Electronic Supplementary Information to:

Photodissociation Dynamics of Propargylene, HCCCH

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Table S1: Excited electronic states of propargylene obtained using CASSCF (8 electrons in 8 orbitals, pVDZ basis). Dominant configurations with weights larger than 10 % are given.

State	E (CASSCF) /eV	Dominant configuration	Character	f_e
T_0	0.00	2 2 2 / / 0 0 0 (86 %)	Ground state	-
T_1	3.88	2 / 2 2 / 0 0 0 (57 %) 2 2 2 0 / / 0 0 (17 %)	$\pi\pi^*$ Rydberg s	0.0110
T_2	4.24	2 2 / 2 / 0 0 0 (75 %)	$\pi\pi^*$	0.0003
T_3	4.39	2 2 / / 2 0 0 0 (67 %) 2 / 2 2 / 0 0 0 (15 %)	$\pi\pi^*$ $\pi\pi^*$	0.0037
T_4	4.73	2 / 2 / 2 0 0 0 (77 %)	$\pi\pi^*$	0.0001
T_5	6.23	2 2 2 / 0 / 0 0 (74 %)	Rydberg s	0.0005
T_6	6.93	2 2 2 0 / / 0 0 (71 %)	Rydberg s	0.0418

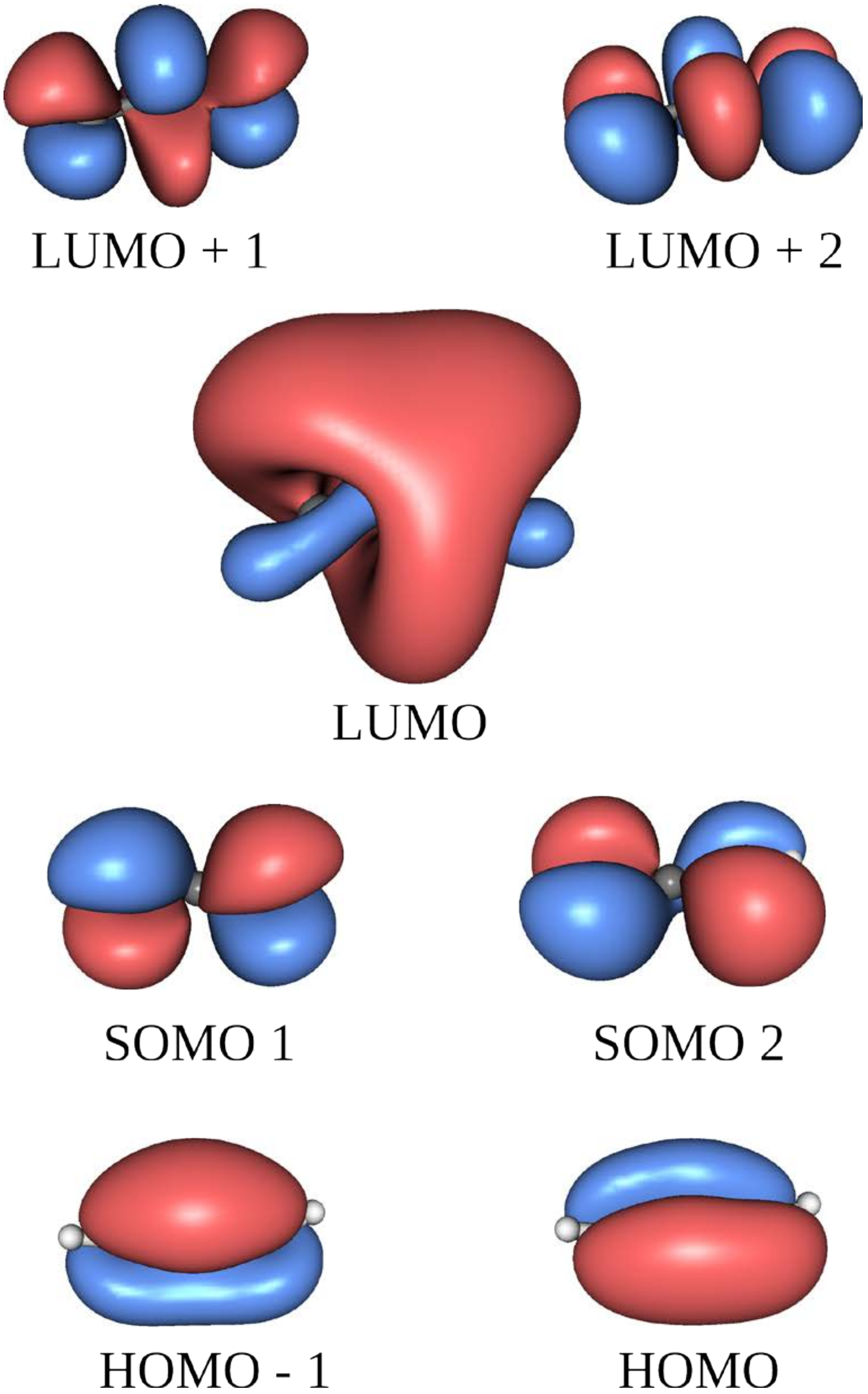

Fig. S1: CASSCF orbitals contributing to the excited electronic states analyzed in Table 1. The orbitals are denoted as highest occupied (HOMO), singly occupied (SOMO) and lowest unoccupied (LUMO) molecular orbitals. A cutoff value of 0.025 has been used. Red and blue colour labels positive and negative lobes respectively.

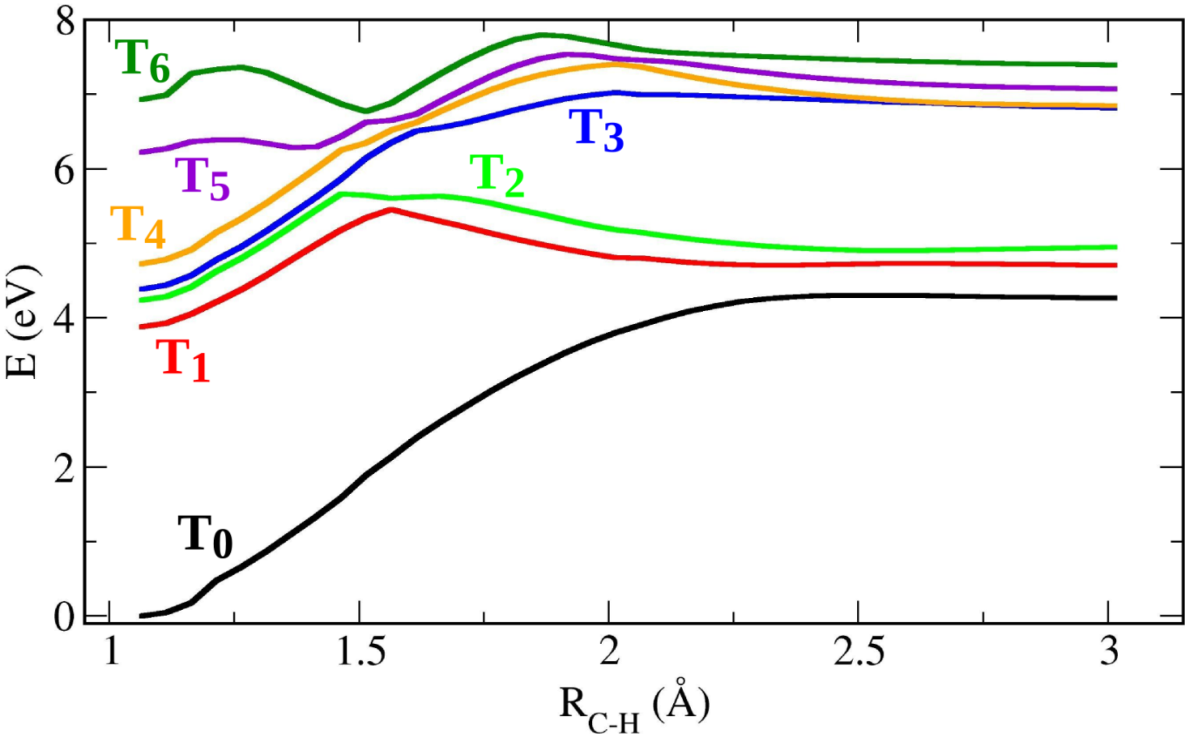

Fig. S2: Energies of the electronic triplet states T_0 – T_6 scanned along the distance between a hydrogen atom and the adjacent carbon atom. The curves have been obtained using CASSCF employing 8 electrons in 8 orbitals and the pVDZ basis set as described in the Computational section. Note that the energies are shifted as compared to the CAS-MRCI computations.

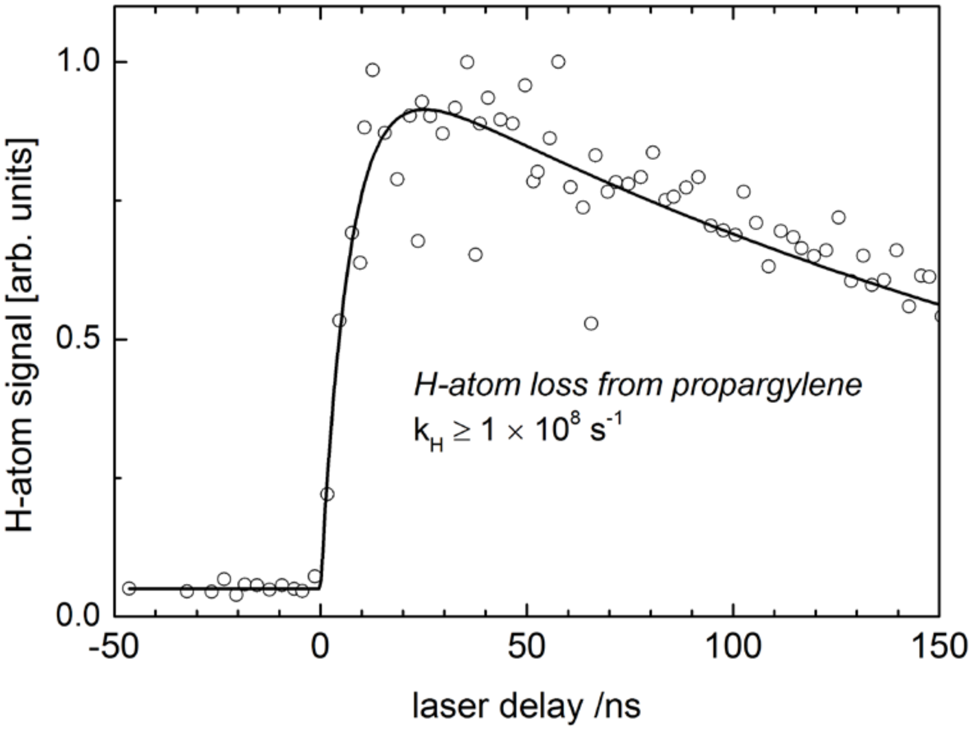

Fig. S3: When the H-atom signal is recorded as a function of the time-delay between the two lasers, a rate for the H-atom loss can be obtained from the rise time of the signal. In the case of HCCCH the signal rise is limited by the instrument response function and only a lower limit can be obtained. The rate of $k_H \geq 1 \cdot 10^8\ s^{-1}$ is thus in agreement with a fast dissociation in an excited state. RRKM computations based on the vibrational frequencies published by Mebel et al (A. M. Mebel, W. M. Jackson, A. H. H. Chang and S. H. Lin, J. Am. Chem. Soc., 1998, 120, 5751) yielded a rate $k_H=1.6 \cdot 10^7\ s^{-1}$ for a statistical dissociation from a hot ground state.

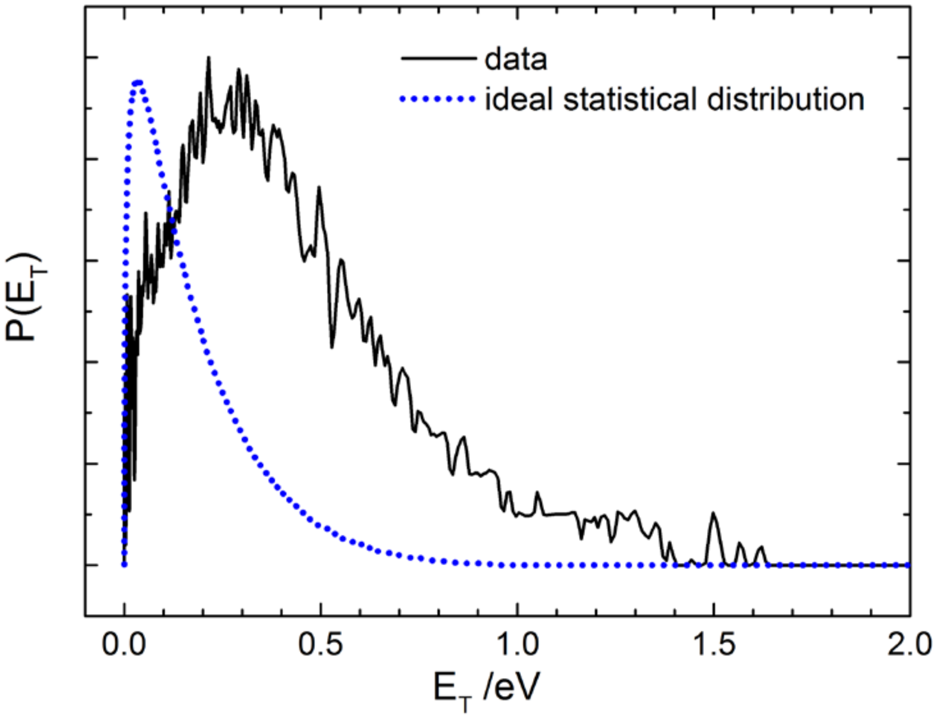

Fig. S4: The dotted blue line represents a translational energy distribution with ideal statistical behaviour. It is given by the expression

$$P(E_T) = C \cdot\ E_T^{1/2} \cdot \rho_{vib}(E_{excess} - E_T)$$

with ρ_{vib} being the vibrational density of states of the reaction products (R. D. Levine and R. B. Bernstein, Acc. Chem. Res., 1974, 7, 393). As visible the distribution does not fit the experimentally observed distribution. A statistical reaction can thus be ruled out.

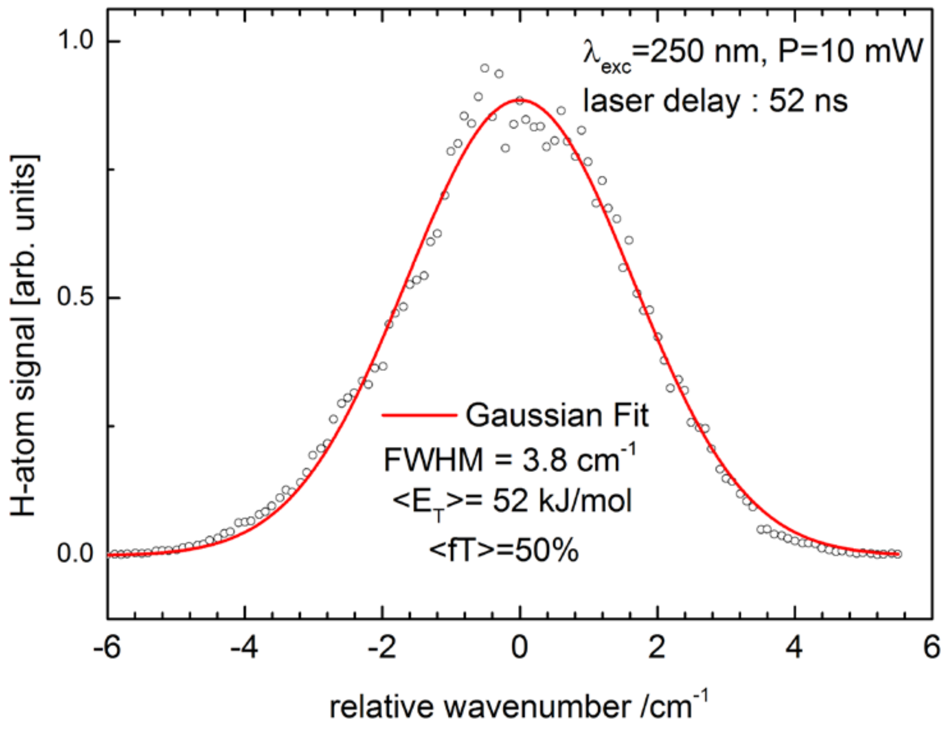

Fig. S5: Doppler profiles were recorded under a variety of conditions, because the measurements are significantly faster. In this case the power of the excitation laser was about half the one used for recording the VMI images. From a Gaussian fit to the profile it is found that 50 % of the excess energy are released as translational energy, very close to the value of 48% obtained from the VM images. Note that a Gaussian does fit the data only approximately, as expected for a non-statistical reaction.