrix}, \qquad (1)$$

where each component is imaginary (e.g. $\varepsilon_{xx}(E) = \varepsilon_{xx}^{(1)}(E) + i\varepsilon_{xx}^{(2)}(E)$). Figures 1 and 2 show both the real and imaginary part of the calculated tensor components for the CuAu-like phase of the studied

Table 1: Calculated and experimental [1] anion displacement for the chalcopyrite phase of the studied compounds.

Material	u_{PBE}	u_{exp}
$AgGaSe_2$	0.278	0.27
		0.276
$AgGaTe_2$	0.266	0.26
$AgInS_2$	0.256	0.25
		0.250
$AgInTe_2$	0.243	0.25
$CuGaS_2$	0.237	0.25
		0.275
		0.2539
		0.272
$CuGaSe_2$	0.244	0.25
		0.250
		0.243
$CuGaTe_2$	0.237	0.25
$CuInS_2$	0.218	0.20
		0.214
		0.2295
$CuInSe_2$	0.217	0.22
		0.224
		0.235
$CuInTe_2$	0.214	0.225

compounds. For completeness, we show the optical dielectric constants in Table 2. It is interesting to note that the choice of the anion (S,Se,Te) in the CuAu-like phase of the I-III-VI$_2$ compounds has a strong influence on the value of their optical dielectric constants. The computational details can be found in Section 2 of the main text.

Table 2: Optical dielectric constants of the CuAu-phase of the studied compounds.

Material	$\varepsilon_{xx}(\infty)$	$\varepsilon_{zz}(\infty)$
$AgGaSe_2$	6.37	6.66
$AgGaTe_2$	8.71	8.61
$AgInS_2$	5.24	5.53
$AgInTe_2$	7.96	8.20
$CuGaS_2$	5.72	6.09
$CuGaSe_2$	6.99	7.34
$CuGaTe_2$	9.00	9.40
$CuInS_2$	5.90	6.34
$CuInSe_2$	7.18	7.69
$CuInTe_2$	8.42	8.99

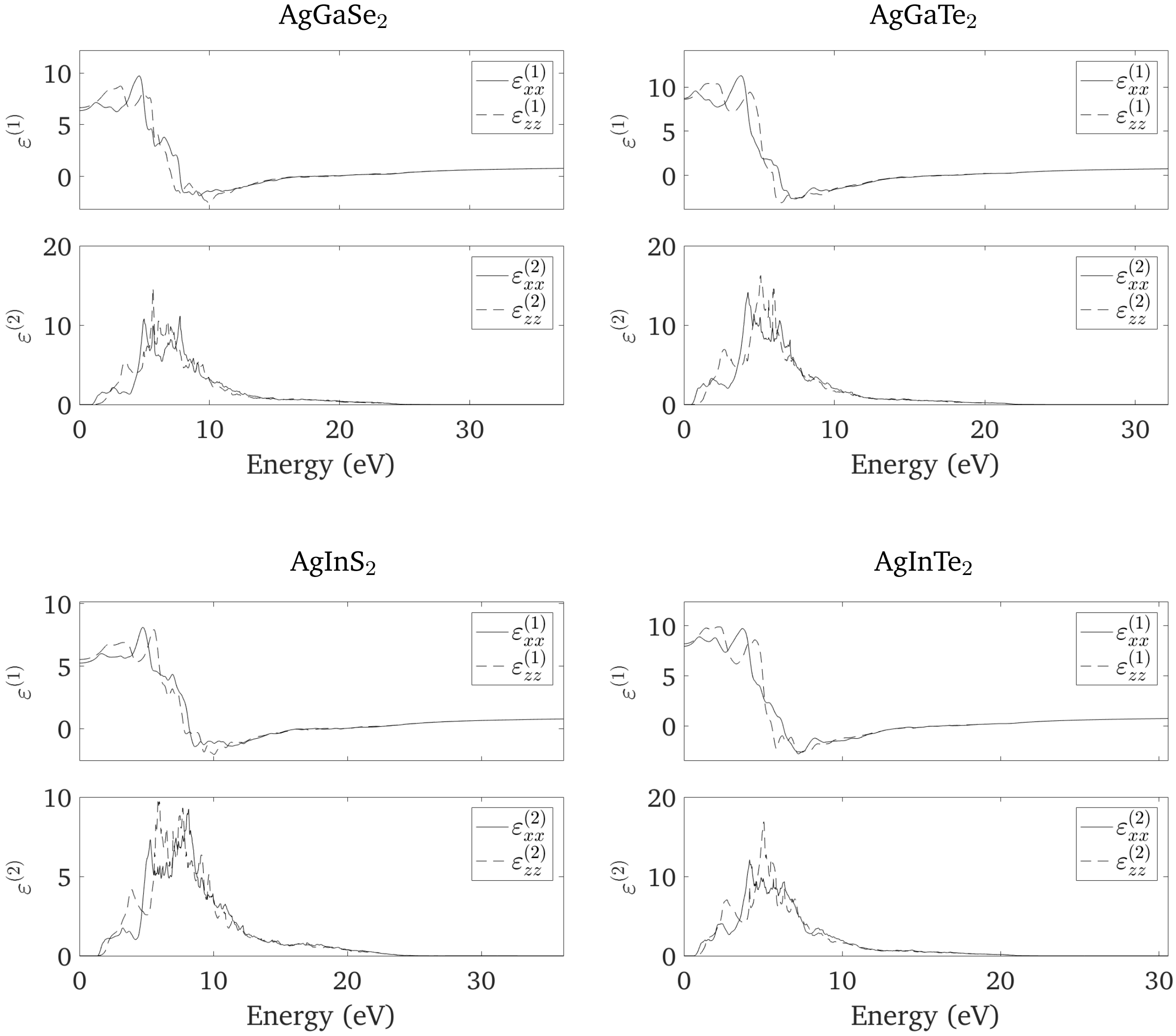

Figure 1: Dielectric functions of the CuAu-like phase of the Ag-III-VI$_2$ compounds.

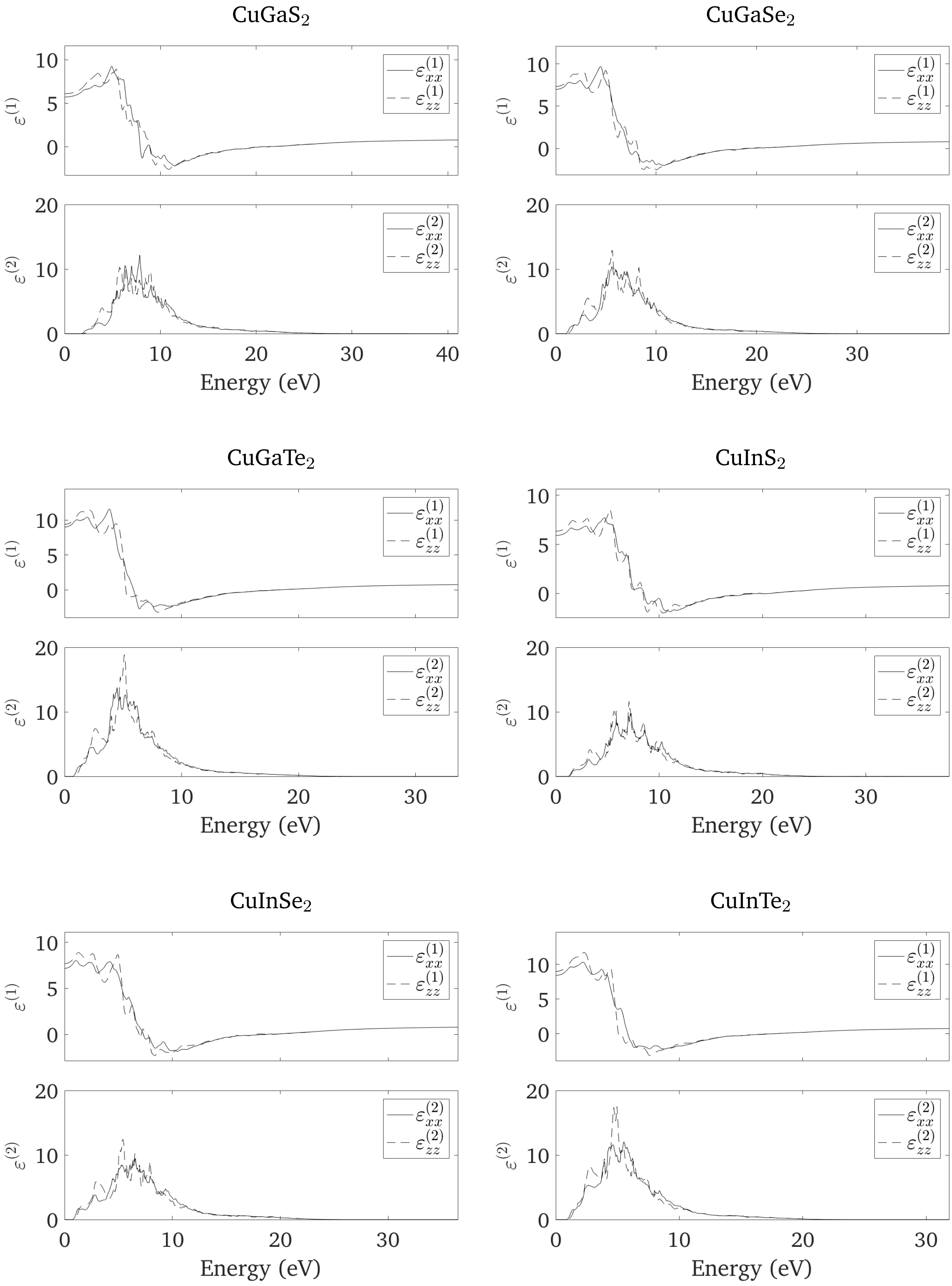

Figure 2: Dielectric functions of the CuAu-like phase of the Cu-III-VI$_2$ compounds.

References

[1] J. E. Jaffe and A. Zunger, “Theory of the band-gap anomaly in AB c 2 chalcopyrite semiconductors”, Phys. Rev. B **29**, 1882–1906 (1984).

[2] J. Vidal, S. Botti, P. Olsson, J.-F. Guillemoles, and L. Reining, “Strong interplay between structure and electronic properties in CuIn (s , se) 2 : a first-principles study”, Phys. Rev. Lett. **104** (2010) `10.1103/physrevlett.104.056401`.