

Supplemental Material for:
Polyynes Electronic and Vibrational Properties under Environmental Interactions

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GEOMETRY BENCHMARK OF C_NH_2

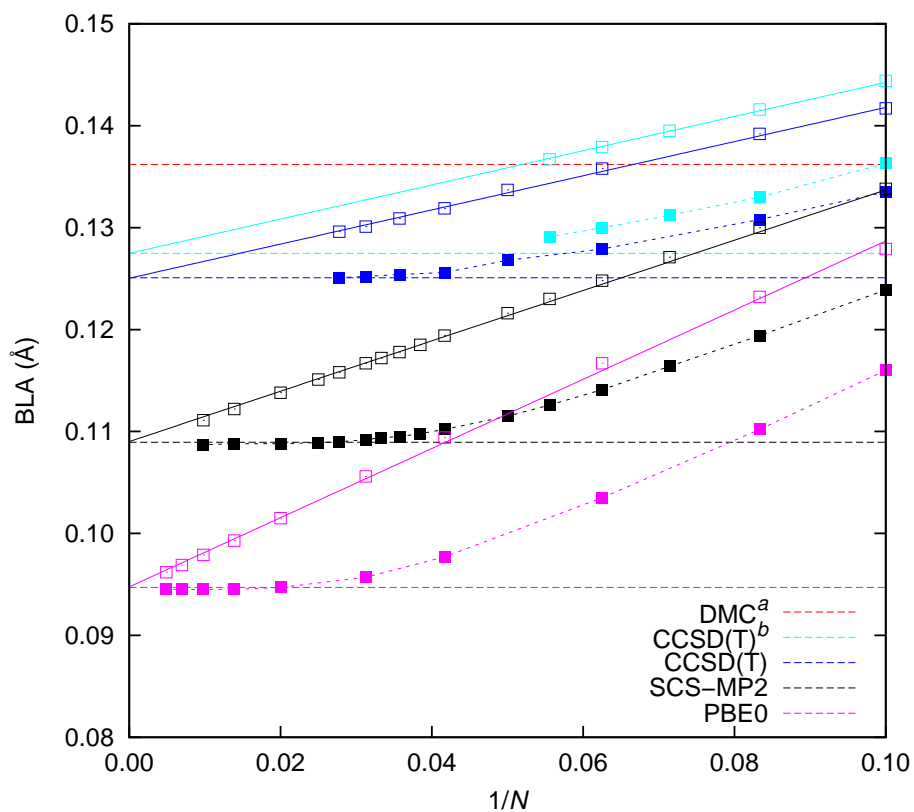


FIG. S1: Bond-length alternation (BLA) as a function of inverse chain length (N is the number of C-atoms). Full symbols show the BLA at the chain center. Empty symbols show the average BLA over the chain (continuous line: linear fit). Horizontal lines mark the BLA of the infinite chain, which is extrapolated from the linear fit in case of CCSD(T). The validity of the linear extrapolation is confirmed by the SCS-MP2 and PBE0 BLA of the converged series (H-termination and circular boundary conditions yield the same value). ^a Coupled-cluster data from Zeinalipour-Yazdi *et al.* [S1]. ^b Diffusion Monte Carlo (DMC) data from Mostaani *et al.* [S2].

TABLE S1: $C_{12}H_2$ RMSD of the energy gradient (atomic units) of the CCSD(T) geometry.

Method	RMSD
CCSD(T)	0.0000
ES-MP2 ^a	0.0028
ES-MP2 ^b	0.0033
SCS-MP2	0.0042
SCS(MI)-MP2	0.0045
B2GP-PLYP	0.0052
mPW2PLYP	0.0053
B3LYP	0.0065
M06	0.0067
PBE0	0.0068
B2PLYP	0.0071
PW6B95	0.0076
BMK	0.0076
TPSS0	0.0078
HISS	0.0119
MP2	0.0136
ω B97XD	0.0143
M062X	0.0146
tHCTh	0.0146
CAM-B3LYP	0.0150
PBE	0.0173
BH&HLYP	0.0188
M11	0.0192
LC-PBE	0.0249
HF	0.0431

^aMP2 with equally-scaled spin components (ES-MP2), optimized scaling parameter of 0.763.

^bES-MP2 with scaling parameter of 0.73.

TABLE S2: Γ -mode frequency (cm^{-1}) and BLA (\AA) of C_8H_2 in vacuo and adsorbed on a graphene sheet.

method	ν_{vacuo}	ν_{sheet}	$\Delta\nu$	$\text{BLA}_{\text{vacuo}}$	$\text{BLA}_{\text{sheet}}$	ΔBLA	D^a	Q_{chain}
SCS-MP2	2209.9	2154.8	-55.1	0.1392	0.1298	-0.0094	3.19	-0.010
PBE-D2	2182.3	2175.9	-6.4	0.1101	0.1094	-0.0007	3.19	-0.020
PBE-D3	2183.8	2180.1	-3.7	0.1099	0.1095	-0.0004	3.37	-0.012

^aAverage separation (\AA) of the chain molecules from the surface.

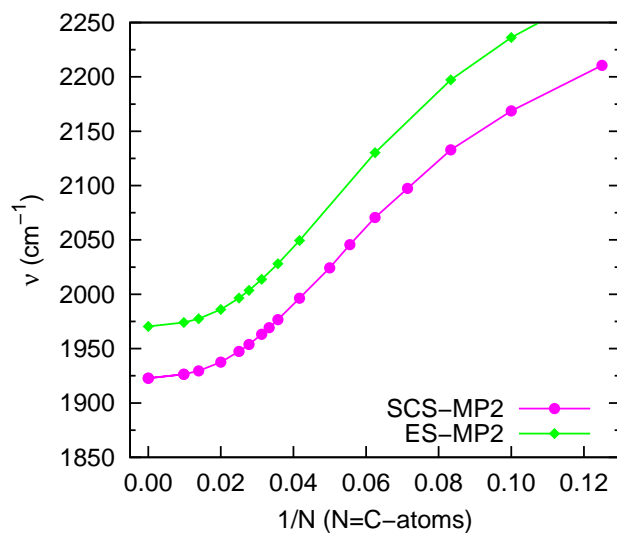


FIG. S2: Γ -mode frequency of C_NH_2 as a function of inverse chain length. Comparison of different MP2 variants.

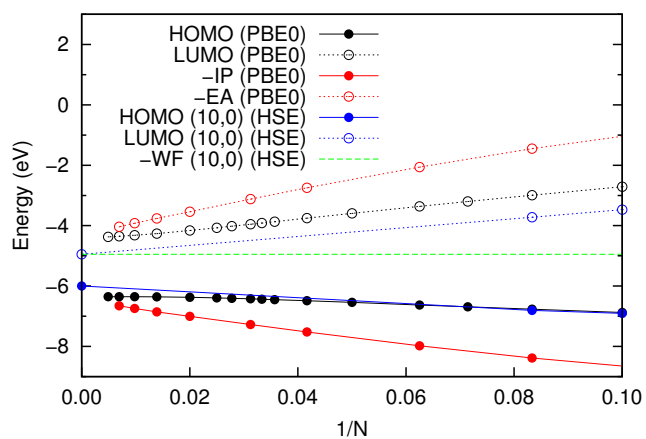


FIG. S3: Comparison of electronic levels, electron affinity (EA), and ionization potential (IP) of C_NH_2 in vacuo and inside SWCNT (HSE calculation) and the work function (WF) of a (10,0) SWCNT (HSE calculation).

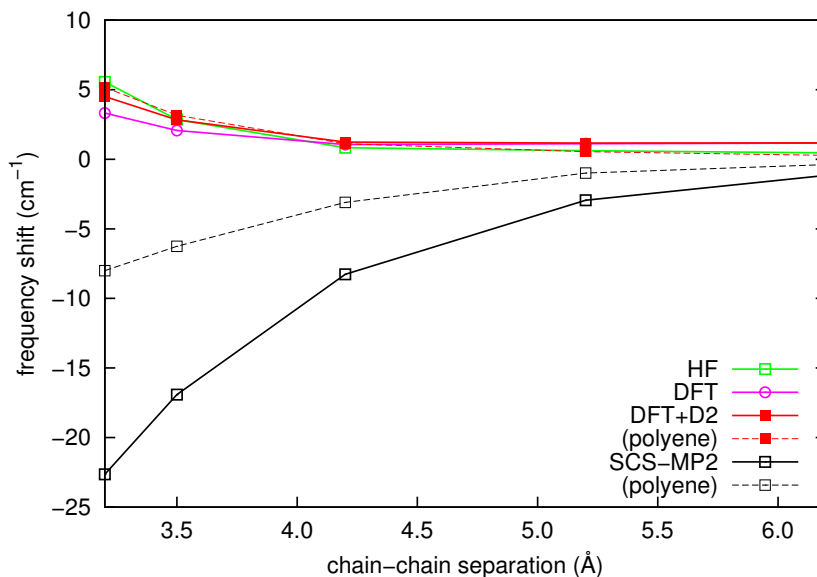


FIG. S4: Frequency shift upon dimerisation of the Γ -mode (symmetric $\text{C}\equiv\text{C}$ stretching mode) of C_8H_2 as a function of the imposed inter-chain separation. The corresponding shift of the $\text{C}=\text{C}$ stretching mode of a polyene dimer (C_8H_{10}) is shown as broken lines. Without explicit treatment of the electron correlation (HF, DFT, DFT-D2) the interaction between the two chains is essentially limited to static polarization and Pauli-exchange repulsion and results in a blue shift. The van der Waals interaction, as described by explicitly correlated methods (here SCS-MP2), overcompensates the other effects and in total leads to a red shift. The effect is visible in both polyenes and polyynes, but is considerably larger in polyynes. The geometry of the two dimers was optimized with atom positions constrained inside two parallel lines (planes in case of polyene) with the current separation. The nature of the van der Waals frequency shift shown here is different from that of vibrations that involve the distance between the weakly interacting objects. Such low-frequency intermolecular vibrations are observed in molecular crystals [S3–S5], ionic liquids [S6], transition metal complexes, and van der Waals heterostructures [S7] and are generally well described by atom pairwise potentials such as the D2 and D3 van der Waals corrections to local density functionals [S8, S9]. We therefore recommend polyyne as a critical test for nonlocal density functionals and self-consistent van der Waals models designed to describe dispersive interactions beyond the pairwise potential approximation.

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