Supplementary Information

for

Association reactions in femtosecond laser filaments of hexane studied by time-of-flight mass spectrometry with velocity screening

Akitaka Matsuda[a,*], Yuya Okumura[a], Kasumi Hashigaya[a], Akiyoshi Hishikawa[a,b,*]

[a] *Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi 464-8602, Japan*

[b] *Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi 464-8602, Japan*

*matsuda.akitaka.f7@f.mail.nagoya-u.ac.jp,
hishikawa.akiyoshi.z6@f.mail.nagoya-u.ac.jp

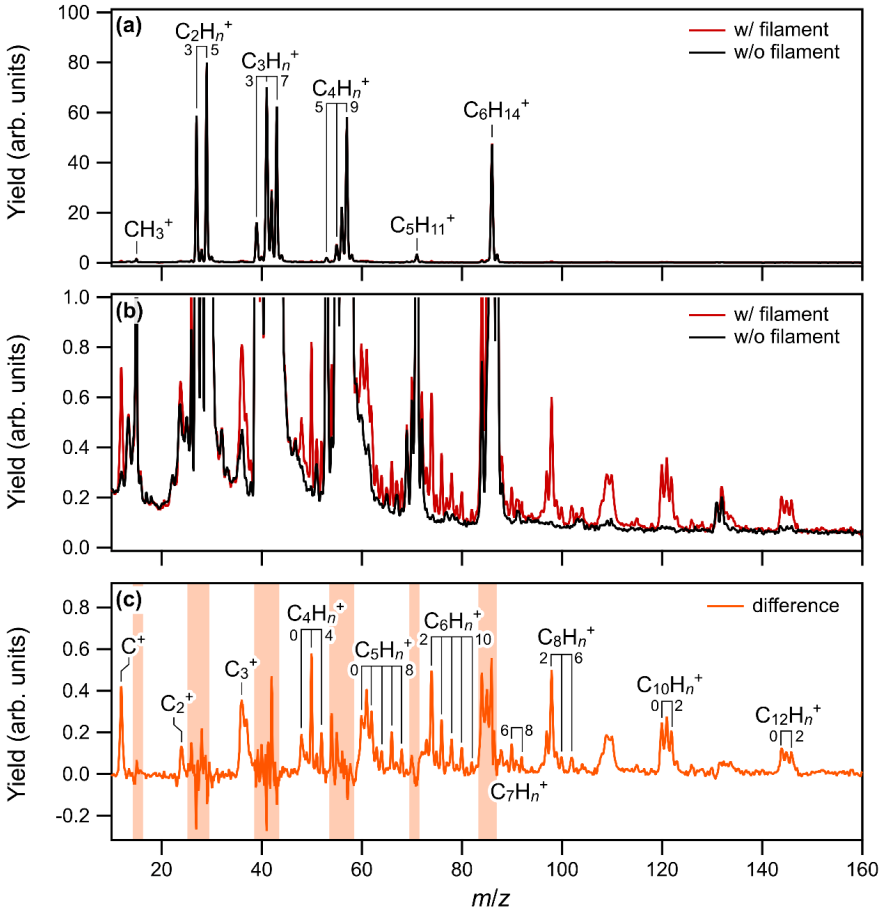

Figure S1 (a) Mass spectra obtained at a probe pulse intensity of 4.9×10^{13} W/cm^2. with (red) and without (black) the filament laser pulse (450 μJ/pulse, 500 Hz). Each spectrum is normalized at *m*/*z* 29. (b) Expanded view of the mass spectra shown in (a). (c) Difference spectrum between the spectra obtained with and without the filamentation laser pulse. The hatched areas indicate spectral regions where strong signals of the probe products from hexane hinder clear identification of the filament products.

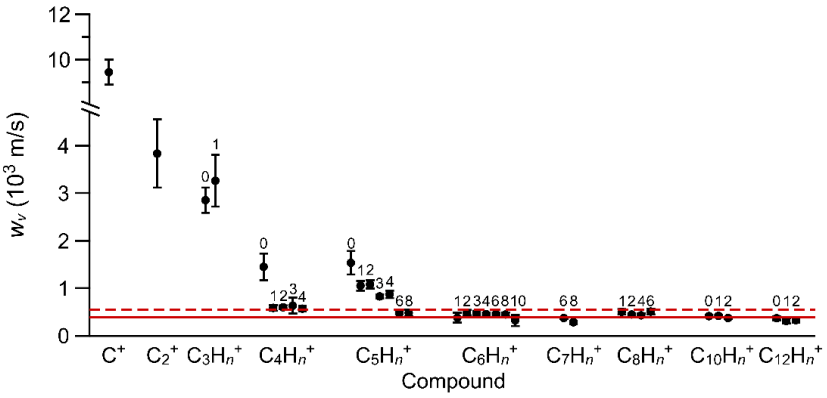

Figure S2 Full-width half maximum of the velocity distribution of the major peaks observed in the difference spectrum (Fig. S1). The horizontal lines represent the reference width w_v^0 and critical width w_v^c, respectively.

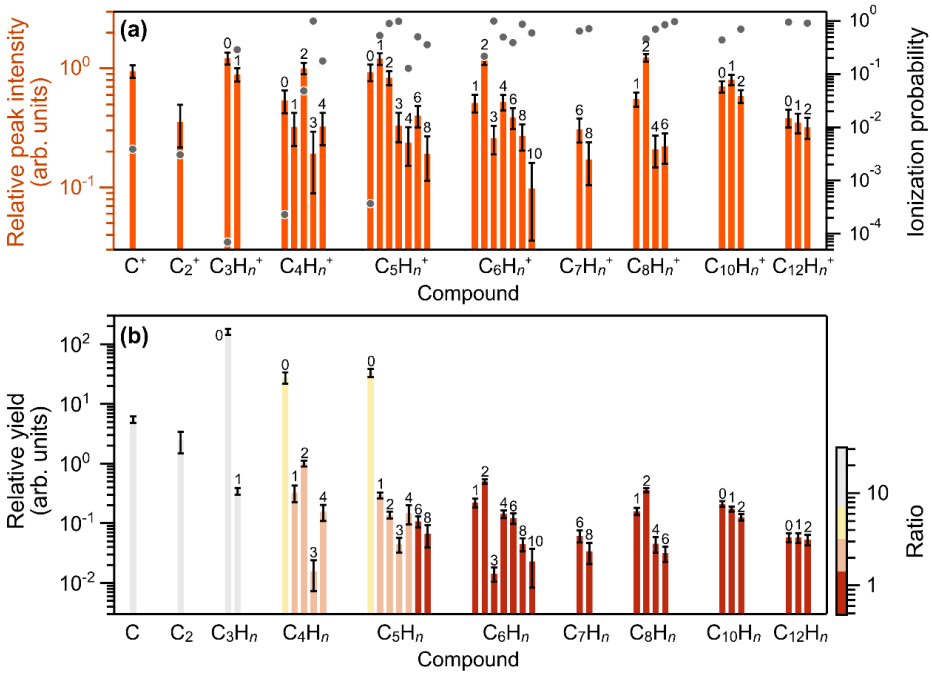

Figure S3 (a) Relative yields of the major peaks observed in Fig. S1(c). The number of hydrogen atoms (n) is indicated above each bar. Tunnel ionization probabilities calculated for the probe pulse with a duration of 50 fs and a peak intensity of 4.9×10^{13} W/cm² are also shown. (b) Relative yields of the products obtained after tunnel ionization efficiency correction. Since the ionization energies of C_nH (n = 4, 6, 8, 10, 12) are unavailable, the ionization potentials of C_nH_2 are used instead for peaks at m/z 49, 73, 97, 121, and 145. The color indicates the ratio w_v/w_v^0 of each peak with w_v^0 being the reference width determined from the $C_6H_{14}^+$ peak. The filament products ($r_v < r_v^c$) are distinguished from the ionization fragments ($r_v \geq r_v^c$). The r_v values for C_4H_2 and C_4H_3 have large uncertainties associated with small signal intensities (see Fig. S2).

Table S1 Ionization energies I_p [1-32] of selected molecules.

m/z	formula	compound	I_p (eV)	ref.
12	C	carbon	11.3	[1]
24	C_2	dicarbon	11.4	[2]
36	C_3	tricarbon	13.0	[3]
37	C_3H	linear C_3H	9.1	[4]
		cyclic C_3H	9.8	[4]
48	C_4	tetracarbon	12.5	[3]
50	C_4H_2	1,3-butadiyne	10.2	[5]
51	C_4H_3	*n*-C_4H_3	7.4	[6]
		i-C_4H_3	8.0	[6]
52	C_4H_4	1-buten-3-yne	9.6	[5]
60	C_5	pentacarbon	12.3	[3]
61	C_5H	*l*-C_5H	8.4	[7]
		t-C_5H	9.8	[7]
62	C_5H_2	pentadiynylidene	8.4	[8]
		3-(didehydrovinylidene)cyclopropene	8.6	[8]
63	C_5H_3	*i*-C_5H_3	8.2	[9]
		n-C_5H_3	8.3	[9]
64	C_5H_4	1,3-pentadiyne	9.5	[5]
		1,4-pentadiyne	10.3	[5]
66	C_5H_6	1,3-cyclopentadiene	8.6	[5]
		1-penten-3-yne	9.1	[5]
		3-penten-1-yne	9.2	[5]
		1-buten-3-yne, 2-methyl-	9.3	[5]
68	C_5H_8	1,3-pentadiene	8.7	[5]
		Isoprene	8.9	[5]
		cyclopentene	9.0	[5]
		2-pentyne	9.4	[5]
		1,4-pentadiene	9.6	[5]
		1-butyne, 3-methyl-	10.0	[5]
		1-pentyne	10.1	[5]
74	C_6H_2	1,3,5-hexatriyne	9.5	[5]
75	C_6H_3	1,3,5-tridehydrobenzene	7.2	[10]
76	C_6H_4	benzyne	9.0	[11]
		hexa-1,5-diyne-3-ene	9.1	[5]
78	C_6H_6	1,5-hexadien-e-yne	8.5	[5]
		2,4-hexadiyne	8.9	[5]
		1,3-hexadien-5-yne	9.2	[5]
		benzene	9.3	[5]
		1,3-hexadiyne	9.4	[12]
		1,4-hexadiyne	9.7	[5]
		1,5-hexadiyne	9.9	[5]

80	C_6H_8	1,3-cyclohexadiene	8.3	[5]
		1,3,5-hexatriene	8.3	[5]
		1,3-cyclopentadiene, 1-methyl-	8.4	[5]
		2-methyl-1,3-cyclopentadiene	8.4	[13]
		1,3-cyclopentadiene, 5-methyl-	8.5	[5]
		1,4-cyclohexadiene	8.8	[5]
		1-hexen-3-yne	8.9	[14]
82	C_6H_{10}	4-methyl-1,3-pentadiene	8.3	[15]
		(Z),(Z)-2,4-hexadiene	8.3	[15]
		1,3-pentadiene, 2-methyl-	8.5	[15]
		1,3-pentadiene, 3-methyl-, (E)-	8.5	[15]
		cis-1,3-hexadiene	8.5	[16]
		(E)-1,3-hexadiene	8.6	[15]
		1,3-butadiene, 2,3-dimethyl-	8.7	[15]
		1,3-butadiene, 2-ethyl-	8.8	[15]
		2,3-hexadiene	8.8	[15]
		cyclohexane	8.9	[17]
		1,2-hexadiene	9.0	[15]
		trans-1,4-hexadiene	9.0	[15]
		1,4-pentadiene, 2-methyl-	9.2	[15]
		1,5-hexadiene	9.3	[18]
		3-hexyne	9.3	[15]
		4-methyl-2-pentyne	9.3	[15]
		1,4-pentadiene, 3-methyl-	9.4	[15]
		2-Hexyne	9.4	[18]
		1-hexyne	10.1	[19]
90	C_7H_6	1,3-cyclopentadiene, 5-ethenylidene-	8.3	[20]
		cyclopropane, 1,1-diethynyl-	9.3	[21]
92	C_7H_8	tetracyclo[3.2.0.0(2,7).0(4,6)]heptane	8.3	[22]
		2,5-norbornadiene	8.4	[18]
		3-methylene-1,4-cyclohexadiene	8.6	[23]
		toluene	8.8	[24]
		1,6-heptadiyne	9.9	[25]
98	C_8H_2	1,3,5,7-octatetrayne	9.1	[26]
100	C_8H_4	vinyltriacetylene	8.8	[26]
102	C_8H_6	(E),(E)-octa-3,5,7-triene-1-yne	7.8	[27]
		2,4,6-octatriyne	8.6	[28]
		phenylethyne	8.8	[29]
104	C_8H_8	1,4-cyclohexadiene,3,6-bis(methylene)-	7.9	[15]
		styrene	8.5	[30]
		1,3,5,7-cyclooctatetraene	8.0	[15]
120	C_{10}	linear C_{10}	8.8	[31]
		cyclic C_{10}	9.6	[31]
122	$C_{10}H_2$	1,3,5,7,9-decapentayne	8.8	[26]
144	C_{12}	cyclic C_{12}	8.4	[31]
146	$C_{12}H_2$	1,3,5,7,9,11-dodecahexayne	8.5	[32]

References

[1] D. R. Lide (Ed.), Ionization potentials of atoms and atomic ions in Handbook of Chem. and Phys. 1992, 10.

[2] C. J. Reid, J. A. Ballantine, S. R. Andrews, F. M. Harris, *Chem. Phys.* 1995, **190**, 113.

[3] R. Ramathan, J. A. Zimmerman, J. R. Eyler, *J. Chem. Phys.* 1993, **98**, 7838.

[4] Y. Wang, B. J. Braams, J. M. Bowman, *J. Phys. Chem. A* 2007, **111**, 4056.

[5] G. Bieri, F. Burger, E. Heilbronner, J. P. Maier, *Helv. Chim. Acta* 1977, **60**, 2213.

[6] R. I. Kaiser, A. Mebel, O. Kostko, M. Ahmed, *Chem. Phys. Lett.* 2010, **485**, 281.

[7] S. C. Bennedjai1, D. Hammoutène1, M. L. Senent, *Astrophys J.* 2019, **871**, 255.

[8] E. Reusch, D. Kaiser, D. Schleier, R. Buschmann, A. Krueger, T. Hermann, B. Engels, I. Fischer, P. Hemberger, *J. Phys. Chem. A* 2019, **123**, 2008.

[9] B. Yang, C. Huang, L. Wei, J. Wang, L. Sheng, Y. Zhang, F. Qi, W. Zheng, W.-K. Li, *Chem. Phys. Lett.* 2006, **423**, 321.

[10] H. M. T. Nguyen, T. Höltzl, G. Gopakumar, T. Veszprémi, J. Peeters, M. T. Nguyen, *Chem. Phys.* 2005, **316**, 125.

[11] X. Zhang, P. Chen, *J. Am. Chem. Soc.* 1992, **114**, 3147.

[12] H. M. Rosenstock, J. Dannacher, J. F. Liebman, *Radiat. Phys. Chem.* 1982, **20**, 7.

[13] S. Cradock, E. A. V. Ebsworth, H. Moretto, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.* 1975, 390.

[14] P. Carlier, G. Mouvier, D. Mesnard, L. Miginiac, *J. Electron Spectrosc. Relat. Phenom.* 1979, **16**, 147.

[15] S. G. Lias, R. D. Levin, S. A. Kafafi, "Ion Energetics Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303.

[16] F. P. Lossing, J. C. Traeger, *J. Am. Chem. Soc.* 1975, **97**, 1579.

[17] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, Ionization energies, Ab initio assignments, and valence electronic structure for 200 molecules in Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds, Japan Scientific Soc. Press, Tokyo, 1981.

[18] S. G. Lias, "Ionization Energy Evaluation" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303.

[19] H. M. Rosenstock, K. Draxl, B. W. Steiner, J. T. Herron, "Ion Energetics Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899,

https://doi.org/10.18434/T4D303.

[20] C. Muller, A. Schweig, W. Thiel, W. Grahn, R. G. Bergman, K. P. C. Vollhardt, *J. Am. Chem. Soc.* 1979, **101**, 5579.

[21] M. Eckert-Maksie, R. Gleiter, N. S. Zefirov, S. I. Kozhushkov, T. S. Kuznetsova, *Chem. Ber.* 1991, **124**, 371.

[22] H.-D. Martin, C. Heller, E. Haselbach, Z. Lanyjova, *Helv. Chim. Acta* 1974, **57**, 465.

[23] J. E. Bartmess, *J. Am. Chem. Soc.* 1982, **104**, 335.

[24] K.-T. Lu, G. C. Eiden, J. C. Weisshaar, *J. Phys. Chem.* 1992, **96**, 9742.

[25] J. C. Traeger, R. G. McLoughlin, *Int. J. Mass Spectrom. Ion Phys.* 1978, **27**, 319.

[26] N. Hansen, S. J. Klippenstein, P. R. Westmoreland, T. Kasper, K. Kohse-Höinghous, J. Wang, T. A. Cool, *Phys. Chem. Chem. Phys.* 2008, **10**, 366.

[27] C. Koppel, H. Schwarz, F. Bohlmann, *Org. Mass Spectrom.* 1974, **9**, 324.

[28] C. Baker, D. W. Turner, *Proc. Roy. Soc. (London)* 1968, **A308**, 19.

[29] D. L. Lichtenberger, S. K. Renshaw, R. M. Bullock, *J. Am. Chem. Soc.* 1993, **115**, 3276.

[30] J. M. Dyke, H. Ozeki, M. Takahashi, M. C. R. Cockett, K. Kimura, *J. Chem. Phys.* 1992, **97**, 8926.

[31] L. Belau, S. E. Wheeler, B. W. Ticknor, M. Ahmed, S. R. Leone, W. D. Allen, H. F. Schaefer III, M. A. Duncan, *J. Am. Chem. Soc.* 2007, **129**, 10229.

[32] R. I. Kaiser, B. J. Sun, H. M. Lin, A. H. H. Chang, A. M. Mebel, O. Kostko, M. Ahmed, *Astrophys J.* 2010, **719**, 1884.