Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Gas-phase $C_{60}H_n{}^{+q}$ (n = 0–4, q = 0,1) Fullerenes and Fulleranes: Spectroscopic Simulations Shed Light on Cosmic Molecular Structures

Ricardo R. Oliveira[a*], Germán Molpeceres[b*], Ricardo Montserrat[a], Felipe Fantuzzi[c], Alexandre B. Rocha[a] and Johannes Kästner[d]

[a] *Chemistry Institute, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*
[*] *e-mail: rrodrigues.iq@gmail.com*
[b] *Department of Astronomy, Graduate School of Science, The University of Tokyo, Tokyo 113 0033, Japan*
[*] *e-mail: molpeceres@astron.s.u-tokyo.ac.jp*
[c] *School of Chemistry and Forensic Science, University of Kent, Canterbury CT2 7NH, UK.*
[d] *Institute for Theoretical Chemistry, University of Stuttgart, Stuttgart, Germany*

Contents

S1 Molecular structures and relative enthalpies

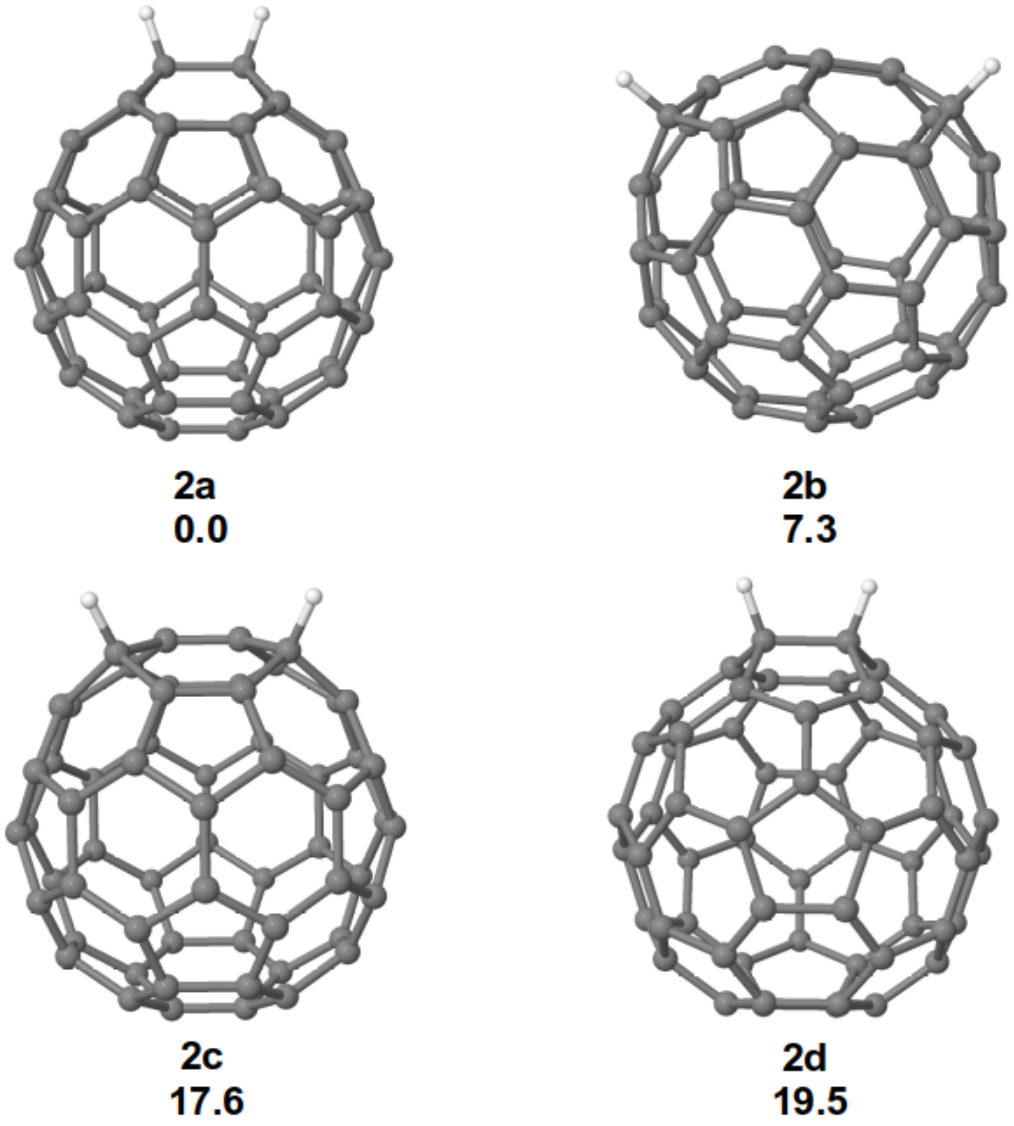

Figure S1 Molecular structures of $C_{60}H_2$ obtained at B3LYP-D3/def2-TZVP level. All energies are in kcal mol^{-1} units.

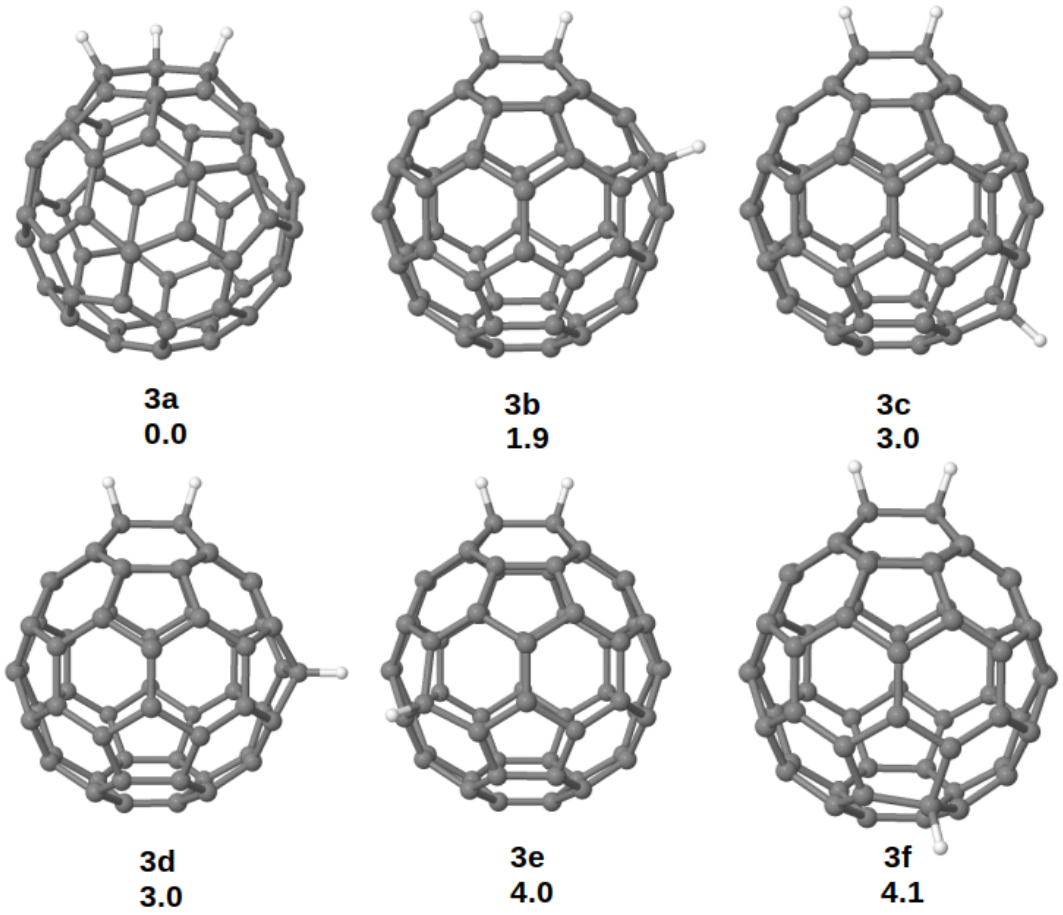

Figure S2 Molecular structures of $C_{60}H_3$ obtained at B3LYP-D3/def2-TZVP level. All energies are in kcal mol^{-1} units.

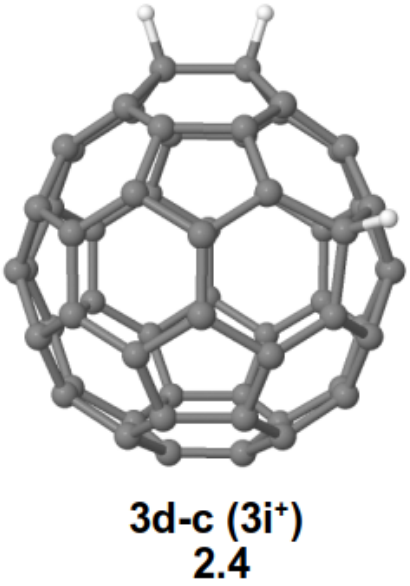

Figure S3 Molecular structure of $3i^+$ isomer of $C_{60}H_3^+$ obtained at B3LYP-D3/def2-TZVP level. All energies are in kcal mol^{-1} units.

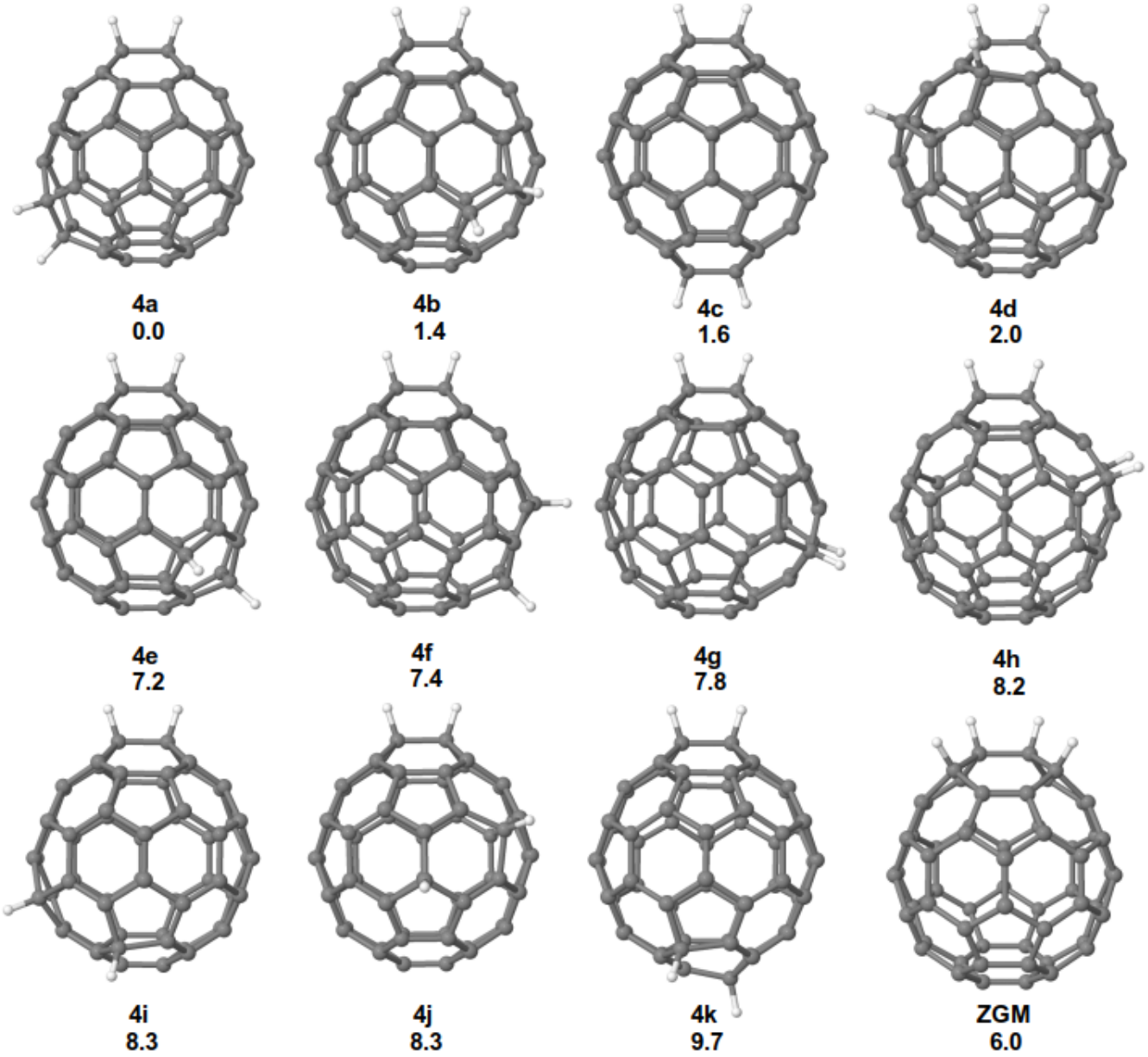

Figure S4 Molecular structures of $C_{60}H_4$ obtained at B3LYP-D3/def2-TZVP level. All energies are in kcal mol^{-1} units.

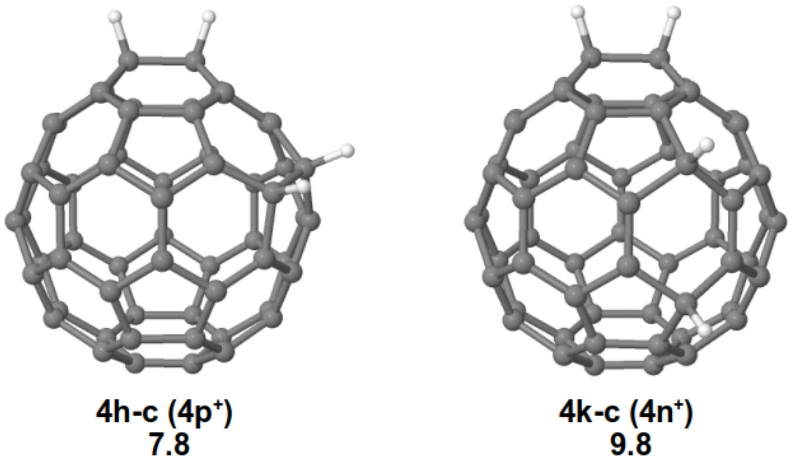

Figure S5 Molecular structure of $4p^+$ and $4n^+$ isomer of $C_{60}H_4^+$ obtained at B3LYP-D3/def2-TZVP level. All energies are in kcal mol^{-1} units.

Table S1 Relative enthalpies of $C_{60}H_2$ and $C_{60}H_2^+$ species obtained at B3LYP-D3/def2-TZVP level.

Specie	Enthalpy (kcal mol^{-1})	Specie	Enthalpy (kcal mol^{-1})
2a	0.00	2a-c ($2a^+$)	0.00
2b	7.29	2b-c ($2b^+$)	7.52
2c	17.64	2c-c ($2d^+$)	9.95
2d	19.49	2d-c ($2c^+$)	10.01
2e	22.89	2e-c ($2f^+$)	11.81
2f	25.29	2f-c ($2e^+$)	12.12
2g	28.81	2g-c ($2g^+$)	14.54
2h	30.09	2h-c ($2i^+$)	14.72
2i	33.09	2i-c ($2h^+$)	15.08
2j	36.13	2j-c ($2j^+$)	16.28
2k	73.32	2k-c ($2k^+$)	61.14

Table S2 Relative enthalpies of $C_{60}H_3$ and $C_{60}H_3^+$ species obtained at B3LYP-D3/def2-TZVP level.

Specie	Enthalpy (kcal mol^{-1})	Specie	Enthalpy (kcal mol^{-1})
3a	0.00	3a-c (3b$^+$)	0.00
3b	1.88	3b-c (3a$^+$)	0.43
3c	2.95	3c-c (3d$^+$)	1.24
3d	3.01	3d-c (3i$^+$)	2.14
3e	3.98	3e-c (3c$^+$)	2.40
3f	4.14	3f-c (3e$^+$)	2.61
3g	5.00	3g-c (3f$^+$)	3.29
3h	5.18	3h-c (3h$^+$)	5.14
3i	5.36	3i-c (3g$^+$)	6.04
3j	6.50	3j-c (3j$^+$)	7.23
3k	9.23	3k-c (3k$^+$)	7.30

Table S3 Relative enthalpies of $C_{60}H_4$ and $C_{60}H_4^+$ species obtained at B3LYP-D3/def2-TZVP level.

Specie	Enthalpy (kcal mol^{-1})	Specie	Enthalpy (kcal mol^{-1})
4a	0.00	4a-c (4a$^+$)	0.00
4b	1.41	4b-c (4b$^+$)	0.42
4c	1.57	4c-c (4c$^+$)	2.22
4d	2.04	4d-c (4d$^+$)	3.54
4e	7.23	4e-c (4h$^+$)	4.03
4f	7.35	4f-c (4j$^+$)	6.59
4g	7.81	4g-c (4i$^+$)	7.70
4h	8.23	4h-c (4p$^+$)	7.75
4i	8.29	4i-c (4e$^+$)	8.68
4j	8.30	4j-c (4f$^+$)	8.72
4k	9.69	4k-c (4n$^+$)	9.03
ZGM	6.00	-	-

S2 Infrared spectra: C—C region

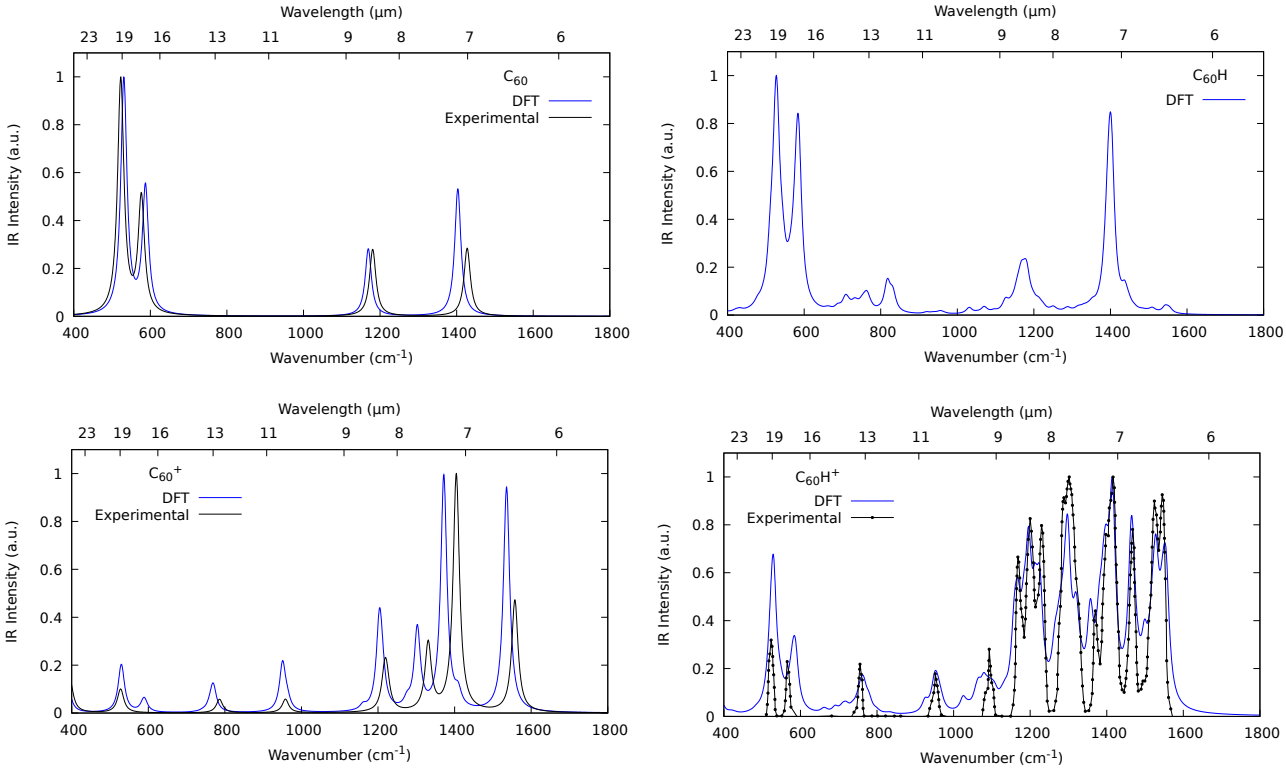

Figure S6 Simulated infrared spectra of C_{60}, C_{60}^{+}, $C_{60}H$ and $C_{60}H^{+}$ at B3LYP-D3/def2-TZVP level of theory. Experimental results for C_{60}, C_{60}^{+} and $C_{60}H^{+}$ were obtained by Yamanoto and co-workers,[1] Strelnikov and co-workers,[2] and Palotás and co-workers[3] respectively.

S3 Electronic absorption spectra of C_{60}, $C_{60}H$ and $C_{60}H^+$

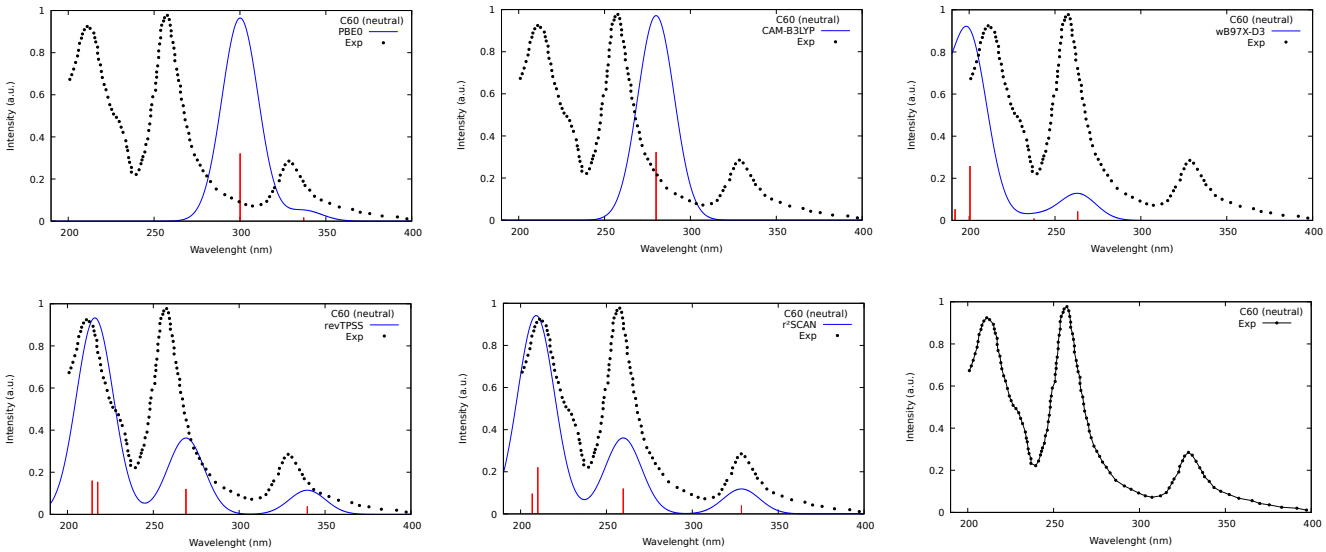

Figure S7 Simulated electronic absorption spectra of C_{60} applying several functionals combined with def2-TZVP basis set. The experimental result for C_{60} was obtained by Leach and co-workers.[4]

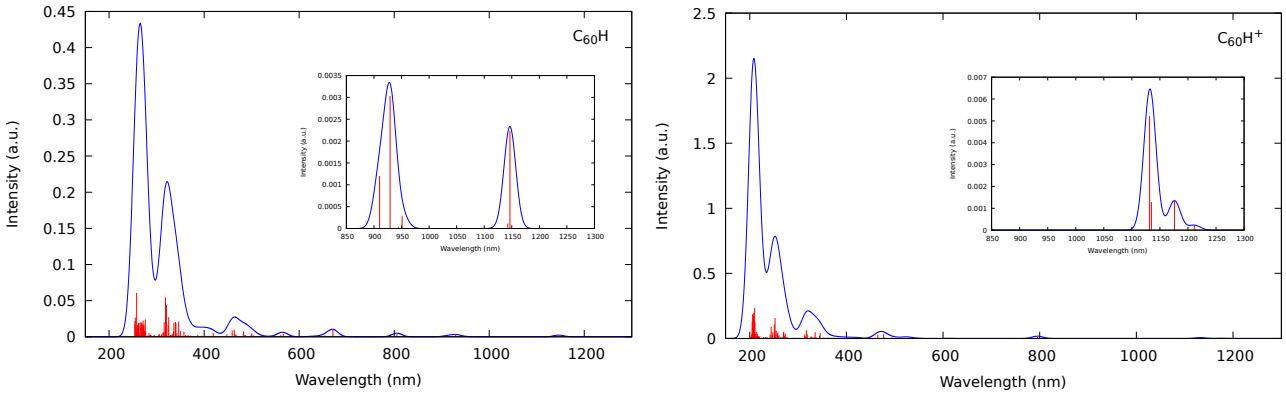

Figure S8 Simulated electronic absorption spectra of $C_{60}H$ and $C_{60}H^+$.

S4 Infrared spectra: C—H region

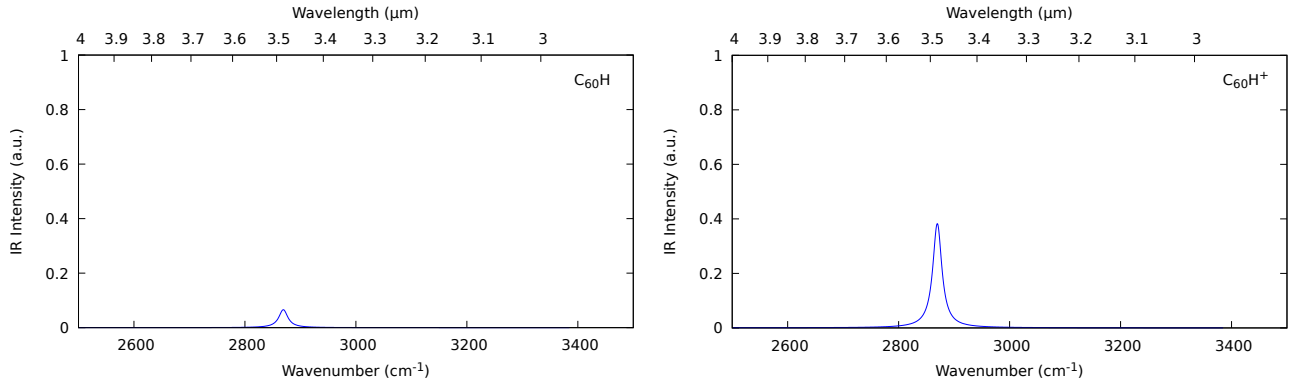

Figure S9 Simulated infrared spectra (C—H region) of $C_{60}H$ and $C_{60}H^+$ at B3LYP-D3/def2-TZVP level of theory.

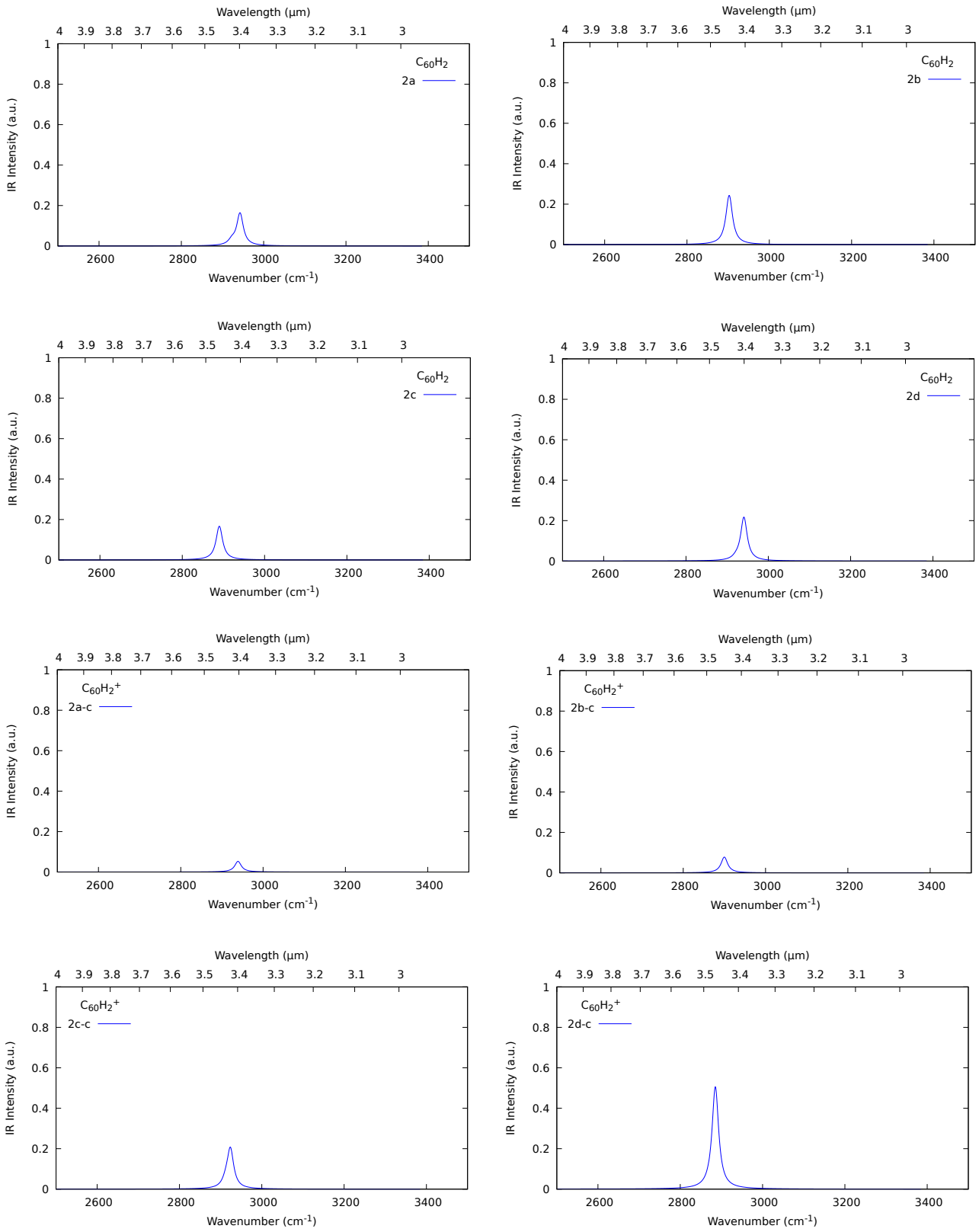

Figure S10 Simulated infrared spectra (C—H region) of $C_{60}H_2$ and $C_{60}H_2^+$ isomers at B3LYP-D3/def2-TZVP level of theory.

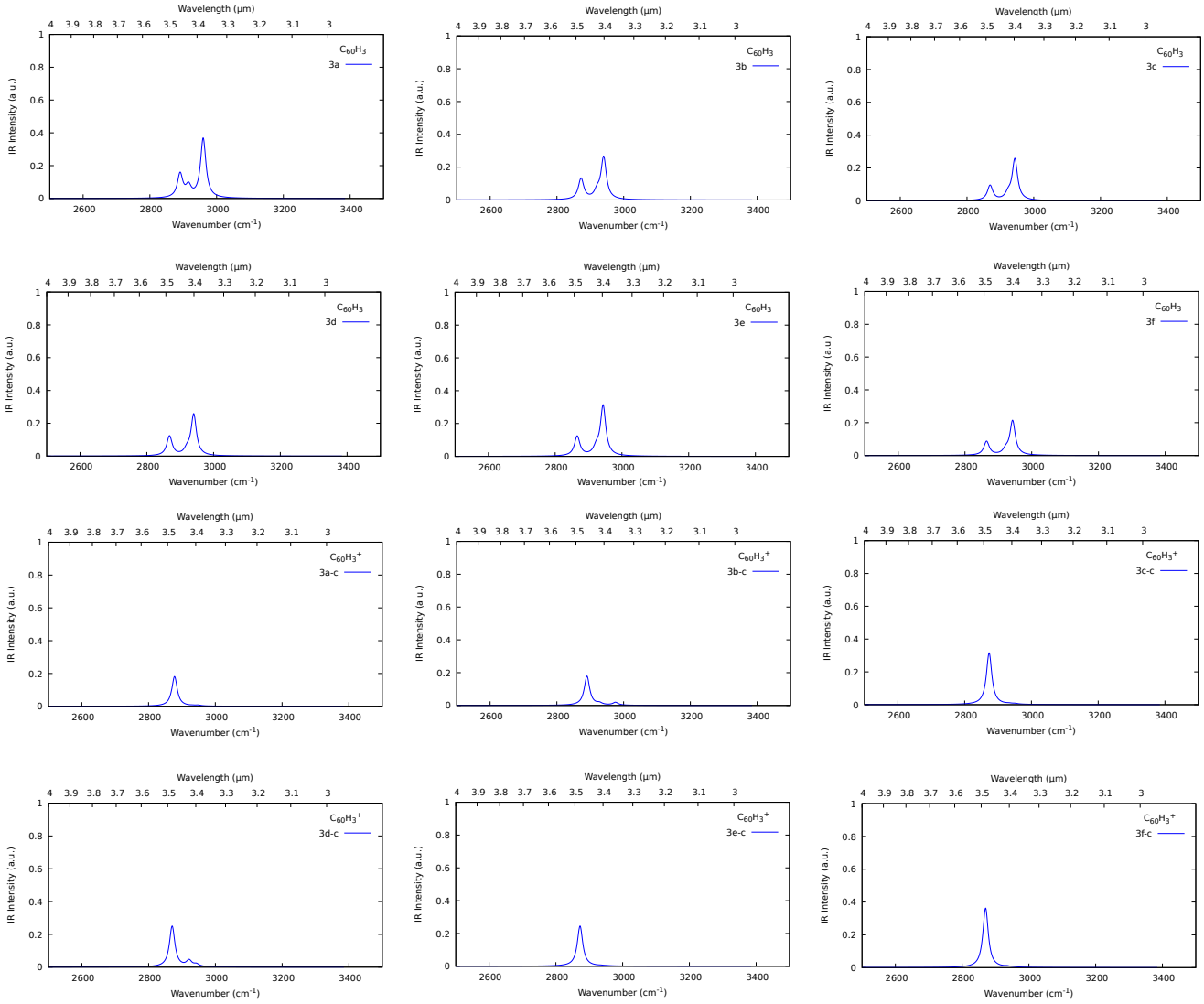

Figure S11 Simulated infrared spectra (C—H region) of $C_{60}H_3$ and $C_{60}H_3^+$ isomers at B3LYP-D3/def2-TZVP level of theory.

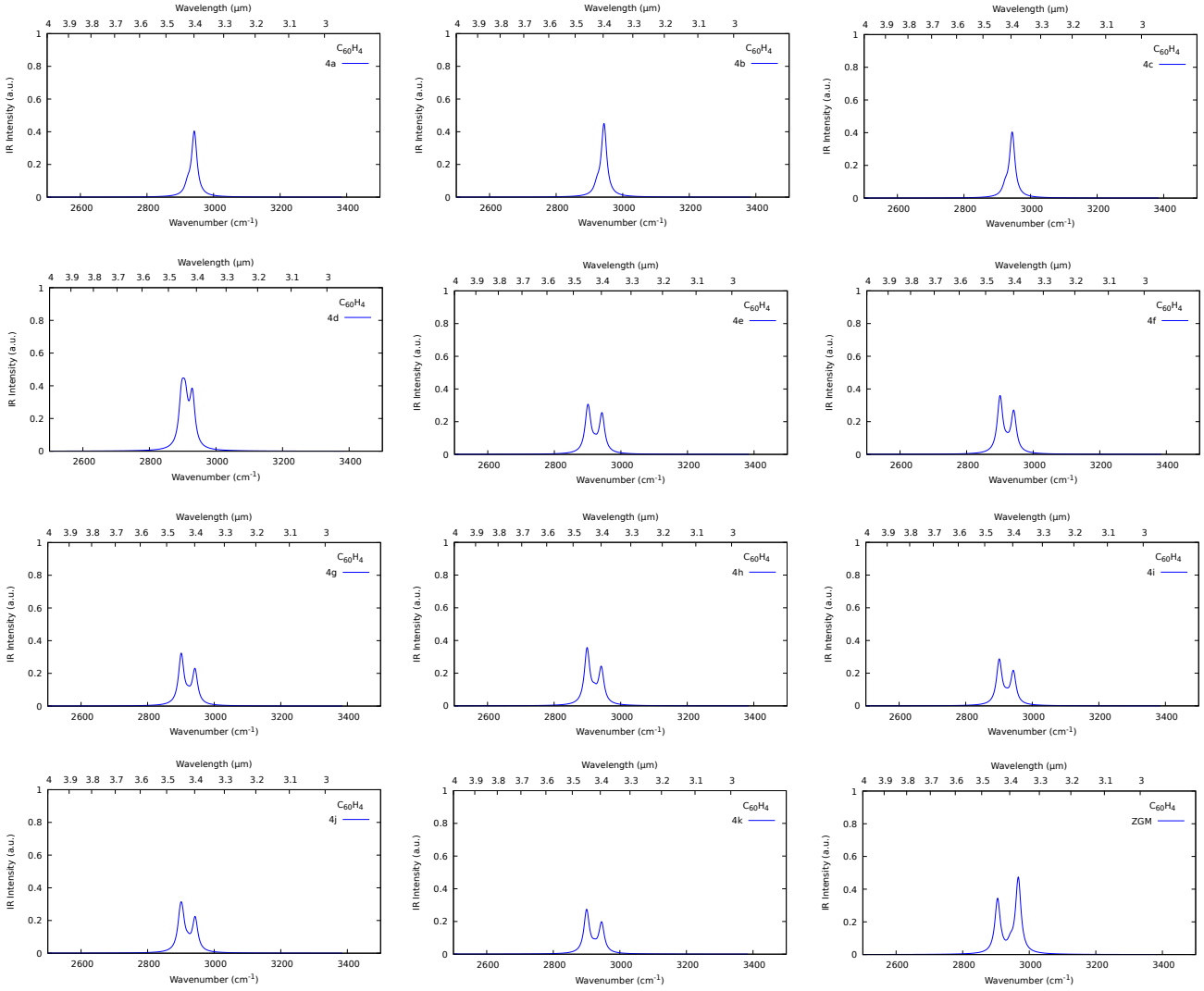

Figure S12 Simulated infrared spectra (C—H region) of $C_{60}H_4$ isomers at B3LYP-D3/def2-TZVP level of theory.

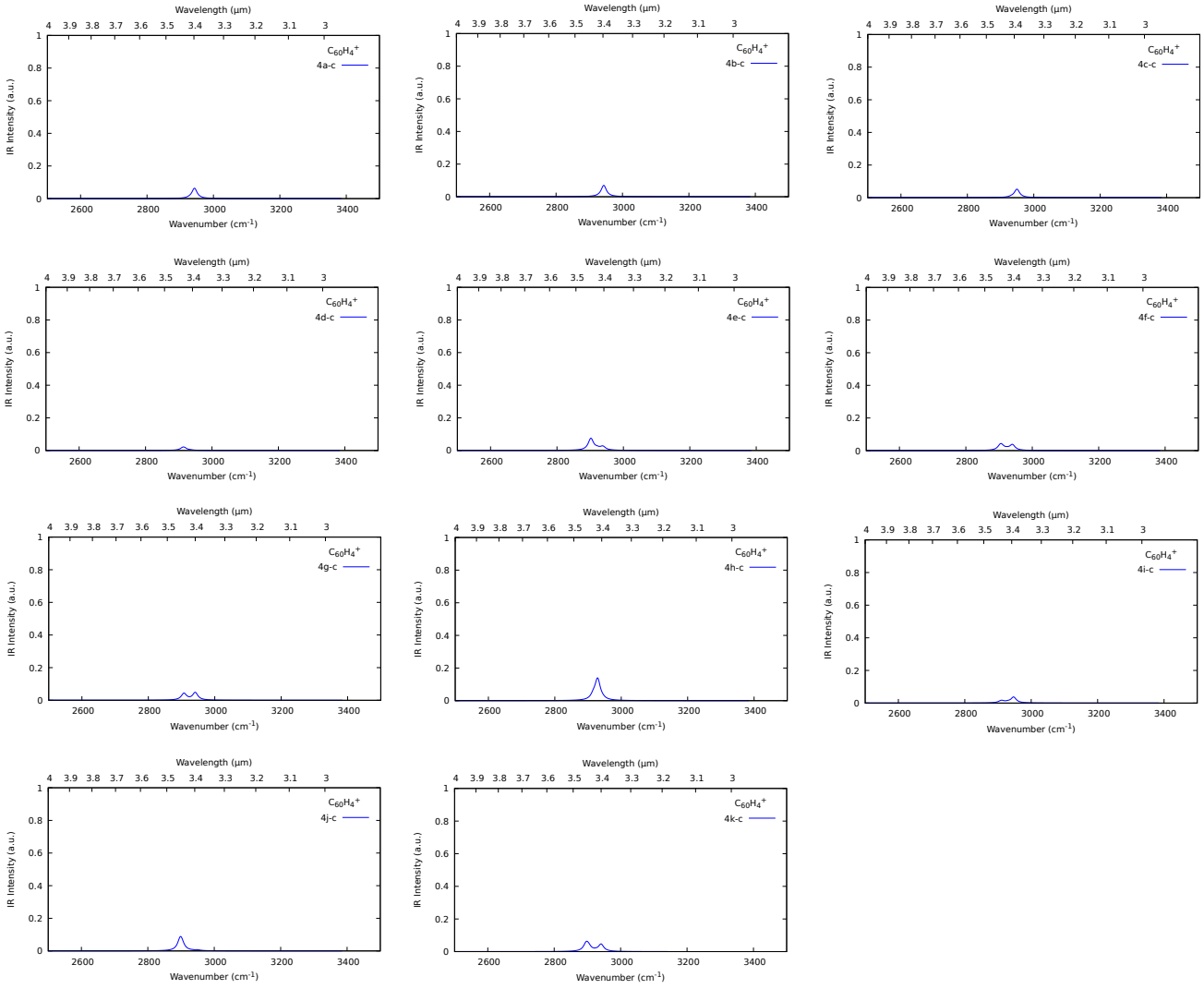

Figure S13 Simulated infrared spectra (C—H region) of $C_{60}H_4^+$ isomers at B3LYP-D3/def2-TZVP level of theory.

S5 Electronic absorption spectra of $C_{60}H_2$ and $C_{60}H_4$

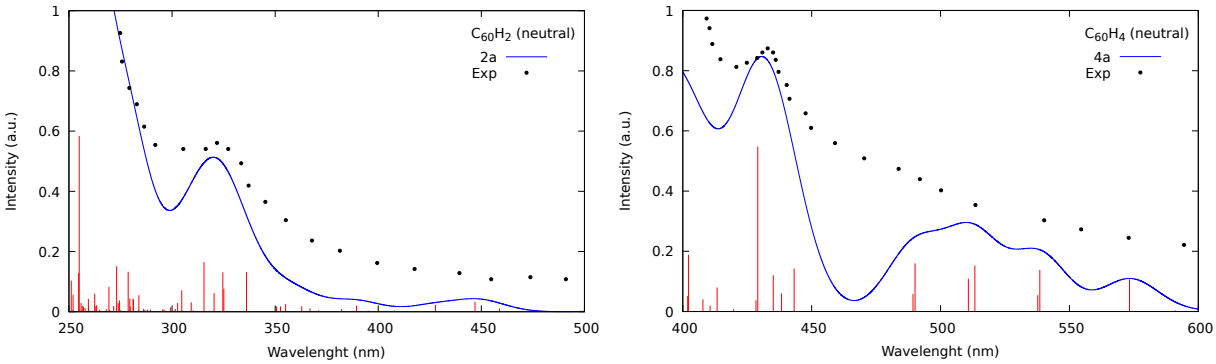

Figure S14 Simulated electronic absorption spectra of $C_{60}H_2$ (left) and $C_{60}H_4$ (right) applying r^{2}SCAN functional combined with def2-TZVP basis set. The experimental result was obtained by Henderson and Cahill,[5] and Bensasson and co-workers.[6]

S6 Electronic transitions

Table S4 Wavelength (in nm) and optical oscillator strength (OOS) of main electronic transitions of C_{60} and C_{60}^{+} species obtained at r^{2}SCAN/def2-TZVP level. In parentheses are the transition energy values in eV.

C_{60}		
Wavelength (this work)	Wavelength	OOS
328.6 (3.77)	328.4[a] (3.78)	0.1039
259.8 (4.77)	256.6[a] (4.83)	0.3162
210.0 (5.90)	211.0[a] (5.88)	0.5810
C_{60}^{+}		
Wavelength (this work)	Wavelength	OOS
895.0 (1.39)	879.3[b] (1.41) 892.0[c] (1.39)	0.0057
764.2 (1.62)	784.7[b] (1.58) 801.0[c] (1.55)	0.0430

[a] Experimental results from Leach and co-workers.[4]

[b] Theoretical results from Lykhin and co-workers.[7]

[c] Theoretical results from Soler and co-workers.[8]

Table S5 Wavelength (nm), energy (eV) and optical oscillator strength (OOS) of the first electronic transitions of $C_{60}H$ ($q = 0$) and $C_{60}H^+$ ($q = +1$) species obtained at r^{2}SCAN/def2-TZVP level.

Specie	E (nm)	E (eV)	OOS
$C_{60}H$	1147	1.08	0.0022
	1143	1.08	0.0001
	951	1.30	0.0003
	944	1.31	0.0000
	929	1.33	0.0030
	910	1.36	0.0012
$C_{60}H^+$	1211	1.02	0.0002
	1176	1.05	0.0013
	1135	1.09	0.0013
	1132	1.10	0.0052

Table S6 Wavelength (nm), energy (eV) and optical oscillator strength (OOS) of the first electronic transitions of $C_{60}H_2$ ($q = 0$) and $C_{60}H_2{}^+$ ($q = +1$) isomers obtained at r^{2}SCAN/def2-TZVP level. Only transitions with $\lambda > 900$ nm are shown.

$q = 0$				$q = +1$			
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
					3873	0.32	0.0000
					3832	0.32	0.0001
2a	-	-	-	**2a-c**	3144	0.39	0.0006
					1778	0.70	0.0020
					994	1.25	0.0188
					4429	0.28	0.0001
					3903	0.32	0.0005
2b	-	-	-	**2b-c**	3574	0.35	0.0013
					1576	0.79	0.0012
					1533	0.81	0.0085

Continuation

$q = 0$				$q = +1$			
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
	963	1.29	0.0064		1724	0.72	0.0019
					1700	0.73	0.0013
					1687	0.73	0.0007
					1621	0.76	0.0005
2c				**2c-c**	1144	1.08	0.0033
					1082	1.15	0.0004
					1074	1.15	0.0004
					1032	1.20	0.0001
					921	1.35	0.0000
	1140	1.09	0.0043		1917	0.65	0.0020
	934	1.33	0.0022		1865	0.66	0.0001
					1783	0.70	0.0018
2d				**2d-c**	1135	1.09	0.0011
					1110	1.12	0.0090
					1101	1.13	0.0056

Table S7 Wavelength (nm), energy (eV) and optical oscillator strength (OOS) of the first electronic transitions of $C_{60}H_3$ ($q = 0$) and $C_{60}H_3{}^+$ ($q = +1$) isomers obtained at r^{2}SCAN/def2-TZVP level.

$q = 0$				$q = +1$			
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
3a	1155	1.07	0.0018	**3a-c**	1272	0.97	0.0073
	1020	1.22	0.0009		1168	1.06	0.0000
	958	1.29	0.0010		1103	1.12	0.0039
	914	1.36	0.0002				
3b	1176	1.05	0.0008	**3b-c**	1482	0.84	0.0012
	1041	1.19	0.0032		1188	1.04	0.0001
	973	1.27	0.0000		1169	1.06	0.0039
	939	1.32	0.0010		957	1.30	0.0020
	919	1.35	0.0042				
3c	1150	1.078	0.0009	**3c-c**	1155	1.07	0.0055
	1047	1.185	0.0023		1089	1.14	0.0020
	983	1.261	0.0015		1081	1.15	0.0027
	950	1.306	0.0006				
	930	1.333	0.0021				
3d	1252	0.990	0.0004	**3d-c**	1218	1.02	0.0032
	950	1.305	0.0006		1049	1.18	0.0037
	917	1.353	0.0028		1007	1.23	0.0023
	906	1.369	0.0009				

Continuation

$q = 0$				$q = +1$			
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
	1196	1.04	0.0002		1329	0.93	0.0037
	1102	1.13	0.0001		1173	1.06	0.0005
3e	1043	1.19	0.0044	**3e-c**	1108	1.12	0.0028
	922	1.35	0.0040		958	1.29	0.0093
	907	1.37	0.0019				
	1184	1,05	0.0033		1322	0.94	0.0027
	1056	1,17	0.0016		1094	1.13	0.0054
3f	975	1,27	0.0019	**3f-c**	1088	1.14	0.0039
	960	1,29	0.0001				
	931	1,33	0.0040				

Table S8 Wavelength (nm), energy (eV) and optical oscillator strength (OOS) of the first electronic transitions of $C_{60}H_4^+$ ($q = +1$) isomers obtained at r^{2}SCAN/def2-TZVP level.

$q = +1$							
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
	3436	0.36	0.0017		3016	0.41	0.0000
	3087	0.40	0.0000		2619	0.47	0.0024
4a-c	1899	0.65	0.0042	**4g-c**	2395	0.52	0.0038
	1661	0.75	0.0024		1443	0.86	0.0014
	960	1.29	0.0015		1036	1.20	0.0118
	3223	0.38	0.0006		2155	0.58	0.0015
	2394	0.52	0.0018		1787	0.69	0.0010
	1900	0.65	0.0000		1386	0.89	0.0003
	1248	0.99	0.0049		1322	0.94	0.0024
4b-c	907	1.37	0.0263	**4h-c**	1089	1.14	0.0011
					1041	1.19	0.0002
					949	1.31	0.0001
					904	1.37	0.0011
	3442	0.36	0.0000		5009	0.25	0.0003
	3358	0.37	0.0000		3134	0.40	0.0006
	2618	0.47	0.0000		2114	0.59	0.0025
4c-c	1554	0.80	0.0168	**4i-c**	1712	0.72	0.0036
					1333	0.93	0.0022
					938	1.32	0.0109

Continuation							
$q = +1$							
Specie	E (nm)	E (eV)	OOS	Specie	E (nm)	E (eV)	OOS
4d-c	3829	0.32	0.0000	**4j-c**	4040	0.31	0.0005
	3096	0.40	0.0002		3268	0.38	0.0013
	1895	0.65	0.0012		2159	0.57	0.0002
	1449	0.86	0.0016		1596	0.78	0.0029
	1339	0.93	0.0096		1321	0.94	0.0124
					956	1.30	0.0060
4e-c	2575	0.48	0.0000	**4k-c**	2221	0.56	0.0026
	2224	0.56	0.0023		2081	0.60	0,0014
	1881	0.66	0.0029		1575	0.79	0.0017
	1208	1.03	0.0003		1170	1.06	0.0066
	1197	1.04	0.0051		1077	1.15	0.0073
	1017	1.22	0.0025		972	1.28	0.0038
					902	1.38	0.0012
4f-c	3112	0.40	0.0015				
	2561	0.48	0.0005				
	1819	0.68	0.0025				
	1332	0.93	0.0015				
	1074	1.15	0.0076				

S7 Ionization potentials

Table S9 Ionization potentials (IP) of $C_{60}H_2$, $C_{60}H_3$ and $C_{60}H_4$ species obtained at B3LYP-D3/def2-TZVP level.

Specie	IP (eV)
2a	7.03
2b	7.04
2c	6.70
2d	6.70
Mean value	6.87
3a	6.40
3b	6.30
3c	6.36
3d	6.36
3e	6.30
3f	6.32
Mean value	6.34
4a	6.82
4b	6.77
4c	6.84
4d	6.88
4e	6.84
4f	6.87
4g	-
4h	6.63
4i	6.79
4j	6.74
4k	-
Mean value	6.80

S8 Property trends

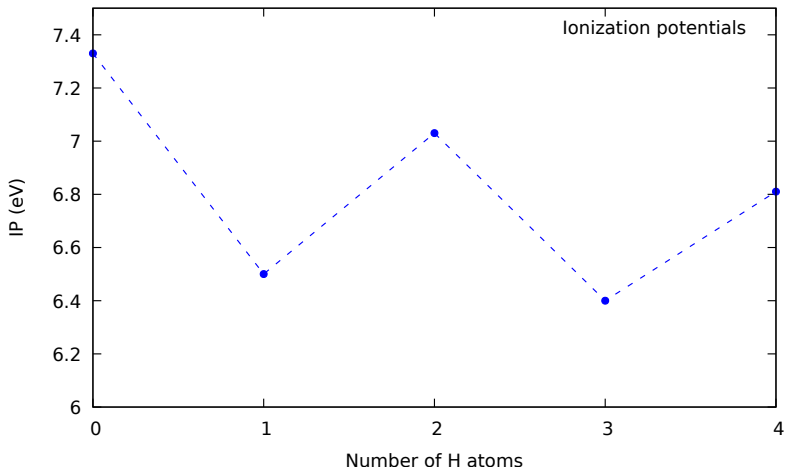

Figure S15 Ionization potentials in function of number of hydrogen atoms.

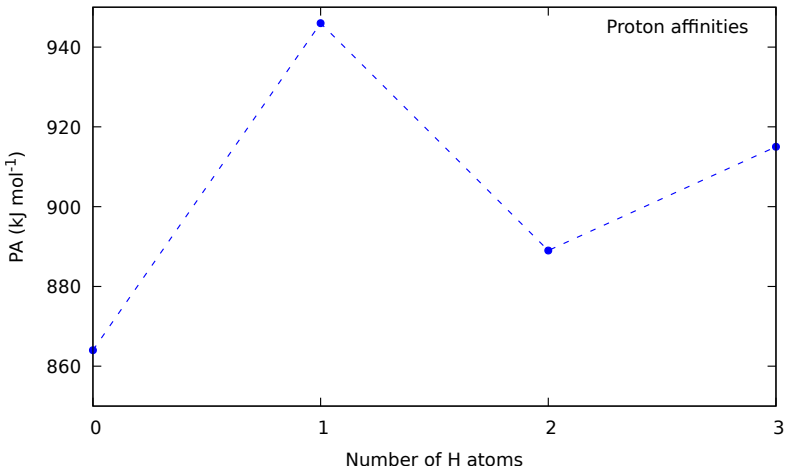

Figure S16 Proton affinities in function of number of hydrogen atoms.

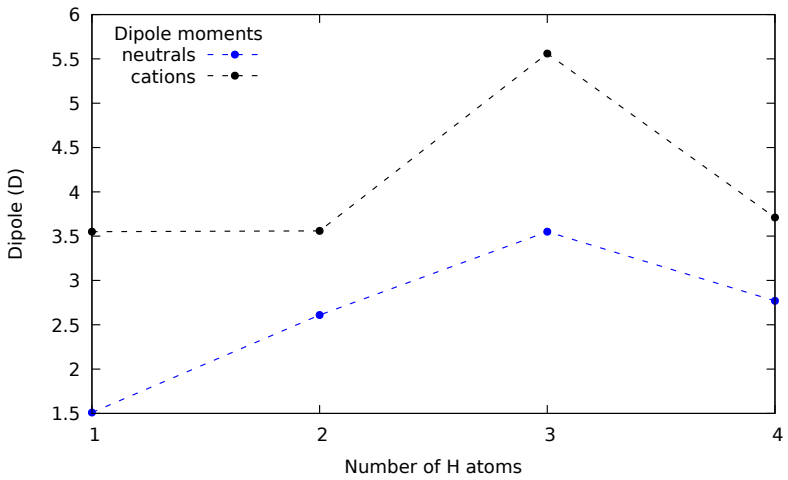

Figure S17 Dipole moments in function of number of hydrogen atoms.

References

[1] K. Yamamoto, M. Saunders, A. Khong, R. J. Cross, M. Grayson, M. L. Gross, A. F. Benedetto and R. B. Weisman, *Journal of the American Chemical Society*, 1999, **121**, 1591–1596.

[2] D. Strelnikov, B. Kern and M. M. Kappes, *Astronomy & Astrophysics*, 2015, **584**, A55.

[3] J. Palotás, J. Martens, G. Berden and J. Oomens, *Nature Astronomy*, 2020, **4**, 240–245.

[4] S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J. P. Hare, T. John Dennis, H. W. Kroto, R. Taylor and D. R. Walton, *Chemical Physics*, 1992, **160**, 451–466.

[5] C. C. Henderson and P. A. Cahill, *Science*, 1993, **259**, 1885–1887.

[6] R. Bensasson, E. Bienvenue, J.-M. Janot, S. Leach, P. Seta, D. Schuster, S. Wilson and H. Zhao, *Chemical Physics Letters*, 1995, **245**, 566–570.

[7] A. O. Lykhin, S. Ahmadvand and S. A. Varganov, *Journal of Physical Chemistry Letters*, 2019, **10**, 115–120.

[8] J. Soler, R. Sarkar and M. Boggio-Pasqua, *The Journal of Physical Chemistry A*, 2019, **123**, 1824–1829.