

# Supplementary Information

## Symmetry breaking in core-valence double ionisation of allene

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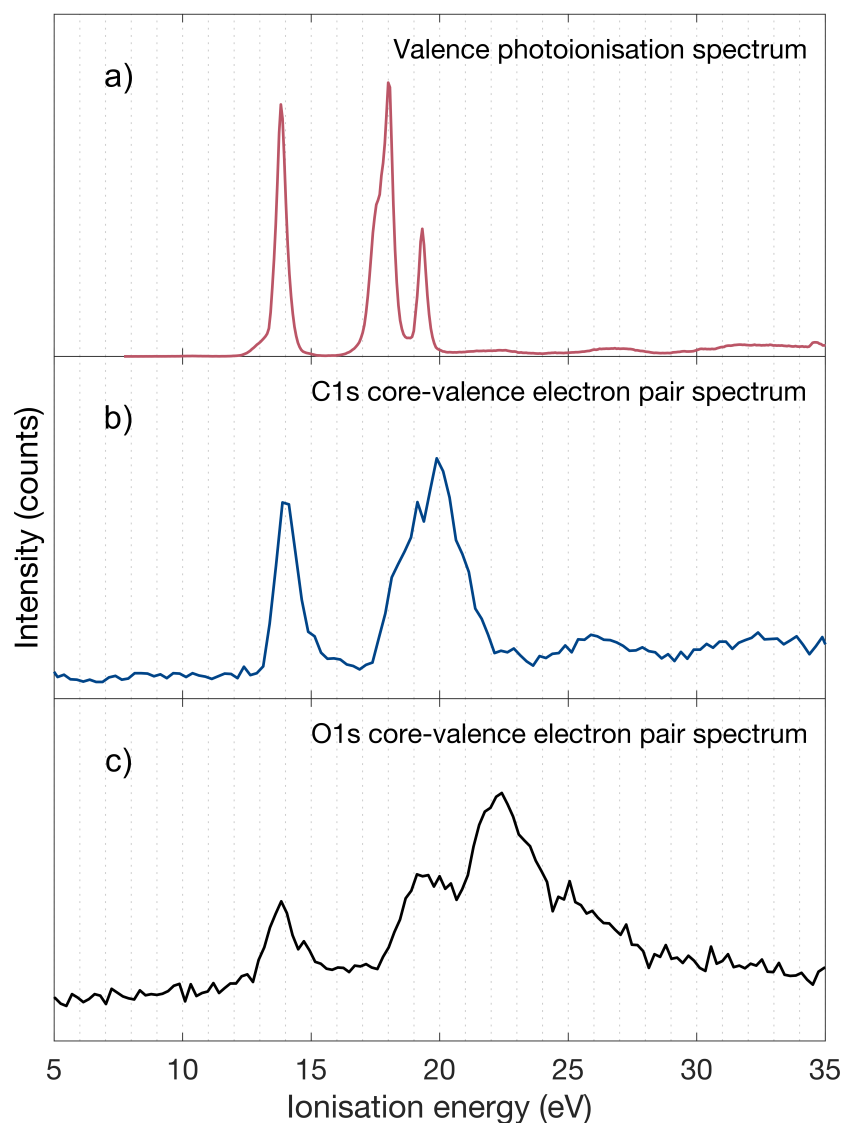
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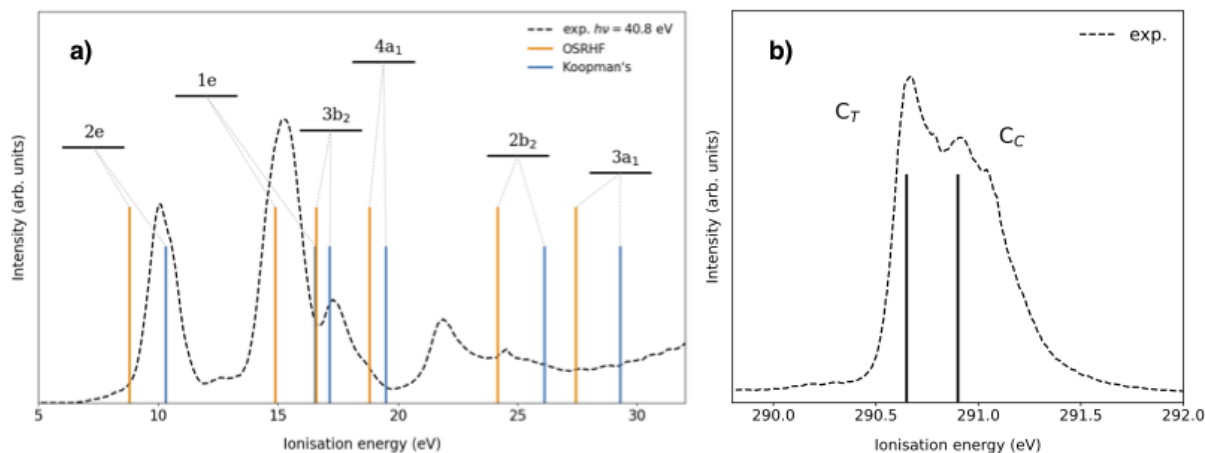
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## Supplementary Note 1: Experimental core-valence double ionisation spectra of CO<sub>2</sub>



**Supplementary Figure 1.** Core-valence spectra of CO<sub>2</sub> obtained at photon energies of 360 eV for the C1s edge (panel b)) and 603 eV for the O1s edge (panel c)), respectively, in comparison with the valence photoelectron spectrum (panel a)) obtained at 40.81 eV photon energy. The core-valence spectra were shifted by 308.1 eV (panel b)) and 554.1 eV (panel c)), respectively, to line up with the lowest spectral feature of the valence photoelectron spectrum. Similar core-valence spectra of CO<sub>2</sub> have been published previously by some of us<sup>1,2</sup>.

## Supplementary Note 2: Experimental valence and carbon 1s ionisation spectra of allene in comparison with theoretical calculations



**Supplementary Figure 2.** Panel a): Theoretical calculations of the valence single ionisation energies of allene, in comparison to our experimental data. Panel b): Theoretical calculations of the single carbon 1s core-ionisation energies of allene, in comparison to the experimental data (taken with permission from the PhD thesis of Oksana Travnikova<sup>3</sup>). C<sub>C</sub> and C<sub>T</sub> denote the central and terminal carbon atoms, respectively.

## Supplementary References

1. Eland, J. H. D. *et al.* Triple ionization of CO<sub>2</sub> by valence and inner shell photoionization. *J. Chem. Phys.* **135**, 134309, DOI: [10.1063/1.3643121](https://doi.org/10.1063/1.3643121) (2011). <https://doi.org/10.1063/1.3643121>.
2. Eland, J. H. D. & Feifel, R. *Double photoionisation spectra of molecules* (Oxford University Press, 2018).
3. Travnikova, O. *Structure and Dynamics of Core-Excited Species*. Ph.D. thesis, Acta Universitatis Upsaliensis (2008).