

Supplementary Information

Single photon double and triple ionization of allene

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Computational Supporting Information

Allene in its neutral form has 22 electrons ($3 \times 1s^2 2s^2 2p^2$ from the C atoms, $4 \times 1s^1$ from the H atoms) and a D_{2d} geometry. Its ground state electronic configuration can be denoted as $(1a_1)^2 (1b_2)^2 (2a_1)^2 (3a_1)^2 (2b_2)^2 (4a_1)^2 (3b_2)^2 (1e)^4 (2e)^4$ [1] where double ionization from the outermost $2e$ (π_{C-C} in character) orbitals corresponds to the first four bands seen in the experimental spectrum. $1e$ and $2e$ are π orbitals and $3b_2$ is a σ -orbital. Removal of two electrons from the $2e$ orbitals gives rise to four states: 3A_2 , 1A_1 , 1B_1 and 1B_2 . The lowest energy singlet state (1A_1) of allene⁺⁺ undergoes a geometric distortion ($D_{2d} \rightarrow D_{2h}$) to remove orbital degeneracy. This D_{2h} dication has 20 electrons, and its ground state electronic configuration is $(1a_g)^2 (1b_{1u})^2 (2a_g)^2 (3a_g)^2 (2b_{1u})^2 (4a_g)^2 (3b_{1u})^2 (1b_{3u})^2 (1b_{2g})^2 (1b_{2u})^2$; the geometric distortion transforms $^1A_1 (D_{2d}) [----(2e)^2]$ into $^1A_g (D_{2h}) [----(1b_{2u})^2 (2b_{3u})^0]$.

All calculations were carried out using the ORCA program (v 4.1.2). Optimisations were carried out at the CASSCF(4,4) and CASSCF(2,4) levels with the def2-TZVP basis set for neutral and doubly-ionised states, respectively, reflecting ionisation from the $2e$ (π) orbitals of allene (Figure S1). Optimisation used ‘tight’ thresholds defined in ORCA, corresponding to an SCF energy convergence of 10^{-8} Ha. Ionisation energies were obtained at the NEVPT2 level based on CASSCF(4,4) and CASSCF(2,4) wavefunctions for neutral and doubly-ionised states, respectively, using the def2-QZVPP basis set. Electronic states were assigned based on the leading CASSCF configuration (see Table S1). Vertical ionisation energies were calculated as the difference in electronic energies between the dication and neutral states at the optimised ground state structure of allene. Each electronic state was fully optimised using the “weights[n]” option in the %casscf block – e.g., to obtain the electronic energy of the 1B_1 state of allene⁺⁺, the input block looks as follows:

```
%casscf
nel 2 # 2 active electrons
norb 4 # 4 active orbitals
mult 1 # singlet multiplicity
nroots 2 # calculate 2 singlet roots
weights[0] = 0, 1 # optimise for second root
end
```

Adiabatic ionization energies were calculated as the difference in the electronic energies between the dication and neutral states, each at their optimised geometry. Excited state geometries were calculated using the same CASSCF procedure as above.

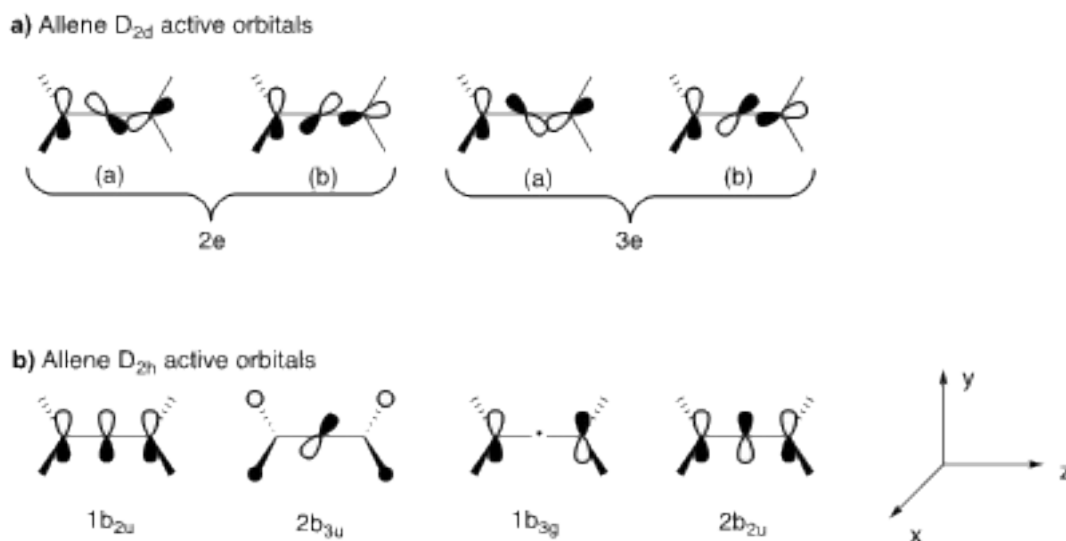


Figure S1. CASSCF active orbitals chosen for $(2e)^{-2}$ double ionization.

Table S1. CASSCF wave functions for the neutral and doubly-ionized species.

Species	State	Point group	CASSCF wave function
C_3H_4	1A_1	D_{2d}	$0.92(2e_{(a)})^2(2e_{(b)})^2(3e_{(a)})^0(3e_{(b)})^0 +$
			$0.03(2e_{(a)})^1(2e_{(b)})^1(3e_{(a)})^1(3e_{(b)})^1 +$
			$0.01(2e_{(a)})^2(2e_{(b)})^0(3e_{(a)})^2(3e_{(b)})^0 +$
			$0.01(2e_{(a)})^0(2e_{(b)})^2(3e_{(a)})^0(3e_{(b)})^2 + \dots$
$C_3H_4^{2+}$	1A_1	D_{2d}	$0.50(2e_{(a)})^2(2e_{(b)})^0(3e_{(a)})^0(3e_{(b)})^0 +$
			$0.50(2e_{(a)})^0(2e_{(b)})^2(3e_{(a)})^0(3e_{(b)})^0 + \dots$
$C_3H_4^{2+}$	1A_g	D_{2h}	$0.96(1b_{2u})^2(2b_{3u})^0(1b_{3g})^0(2b_{2u})^0 +$
			$0.02(1b_{2u})^0(2b_{3u})^0(1b_{3g})^2(2b_{2u})^0 +$
			$0.01(1b_{2u})^0(2b_{3u})^0(1b_{3g})^0(2b_{2u})^2 + \dots$
			$1.00(2e_{(a)})^1(2e_{(b)})^1(3e_{(a)})^0(4e_{(b)})^0 + \dots$
$C_3H_4^{2+}$	3A_2	D_{2d}	
$C_3H_4^{2+}$	1B_1	D_{2d}	$0.98(2e_{(a)})^1(2e_{(b)})^1(3e_{(a)})^0(3e_{(b)})^0 + \dots$
$C_3H_4^{2+}$	1B_2	D_{2d}	$0.97(2e_{(a)})^1(2e_{(b)})^1(3e_{(a)})^0(3e_{(b)})^0 + \dots$

Table S2. Diabatic and adiabatic electronic energies for allene and allene⁺⁺. Energies in Ha.

Species	Allene geometry			Allene ⁺⁺ geometry		
	CASSCF/def2-TZVP energy	CASSCF/def2-QZVPP energy	NEVPT2/def2-QZVPP energy	CASSCF/def2- TZVP energy	CASSCF/def2-QZVPP energy	NEVPT2/def2-QZVPP energy
C ₃ H ₄ (¹ A ₁)	-115.95997	-115.96641	-116.42206	-	-	-
C ₃ H ₄ ²⁺ (¹ A ₁)	-	-114.98861	-115.37193	-115.06627	-115.07284	-115.46263
C ₃ H ₄ ²⁺ (¹ B ₁)	-	-114.94455	-115.33889	-114.95289	-114.95947	-115.34775
C ₃ H ₄ ²⁺ (¹ B ₂)	-	-114.92758	-114.93947	-114.93305	-115.33205	-115.33931
C ₃ H ₄ ²⁺ (³ A ₂)	-	-115.00076	-115.38673	-115.00506	-115.01150	-115.39364

Table S3. Calculated vertical (diabatic) and 0-0 (adiabatic) double ionisation energies, with a def2-QZVPP basis set. Energies in eV.

Electronic state	CASSCF		NEVPT2		Experimental vertical double ionisation
	Vertical double ionisation	0-0 double ionisation	Vertical double ionisation	0-0 double ionisation	
¹ A ₁ (D _{2d}) or ¹ A _g (D _{2h})	26.6	24.3 ^a	28.6	26.1 ^a	28.7
¹ B ₁	27.8	27.4	29.5	29.2	29.5
¹ B ₂	28.3	27.9	29.7	29.5	30.0
³ A ₂	26.3	26.0	28.2	28.0	28.0

^aD_{2h} geometry

Fitting of the First Double Ionization Band

The experimental data were fitted to four Gaussian functions using Matlab R2020b Curve Fitting Toolbox™. The data set was limited to include data points of the energies from 26.81 to 30.21 eV, and the function that was fitted to was

$$y = a1 \cdot \exp(-((x-b1)/c)^2) + a2 \cdot \exp(-((x-b2)/c)^2) + a3 \cdot \exp(-((x-b3)/c)^2) + a4 \cdot \exp(-((x-b4)/c)^2) + d.$$

Here y denotes the counts, x represents the double ionization energy, the a-coefficients are the amplitudes of the Gaussian distributions, c is the (same) width of the peaks, d is a base offset, the b-coefficients are the centers of the Gaussian distributions, and the values are taken as the vertical ionization energies.

In fit options, the a-coefficients are specified to lie in the interval 0 to Inf, with a starting point of 1000, c is set to be between 0 and 1 and d is permitted to lie between 0 and Inf with a starting point of 300. The b-coefficients are all specified to lie within 27 to 30 with separate starting values.

Table S4. The starting points of the coefficients as well as upper and lower bounds for the fit of the Gaussians to the double ionization energy. The Result is the value that Curve Fitting Tool™ calculates and the lower and upper bound make up the span of the 95% confidence interval.

Coefficients	Start point	Lower	Upper	Result	Lower bound	Upper bound
a1	1000	0	Inf	855.5	652	1059
a2	1000	0	Inf	1075	945.2	1168
a3	1000	0	Inf	1138	975.4	1300
a4	1000	0	Inf	491.1	311.6	670.6
b1	26	27	30	29.3	29.11	29.49
b2	27.5	27	30	27.92	27.86	27.98
b3	28	27	30	28.65	28.52	28.77
b4	29	27	30	30	29.79	30.21
c	0.7664 ^b	0	1	0.488	0.4211	0.5548
d	300	0	Inf	384.1	311.7	456.5

^bThe starting value that was automatically generated by Curve Fitting Tool

Besides the fit and the confidence thereof, the goodness of fit is also generated.

Table S5. The parameters that specify the goodness of fit of the result listed above.

Goodness of fit	
Sum of Squares Due to Error	8.638e+04
R-square	0.9882
Degrees of Freedom Adjusted R-square	0.9839
Root Mean Squared Error	58.78

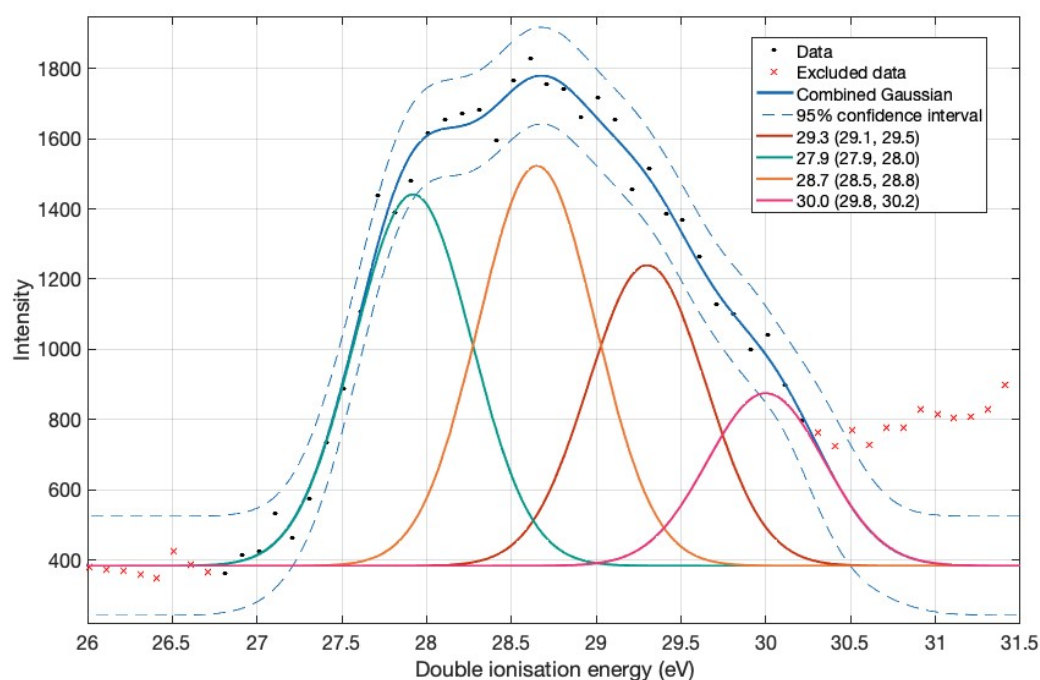


Figure S2: The experimental data of the first double ionization peak are represented by black dots, and the excluded data are marked by red crosses. Individual Gaussian fits of the four peaks are represented by the four last entries in the legend where the mean of the individual Gaussians is the first number and the values in the brackets are the 95% confidence interval of the means. The blue line is the combined function from the four Gaussians and the dashed blue line is the 95% prediction bound calculated by Curve Fitting Tool™.

References

- [1] Y.A. Kruglyak, H. Preuss, and R. Janoschek, *Theor. Exp. Chem.* **7**, 241 (1973).