

Supplementary Information

Symmetry breaking in core-valence double ionisation of allene

Veronica Ideböhn¹, Roberto Linguerri², Lucas M. Cornetta^{3,4}, Emelie Olsson¹, Måns Wallner¹, Richard J. Squibb¹, Rafael C. Couto⁵, Leif Karlsson³, Gunnar Nyman⁶, Majdi Hochlaf², John H.D. Eland⁷, Hans ° Agren³, and Raimund Feifel^{1,*}

¹University of Gothenburg, Department of Physics, Origovägen 6B, 412 58 Gothenburg, Sweden

²Université Gustave Eiffel, COSYS/IMSE, 5 Bd Descartes 77454, Champs sur Marne, France.

³Uppsala University, Department of Physics and Astronomy, Box 516, SE-751 20 Uppsala, Sweden

⁴Department of Applied Physics, Gleb Wataghin Institute of Physics, State University of Campinas, Campinas, Brazil

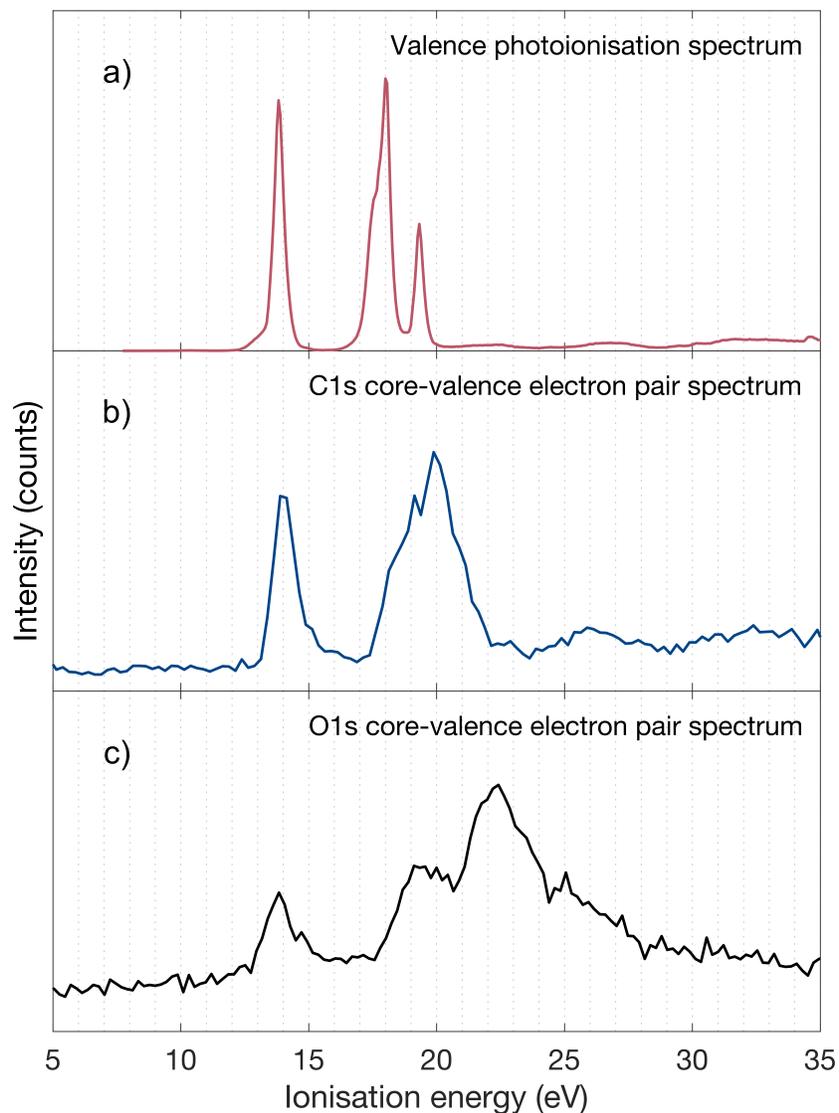
⁵Division of Theoretical Chemistry and Biology, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, SE-106 91 Stockholm, Sweden

⁶University of Gothenburg, Department of Chemistry and Molecular Biology, 405 30 Gothenburg, Sweden

⁷Oxford University, Department of Chemistry, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom

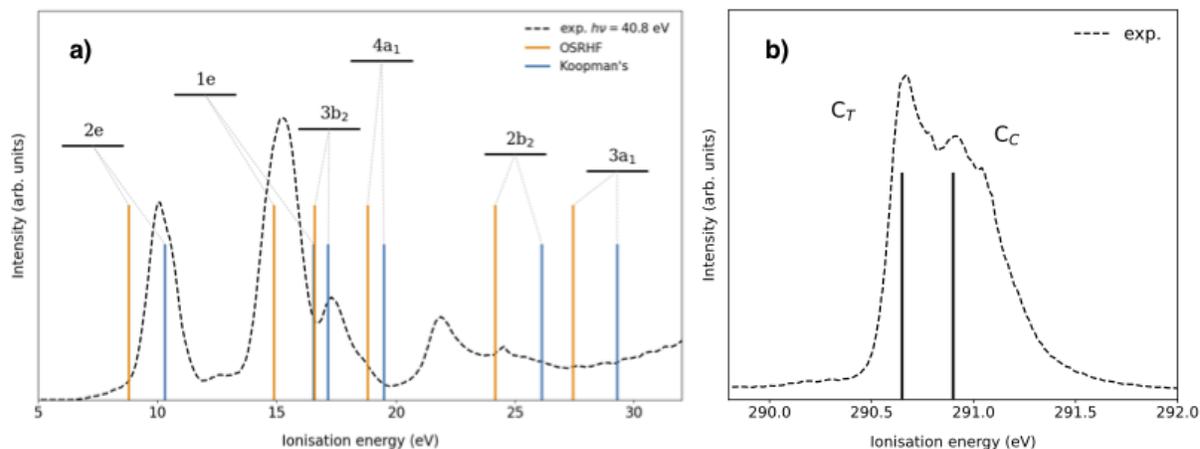
*raimund.feifel@physics.gu.se

Supplementary Note 1: Experimental core-valence double ionisation spectra of CO₂



Supplementary Figure 1. Core-valence spectra of CO₂ 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 CO₂ have been published previously by some of us^{1,2}.

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 Travnikova³). C_C and C_T denote the central and terminal carbon atoms, respectively.

Supplementary References

1. Eland, J. H. D. *et al.* Triple ionization of CO_2 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).