Supporting Information

A Theoretical Study on the Formation Mechanism and Sum-Frequency Generation Spectra of Hydrogenated Graphene

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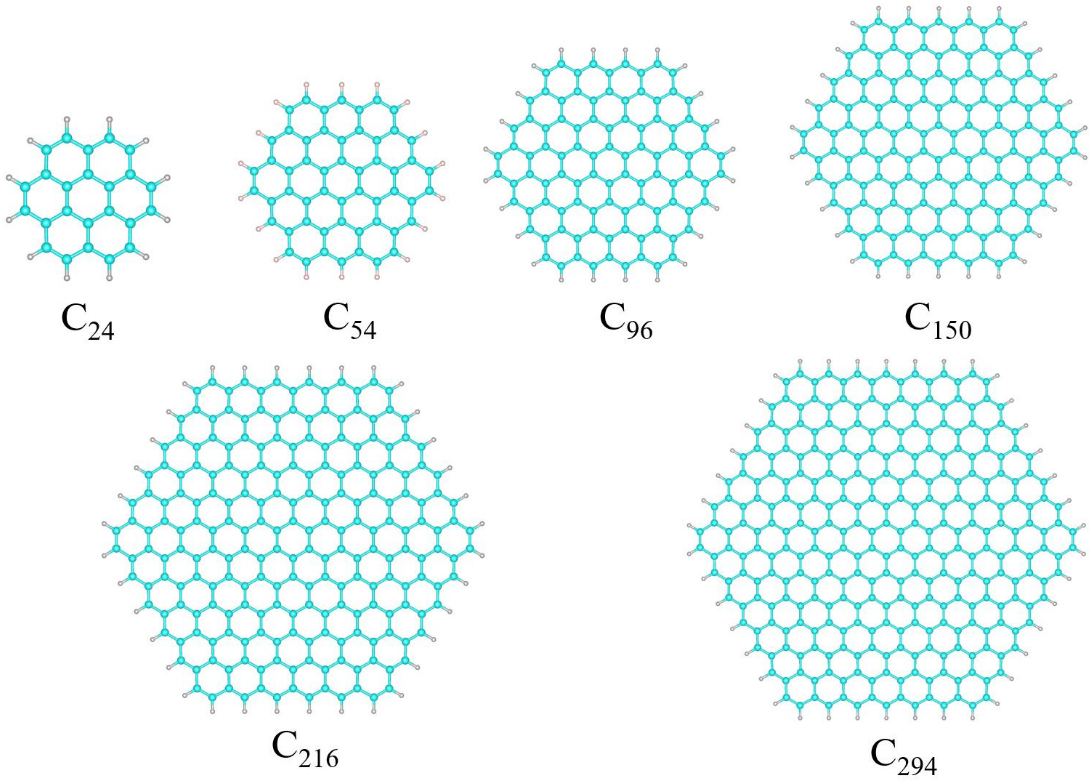


Fig. S1. Various sizes of graphene nanosheets with 24 (C_{24}), 54 (C_{54}), 96 (C_{96}), 150 (C_{150}), 216 (C_{216}), and 294 (C_{294}) carbon atoms. The edges are passivated with hydrogens.

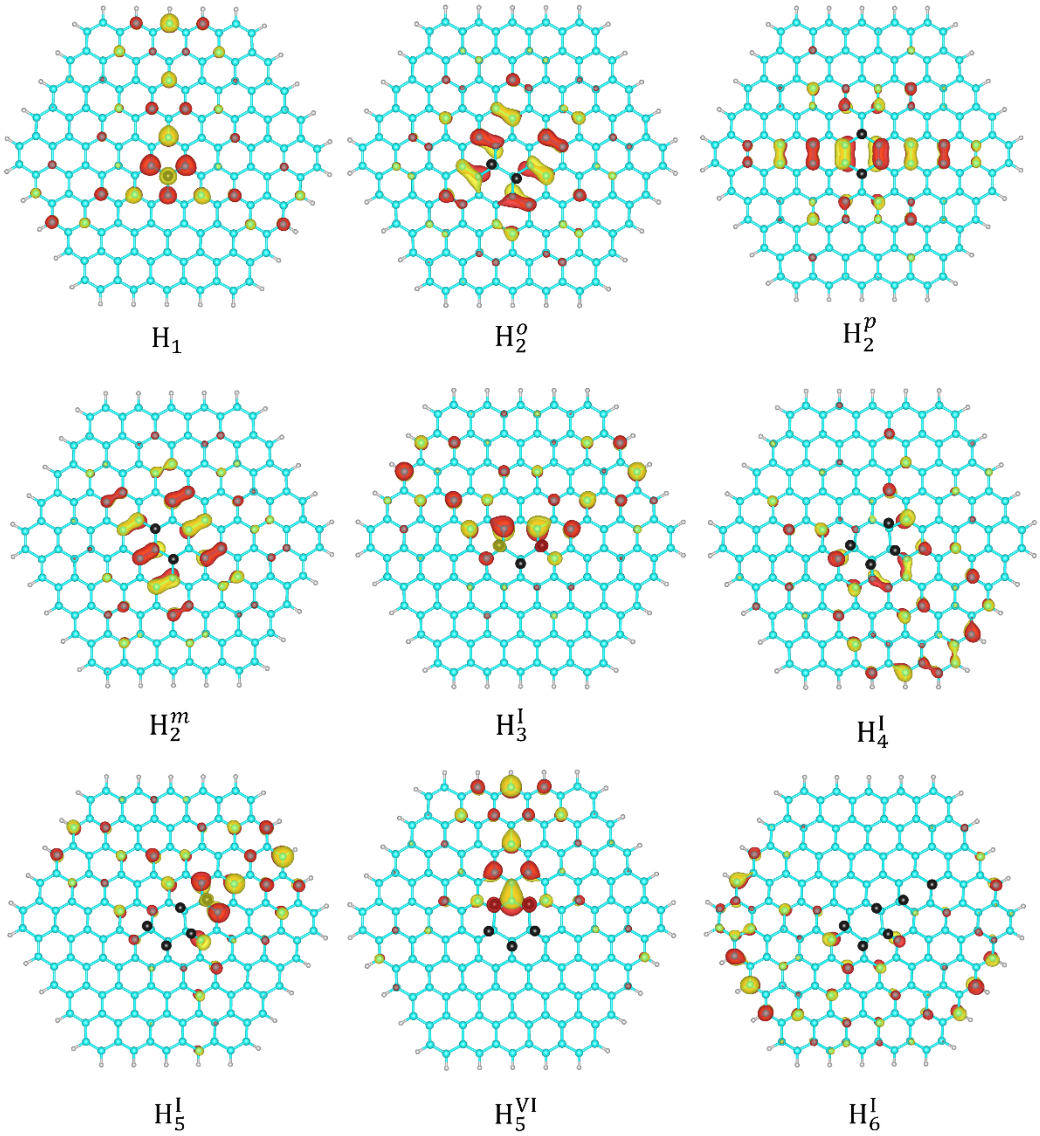


Fig. S2. Lowest unoccupied molecular orbitals (LUMOs) of the titled H-Gra, with an isosurface value of 0.03 e/bohr^3.

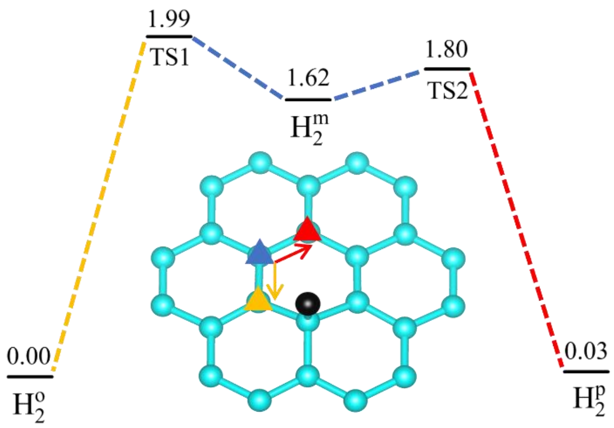


Fig. S3. Energy profile of the meta-dimer (H_2^m) to the ortho- (H_2^o) and para-dimer (H_2^p) configurations.

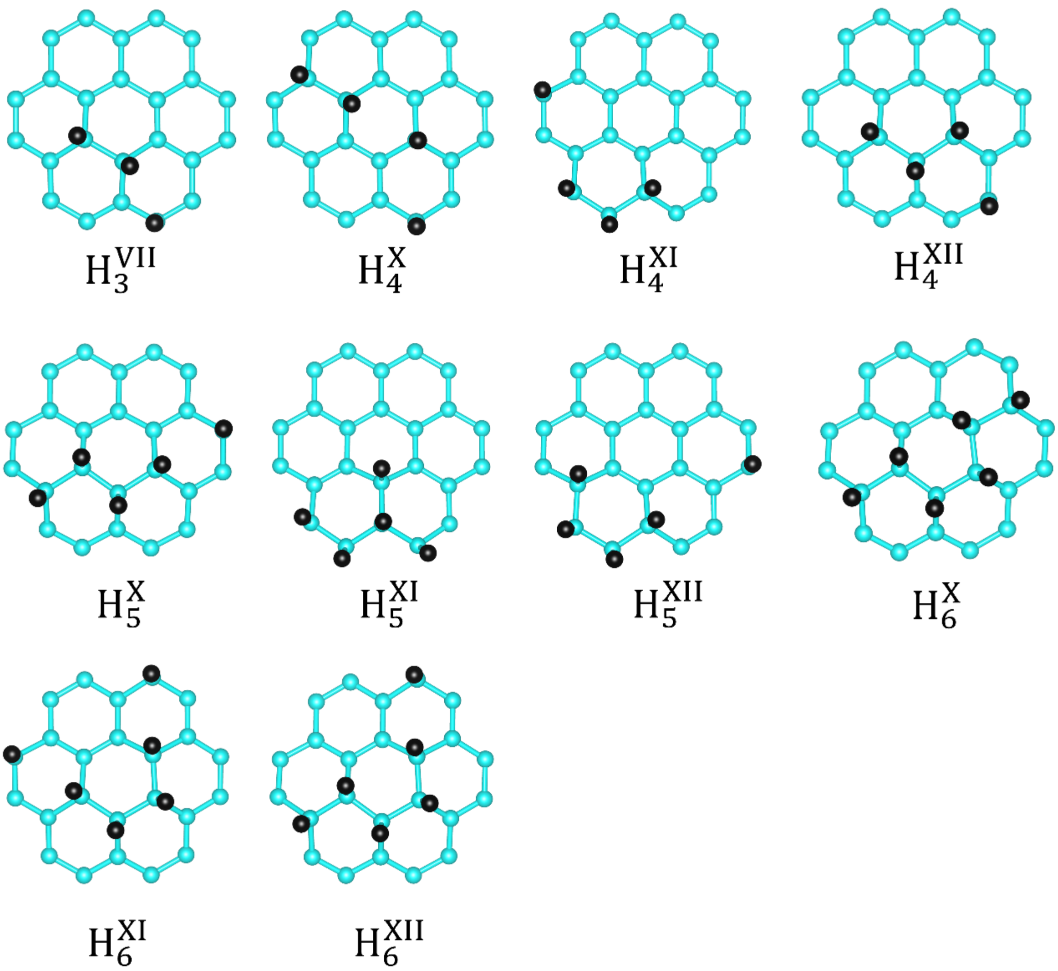


Fig. S4. Titled configurations of H-Gra with 3−6 hydrogen atoms adsorbed on graphene.

Table SI. Comparison of binding energies (E_b, eV) of H-monomer, dimer, and trimer adsorbed on the graphene between this work and previous studies.[a]

XC functional	Binding energy (eV)			
	H_1	H_2^o	H_2^p	H_3^I
PW91[R1]	0.81	1.38		1.41
PBE[R2]	0.83	1.41	1.38	
PBE[R3]	0.81	1.36	1.34	
PBE[R4]	0.77			1.39
PBE[R5]				1.39
B3LYP[b]	0.81	1.47	1.45	1.49

[a]Only the most stable H-trimer (H_3^I) is listed here.

[b]Exchange-correlation (XC) functional used in this work. Refs. [R1-R5] corresponding to Refs. [50,51,48,53,54] in the main text, respectively.

References

[R1] Ž. Šljivančanin, M. Andersen, L. Hornekær, and B. Hammer, Structure and Stability of Small H Clusters on Graphene, *Phys. Rev. B*, 2011, **83**, 205426.

[R2] A. Ranjbar, M. S. Bahramy, M. Khazaei, H. Mizuseki, and Y. Kawazoe, First-Principles Study of Structural Stability, Magnetism, and Hyperfine Coupling in Hydrogen Clusters Adsorbed on Graphene, *Phys. Rev. B*, 2010, **82**, 165446.

[R3] S. Sakong and P. Kratzer, Hydrogen Vibrational Modes on Graphene and Relaxation of the C–H Stretch Excitation from First-Principles Calculations, *J. Chem. Phys*., 2010, **133**, 054505.

[R4] T. Roman, H. Nakanishi, H. Kasai, K. Nobuhara, T. Sugimoto, and K. Tange, Stability of Three-Hydrogen Clusters on Graphene, *J. Phys. Soc. Jpn*., 2009, **78**, 035002.

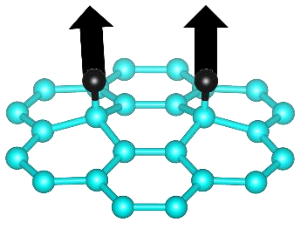
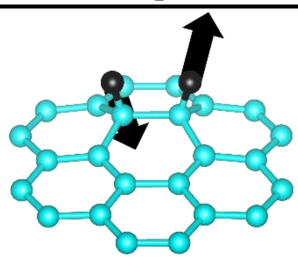
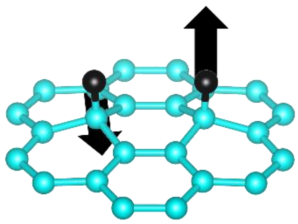
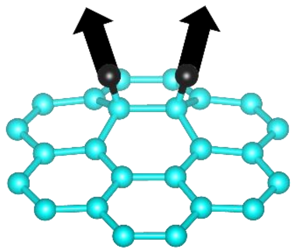
[R5] T. Cao, L. Huang, X. Zheng, P. Gong and Z. Zeng, Understanding the stability and dynamical process of hydrogen trimers on graphene, *J. Appl. Phys.*, 2013, **113**, 173707.

Table SII. Binding energies (E_b, eV) and C−H distances (d_{C-H}, Å) of the corresponding configurations of H-Gra.[a]

configuration	E_b	d_{C-H}
H_3^{VII}	1.25	1.105
H_4^{X}	1.57	1.107
H_4^{XI}	1.42	1.105
H_4^{XII}	1.26	1.109
H_5^{X}	1.62	1.104
H_5^{XI}	1.60	1.101
H_5^{XII}	1.49	1.104
H_6^{X}	1.67	1.101
H_6^{XI}	1.66	1.105
H_6^{XII}	1.65	1.103

[a]The C–H distances in trimers and tetramers are averaged.

Table SIII. The assigned vibrational modes in the simulated SFG spectra as shown in Fig. 9(b), with associated vibrational frequencies (in cm^{-1}) and configurations of H-Gra.[a]

H_2^p	H_2^o
	
υ_{sym}^p (2852.9 cm^{-1})	υ_{asym}^o (2938.2 cm^{-1})
	
υ_{asym}^p (2866.3 cm^{-1})	υ_{sym}^o (2973.0 cm^{-1})

[a]The asymmetric vibrational modes, υ_{asym}^p and υ_{asym}^o, do not appear in the SFG spectra.

Table SIV. The assigned vibrational modes in the simulated SFG spectra as shown in Fig. 10(a), with associated vibrational frequencies (in cm^{-1}) and configurations of H-Gra.

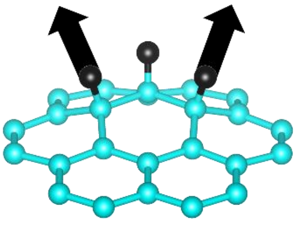
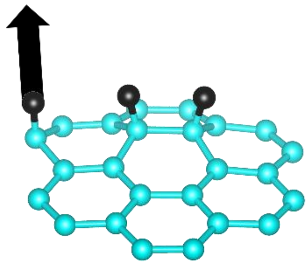
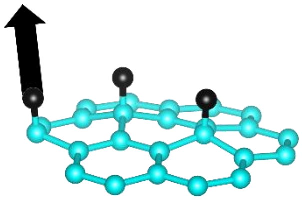
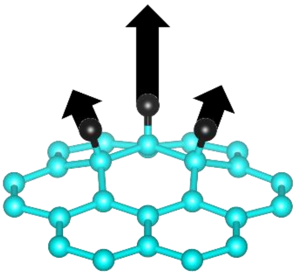
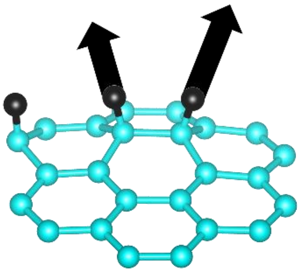
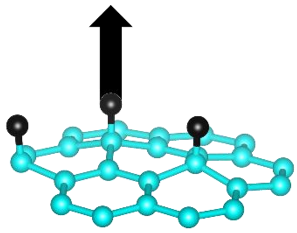
H_3^{I}	H_3^{II}	H_3^{III}
		
υ_{sym}^{m} (2920.3 cm^{-1})	υ^{s} (2837.2 cm^{-1})	υ^{s} (2847.4 cm^{-1})
		
υ_{sym}^{H3} (3020.2 cm^{-1})	υ_{sym}^{o} (2960.3 cm^{-1})	υ^{s} (2881.7 cm^{-1})

Table SV. The assigned vibrational modes in the simulated SFG spectra as shown in Fig. 10(b), with associated vibrational frequencies (in cm^{-1}) and configurations of H-Gra.

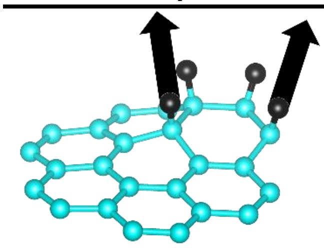
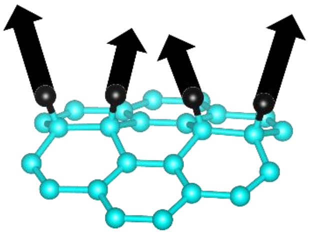
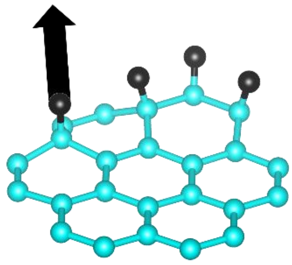
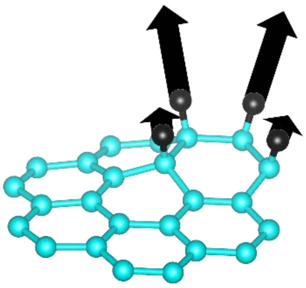
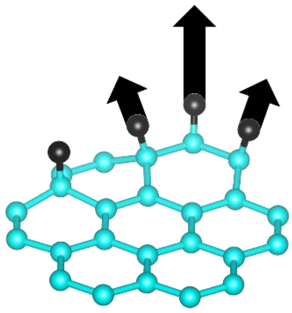
H_4^{I}	H_4^{II}	H_4^{III}
		
υ_{sym}^{p} (2926.5 cm^{-1})	υ_{sym}^{H4} (2956.9 cm^{-1})	υ^{s} (2846.2 cm^{-1})
		
υ_{sym}^{o} (3036.9 cm^{-1})		υ_{sym}^{H3} (3015.8 cm^{-1})

Table SVI. The assigned vibrational modes in the simulated SFG spectra as shown in Fig. 10(c), with associated vibrational frequencies (in cm^{-1}) and configurations of H-Gra.

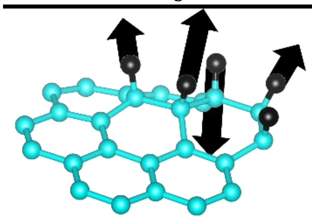
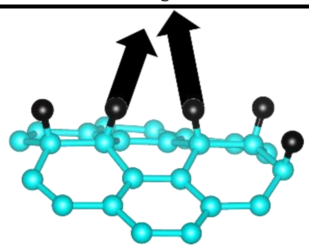
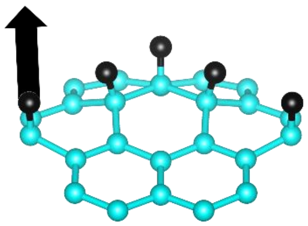
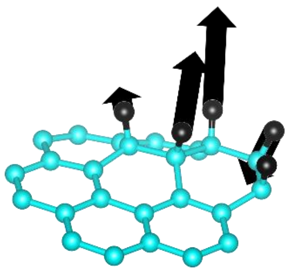
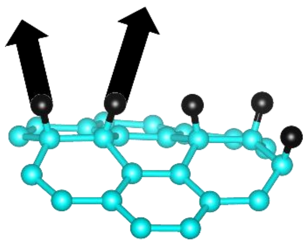
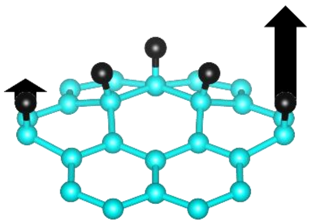
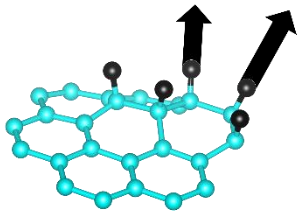
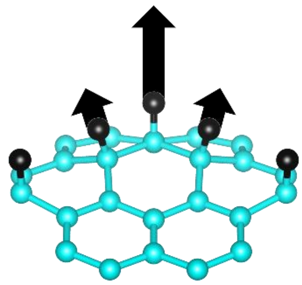
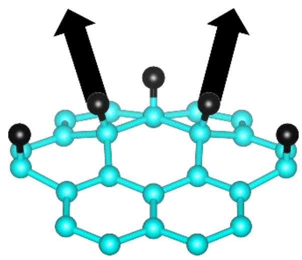
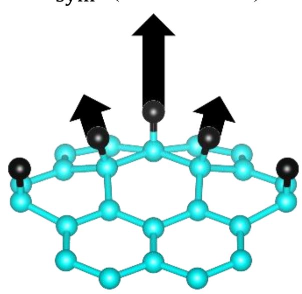
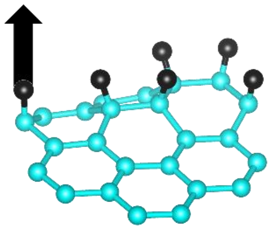
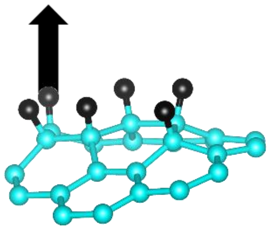
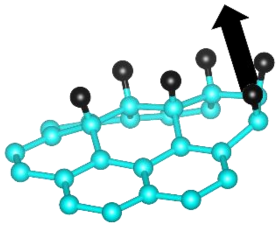
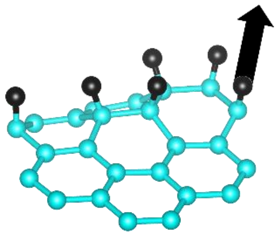
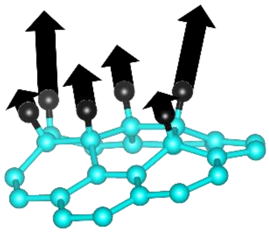
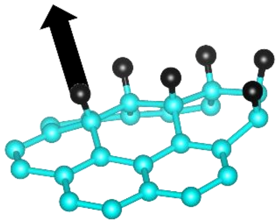
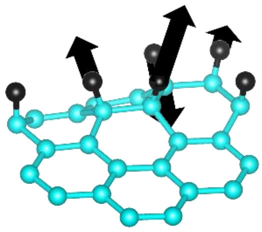
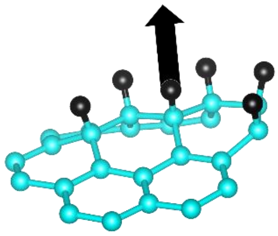
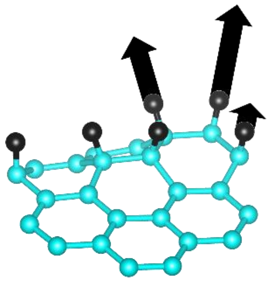
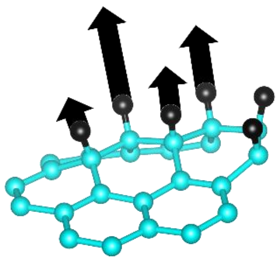
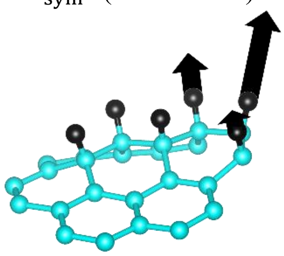
H_5^{I}	H_5^{II}	H_5^{III}
		
υ_{asym}^{H4} (2970.6 cm^{-1})	υ_{sym}^{p} (2912.5 cm^{-1})	υ^{s} (2840.9 cm^{-1})
		
υ_{asym}^{H3} (2992.1 cm^{-1})	υ_{sym}^{o} (2954.5 cm^{-1})	υ^{s} (2841.3 cm^{-1})
		
υ_{sym}^{o} (3027.8 cm^{-1})	υ_{sym}^{H3} (3013.7 cm^{-1})	υ_{sym}^{m} (2931.2 cm^{-1})
		
		υ_{sym}^{H3} (3008.8 cm^{-1})

Table SVII. The assigned vibrational modes in the simulated SFG spectra as shown in Fig. 10(d), with associated vibrational frequencies (in cm^{-1}) and configurations of H-Gra.

H_6^{I}	H_6^{II}	H_6^{III}
 υ^{s} (2857.9 cm^{-1})	 υ^{s} (2919.9 cm^{-1})	 υ^{s} (2920.0 cm^{-1})
 υ^{s} (2919.5 cm^{-1})	 υ_{sym}^{H4} (3024.3 cm^{-1})	 υ^{s} (2936.0 cm^{-1})
 υ_{asym}^{H3} (2968.9 cm^{-1})		 υ^{s} (2947.5 cm^{-1})
 υ_{sym}^{o} (3027.2 cm^{-1})		 υ_{sym}^{H4} (2991.6 cm^{-1})
		 υ_{sym}^{o} (3026.5 cm^{-1})