

# Photoionisation of allene and propyne

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**Synopsis** The cationic states of allene and propyne have been studied using high resolution X-ray photoelectron spectroscopy at 100 eV photon energy and ionized equation-of-motion coupled cluster calculations.

The valence-shell photoionisation of allene and propyne (Figure 1) and the energetics of the lowest-energy cations of these C<sub>3</sub>H<sub>4</sub> structural isomers have been studied by X-ray photoelectron spectroscopy (XPS) and computational methods. The experiments were performed at the PLEIADES beamline at the SOLEIL synchrotron radiation facility that is dedicated to ultra-high resolution soft x-ray studies of dilute samples [1, 2]. The vibrationally-resolved electron spectra were recorded at 100 eV photon energy using a VG Scienta R4000 hemispherical electron analyzer.

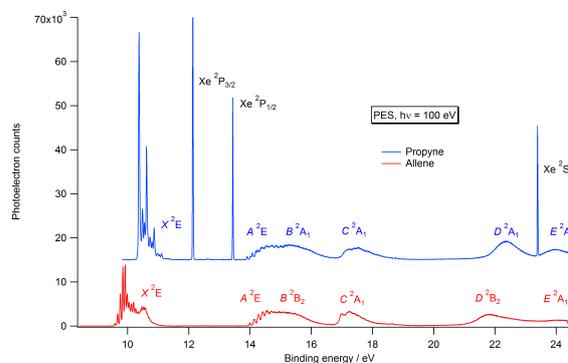


**Figure 1.** Equilibrium geometries of allene (left) and propyne (right).

Despite their different structures, allene and propyne have similar photoionization spectra and molecular orbital (MO) energies. The high symmetry of each molecule (D<sub>2d</sub> for allene and C<sub>3v</sub> for propyne) results in two pairs of degenerate e-symmetry MOs as the highest occupied MOs of each molecule: the 2e HOMO responsible for C–C  $\pi$ -bonding and the 1e HOMO-1 involved in C–H bonding. Because of these degeneracies, removal of a single electron from either the 2e or the 1e MO to give the ground state or first excited state of the cation results in Jahn–Teller distortion to a lower-symmetry geometry, removing the degeneracy and lowering the total energy of the ion.

XPS bands corresponding to six distinct cation states were observed for each isomer for binding energies up to 24 eV, with extended vibrational structure observed with ionisation to the two lowest energy cation states of each molecule (Figure 2).

Ionized equation-of-motion coupled-cluster calculations (IP-EOMCCSD and IP-EOMCCSDt) [3, 4] of the lowest energy cation states of propyne and allene have been performed to aid in the analysis and interpretation of the experimental data. In particular, optimized cation geometries and calculated vibrational frequencies provide insight into the origins of the extensive vibrational structure observed in the electron spectra. In each molecule, ionisation from the degenerate outer valence orbitals leads to significant changes in equilibrium geometry and symmetry lowering, accounting for the significant vibrational excitation of the cations.



**Figure 2.** XPS of propyne and allene recorded at 100 eV photon energy.

## References

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