

Supplementary Materials

Phosphorescence of Hydrogen-Capped Linear Polyynes C_8H_2 , $C_{10}H_2$ and $C_{12}H_2$ in Solid Hexane Matrices at 20 K

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For the assignment of vibrational modes of polyynes, C_8H_2 , $C_{10}H_2$, and $C_{12}H_2$, molecular orbital calculations were performed [S1]. Figure S1 summarizes calculated harmonic frequencies and observed vibrational frequencies in the phosphorescence spectra. Figure S2 illustrates deformation of polyyne molecules relevant to the vibrational-mode excitation upon the electronic transition of phosphorescence.

Figure S1. Harmonic vibrational-mode frequencies of $C_{2n}H_2$ ($n = 4-6$) scaled by 0.975 for anharmonicity correction by using molecular orbital calculations at the B3LYP/cc-pVDZ level of density-functional theory (DFT) [S1]. Markers in red and blue represent observed frequencies in the phosphorescence spectra, while the black markers represent the estimated fundamental frequencies. Open circles indicate the highest-intensity Raman-active modes of σ_g symmetry.

Figure S2. Displacements of atoms in the vibrational modes of (a) C_8H_2 , (b) $C_{10}H_2$, and (c) $C_{12}H_2$.

Reference

[S1] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.V.; Bloino, J.; Janesko, B.G.; Gomperts, R.; Mennucci, B.; Hratchian, H.P.; Ortiz, J.V.; Izmaylov, A.F.; L. Sonnenberg, J.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V.G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.J.; Heyd, J.J.; Brothers, E.N.; Kudin, K.N.; Staroverov, V.N.; Keith, T.A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.P.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Millam, J.M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Farkas, O.; Foresman, J.B.; Fox, D.J. Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2019.

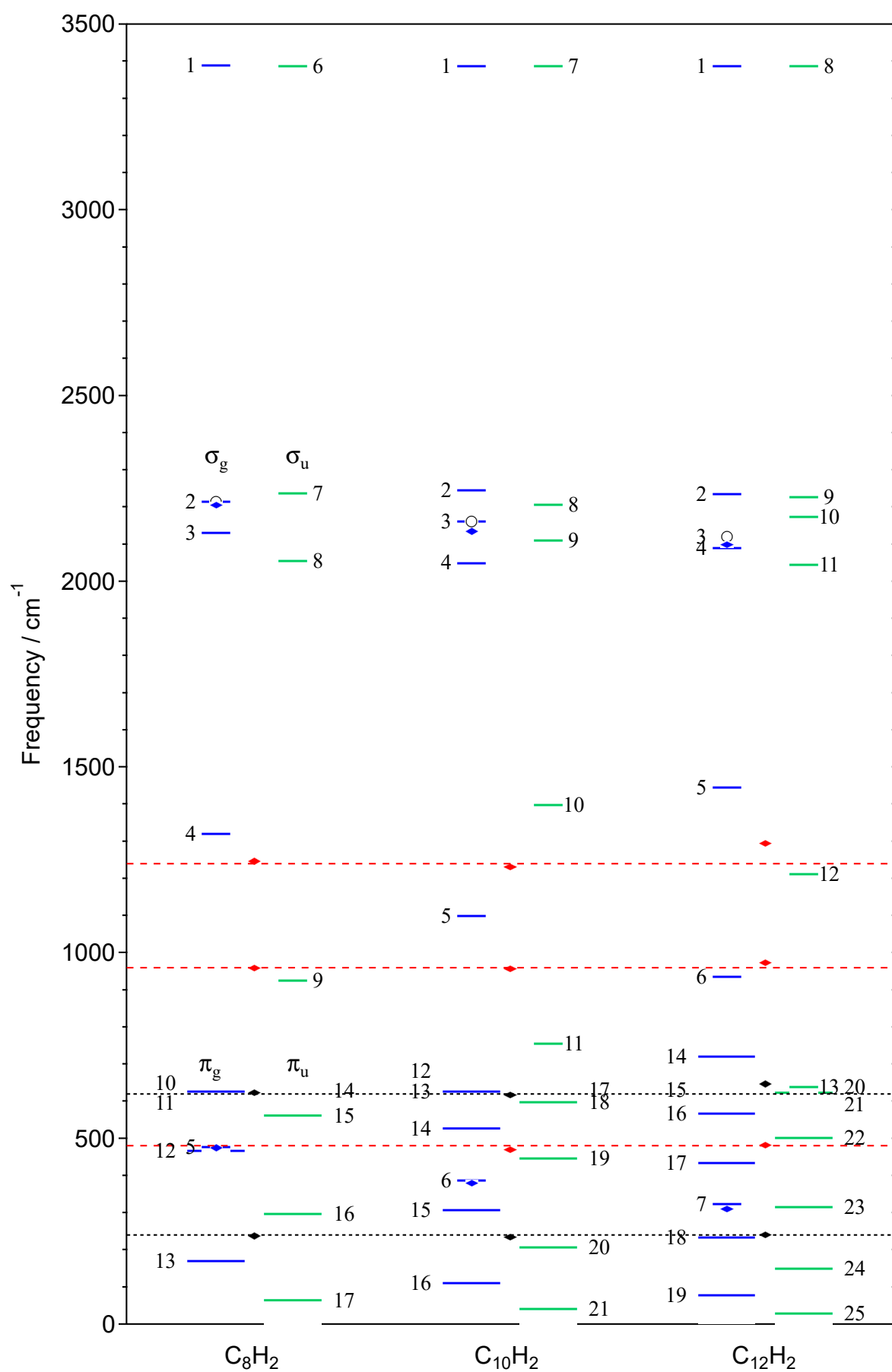
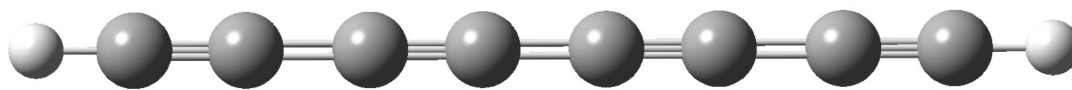
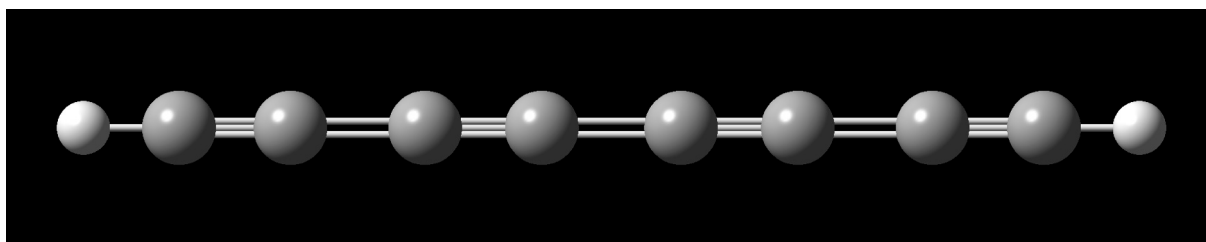


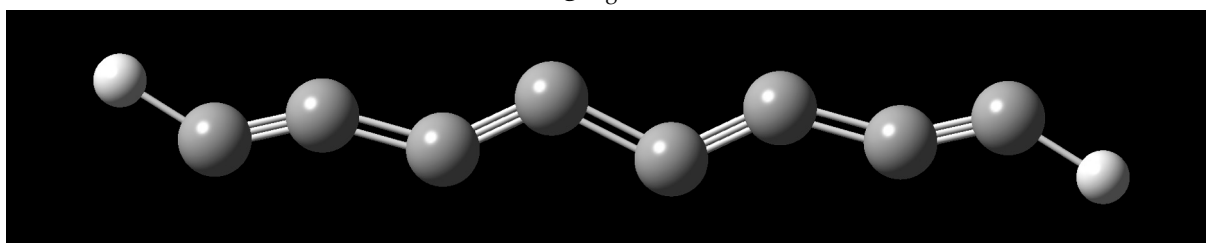
Figure S1.



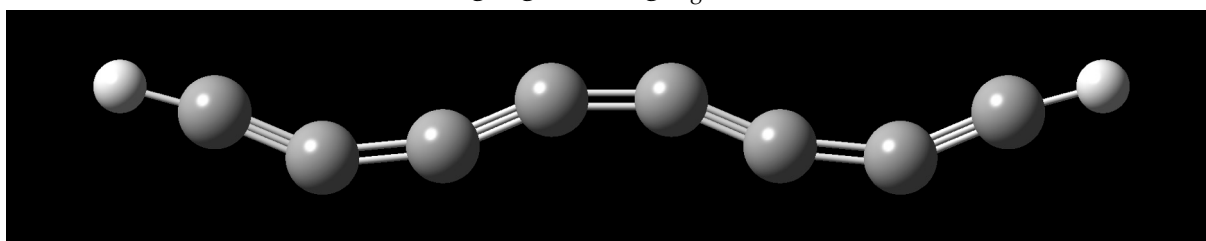
The equilibrium structure of C₈H₂.



(ν₅) breathing σ_g mode of C₈H₂.

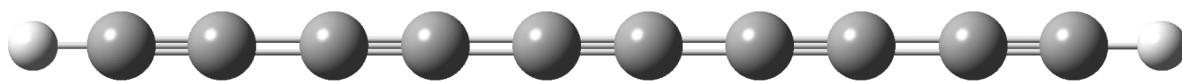


(ν₁₁) *trans*-zigzag bending π_g mode of C₈H₂.

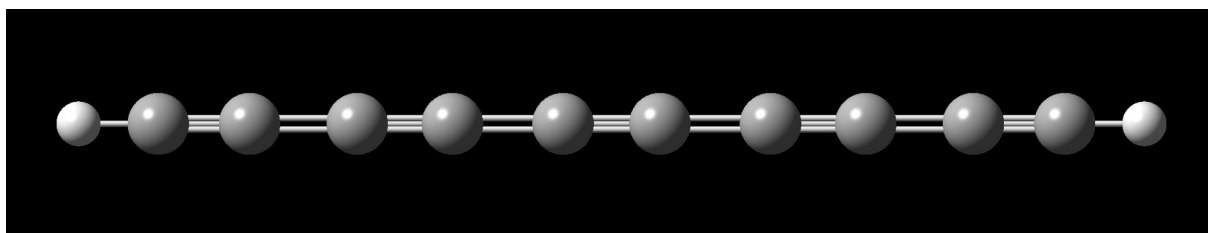


(ν₁₆) *cis*-zigzag bending π_u mode of C₈H₂.

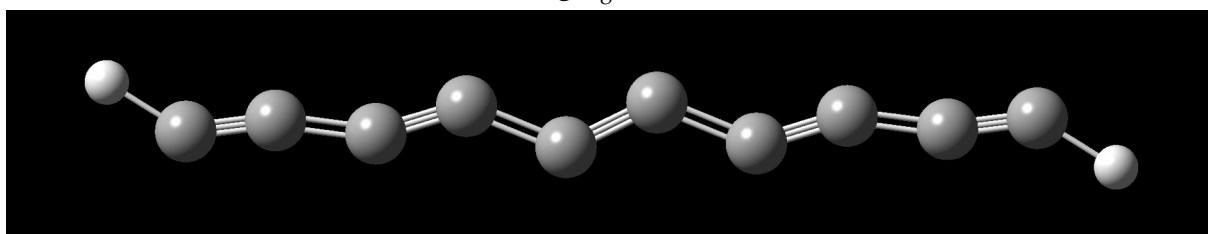
Figure S2. (a) C₈H₂.



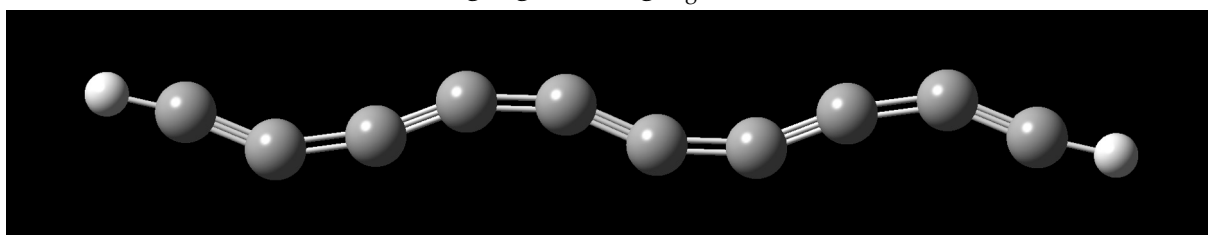
The equilibrium structure of C₁₀H₂.



(ν₆) breathing σ_g mode of C₁₀H₂.

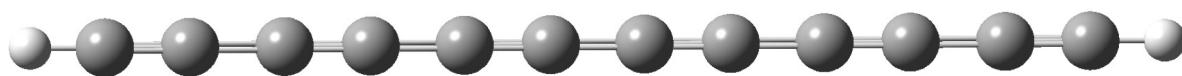


(ν₁₃) *trans*-zigzag bending π_g mode of C₁₀H₂.

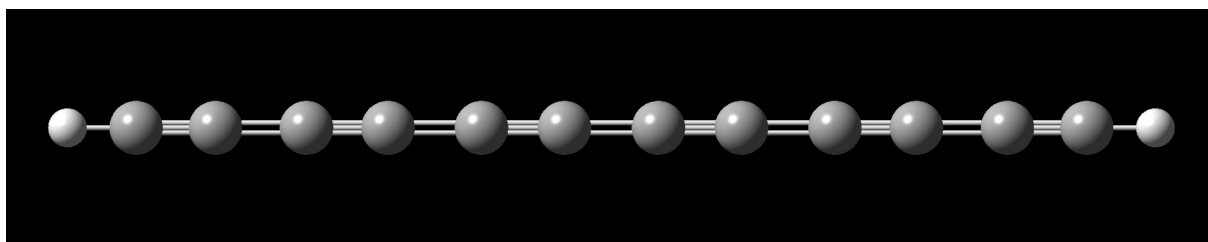


(ν₁₅) *cis*-zigzag bending π_g mode of C₁₀H₂.

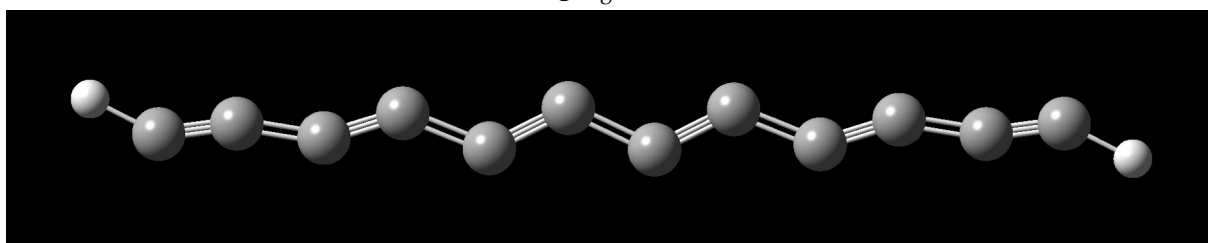
Figure S2. (b) C₁₀H₂.



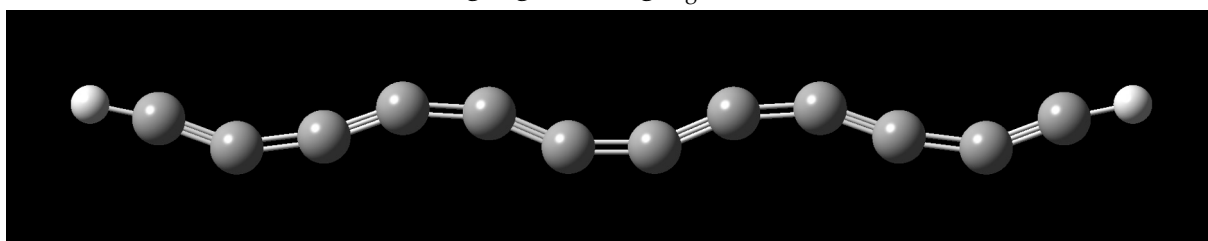
The equilibrium structure of C₁₂H₂.



(v₇) breathing σ_g mode of C₁₂H₂.



(v₁₅) *trans*-zigzag bending π_g mode of C₁₂H₂.



(v₂₃) *cis*-zigzag bending π_u mode of C₁₂H₂.

Figure S2. (c) C₁₂H₂.