Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information for:

Photodissociation Dynamics of Fulvenallene, C_7H_6

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This file contains:

a) Translational energy distribution of H-atoms, P (E_T) produced in the photodissociation of phthalide.

b) Photofragment angular distribution (PAD) of H-atoms produced in the photodissociation of phthalide.

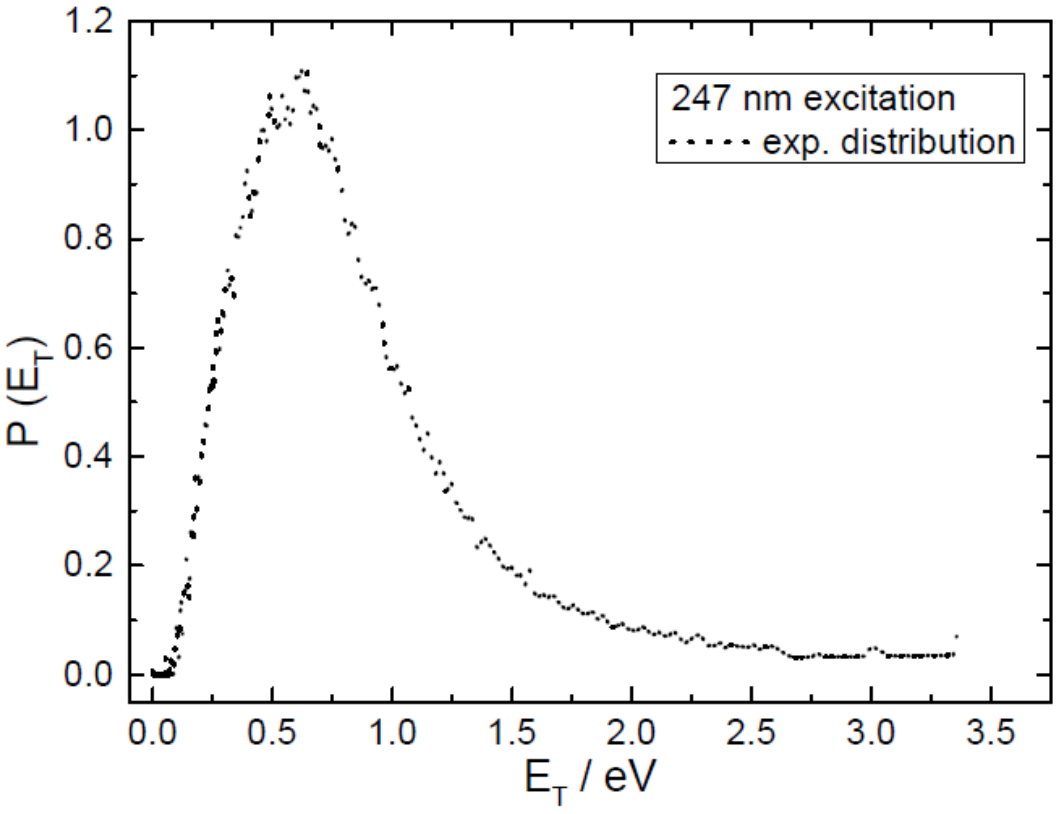
c) Rate for H-atom loss with pyrolysis on.

d) Comparison of translational energy distributions with and without pyrolysis.

e) Dependence of the fit to the translational energy distribution on the parameter n in expression (1) of the main paper.

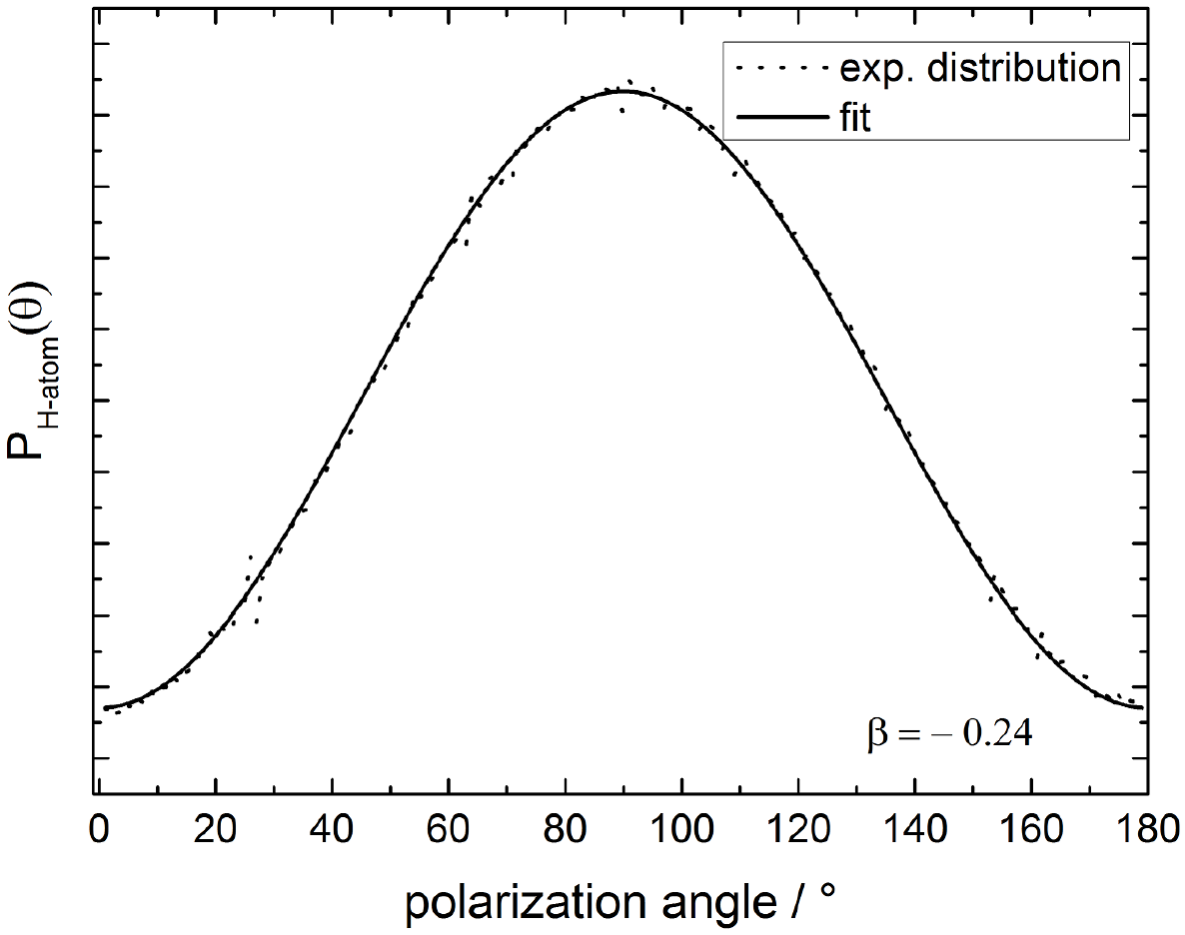
f) Computed geometry of electronic ground state of fulvenallene.

a)



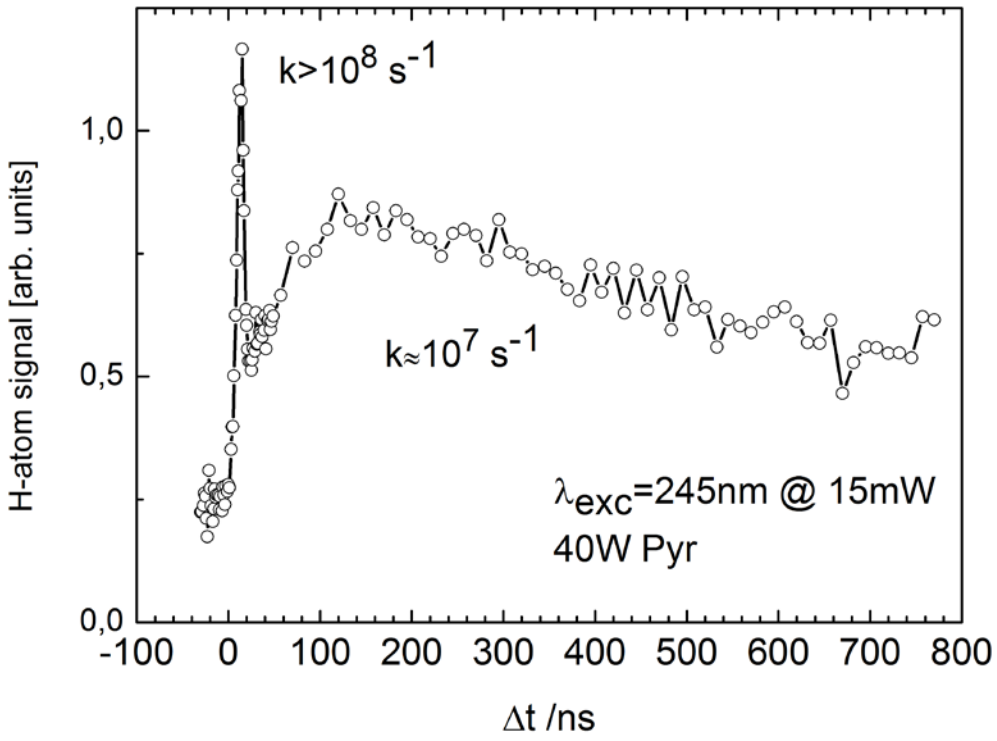
Translational energy distribution of H-atoms produced in the photodissociation of phthalide. The distribution peaks at 0.58 eV, while the distribution of H-atoms from fulvenallene peaks at 0.05 eV. Electrons with a kinetic energy release of up to 3 eV are formed. Overall the distribution differs significantly from the one derived for C_7H_6. Note that the H-atoms originate from a two-photon excitation of phthalide.

b)



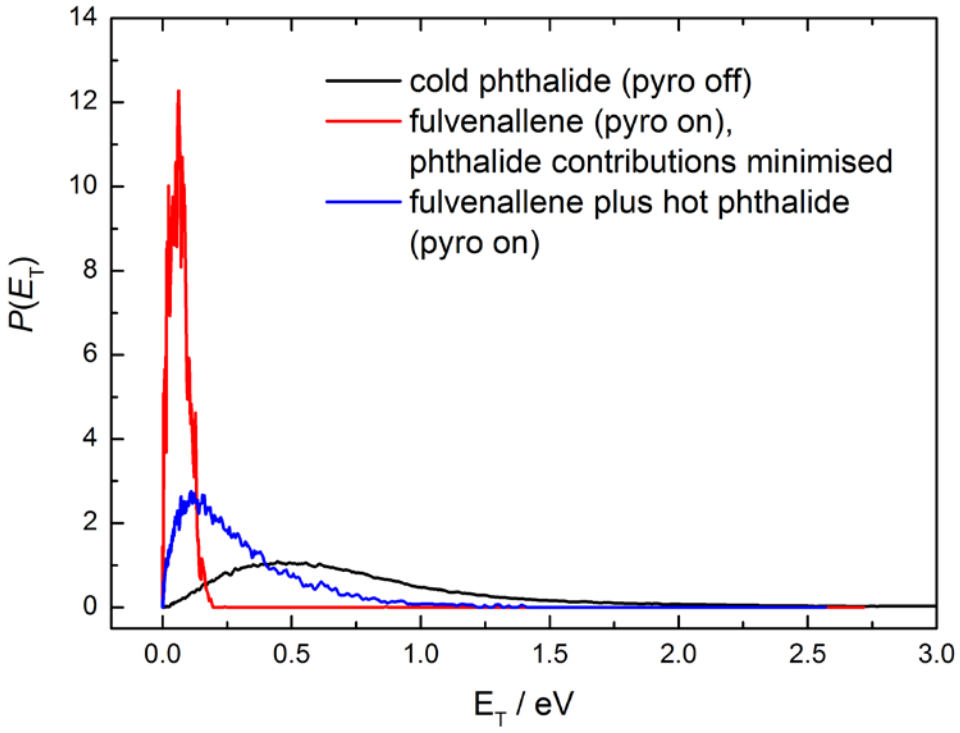
Angular distribution of H-atom photofragments produced in the photodissociation of phthalide. The experimental distribution was fitted with expression (2) as given in the main paper. As visible the distribution is anisotropic and a β-parameter of -0.24 is obtained.

c)



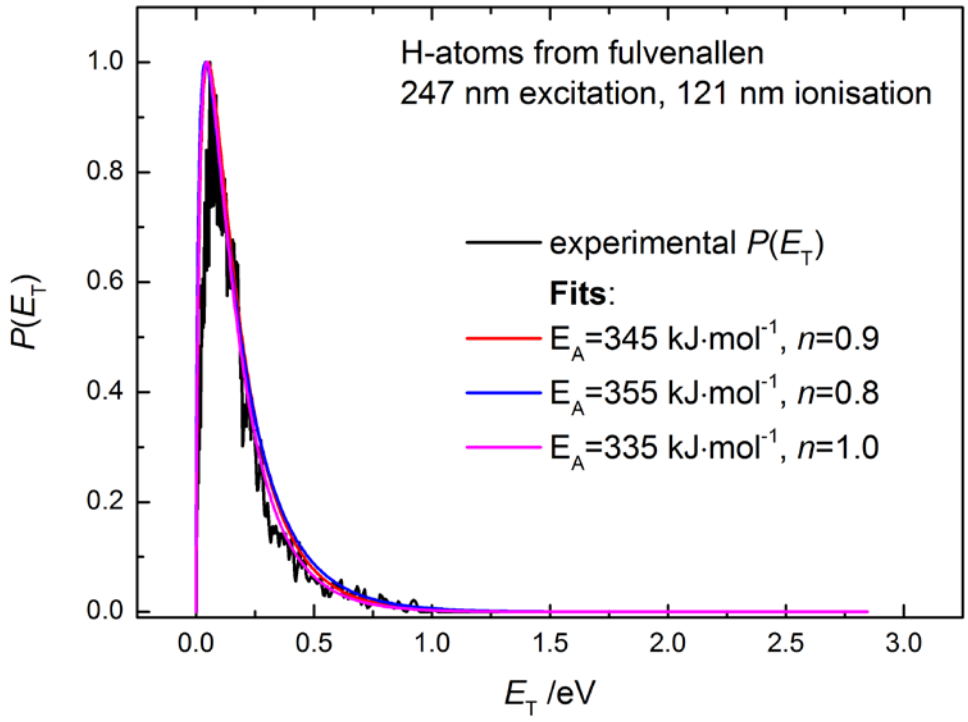
The figure depicts the rate for H-atom loss. Two contributions are visible, a fast one that is also present without pyrolysis and thus assigned to H-atom loss from phthalide and a slower one that is due to H-atom loss from fulvenallene. The spot size of the VUV laser was deliberately chosen to permit a fast fly out of the H-atoms. Under the optimized conditions employed for the data depicted in the main paper, the fly out of H-atoms from phthalide was slower and the two rates could not be separated as well.

d)



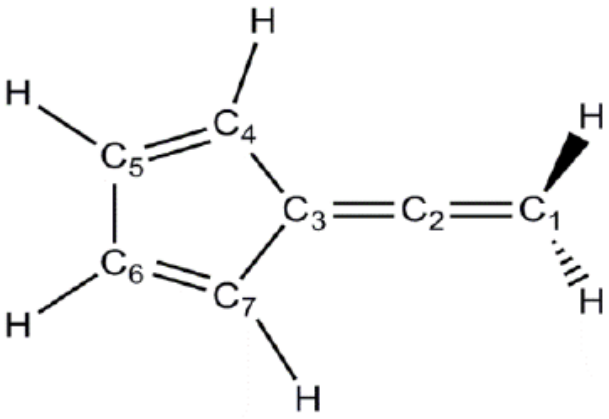
The figure presents a comparison of H-atom translational energy distributions. The black line corresponds to H-atoms from cold phthalide (similar to figure a). The red line represents the distribution from fulvenallene, selected from the image with pyrolysis on around 0° as depicted in figure 6. The blue line finally represents a selected part of the image with pyrolysis on around 90°. It contains both contributions, *i.e.* is perturbations from hot phthalide are present.

e)



The translational energy distribution of H-atoms from fulvenallene is described by expression (1). Here the dependence of the fitting parameter *n* in expression (1) on the activation barrier/excess energy is shown. As visible a change of the activation barrier by ± 10 kJ·mol^{-1} does not change *n* significantly.

f) Computed geometry of electronic ground state of fulvenallene.



fulvenallene	ground state B3LYP 6-311++G**
C_1 - C_2 /pm	129.9
C_2 - C_3	131.8
C_3 - C_4	147.4
C_5 - C_6	135.5
C_1 - H	146.7
C_4 - H	135.5
C_5 - H	146.7
H - C_1 - C_2 /°	121.3
H - C_4 - C_5 /°	128.2
H - C_5 - C_6 /°	124.7
C_1 - C_2 - C_3 /°	180
C_2 - C_3 - C_4 /°	126.8
C_3 - C_4 - C_5 /°	107.5
C_4 - C_5 - C_6 /°	109.3