Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Methane storage capabilities of diamond analogues

Maciej Haranczyk,[a*] Li-Chiang Lin,[b] Kyuho Lee,[b,c] Richard L. Martin,[a] Jeffrey B. Neaton,[c] Berend Smit[a,b,d]

[a] *Lawrence Berkeley National Laboratory, One Cyclotron Road, MS 50F-1650, Berkeley, CA 94720-8139, USA*

[b] *Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA*

[c] *Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, MS 50F-1650, Berkeley, CA 94720-8139, USA*

[d] *Department of Chemistry, University of California, Berkeley, CA 94720, USA*

* *mharanczyk@lbl.gov; Fax +1 510 486 5812; Phone +1 510-486-7749*

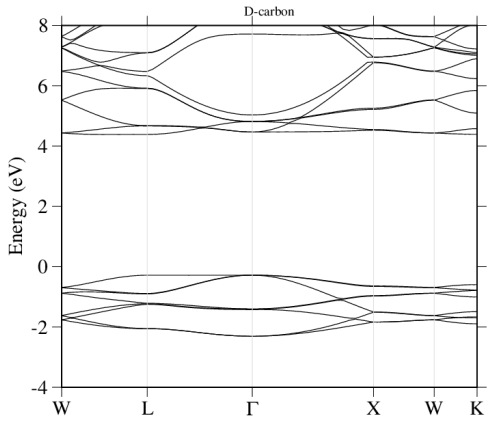
Supporting Materials

1.1 The band structure of diamond analogues

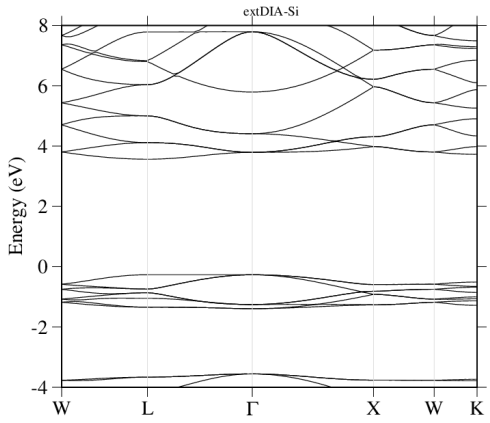
The energy band structure of extDIA, extDIA-Si, extDIA-Ge, extDIA-Si-BN and extDIA-BN was calculated using the fully relaxed structures. We used the VASP code with PBE, 400 eV kinetic energy cutoff and 4×4×4 k-point sampling for self-consistent charge density calculation. Then non-self-consistent band calculations have been done for the band along the high symmetry lines in the first Brillouin zone. Total 105 k-points are sampled for the band plots. The band plots are given in Figure 1S. We found similar energy gaps (~4 eV) across all analogues.

Figure 1S. The electronic band structures of extDIA, extDIA-Si, extDIA-Ge, extDIA-Si-BN, and extDIA-BN.

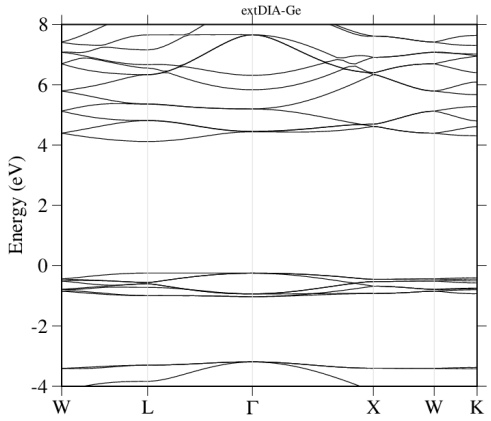
a) extDIA



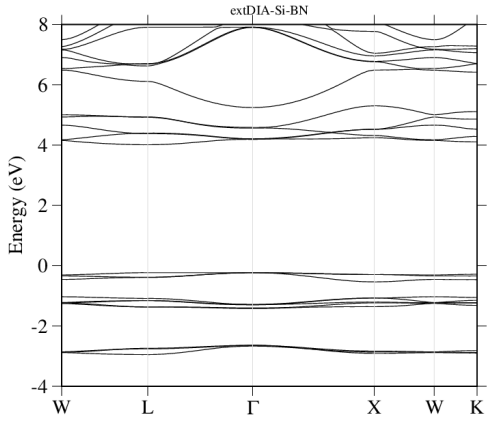
b) extDIA-Si



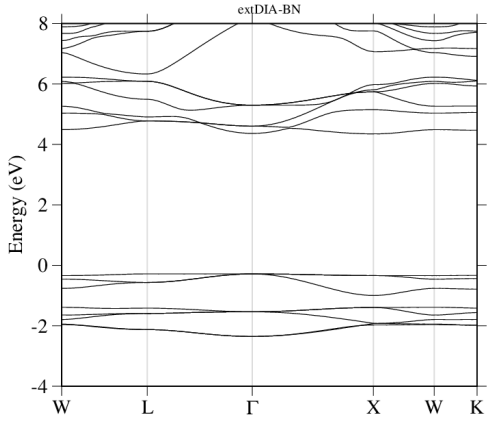
c) extDIA-Ge



d) extDIA-Si-BN



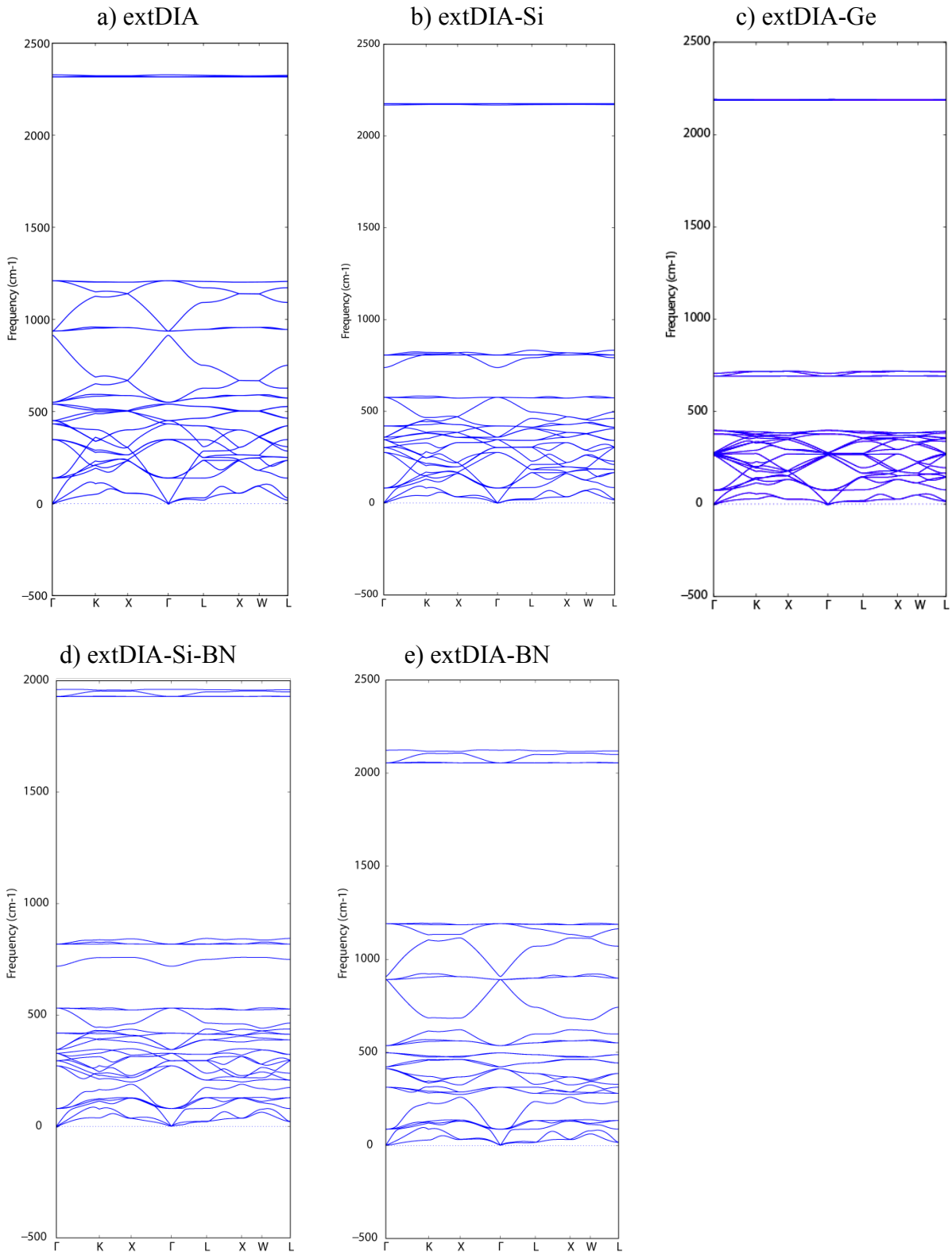
e) extDIA-BN



1.2 Stability of the studied diamond analogues

The stability of extDIA, extDIA-Si, extDIA-Ge, extDIA-Si-BN and extDIA-BN lattice structures was confirmed by calculating zone center gamma phonons, zone boundary phonons. For this step, we used VASP code with PBE, 400 eV kinetic energy cutoff (except extDIA-Si and extDIA-Si-BN in which 520 eV was used). For zone center phonons, a triclinic primitive unit cell with 10 atoms and 4×4×4 k-point sampling were used. For zone boundary phonons, 2×2×2 supercell (80 atoms) of the triclinic primitive unit cell and 2×2×2 k-point sampling were used. We found that both the zone center and the zone boundary phonon frequencies are all real. Three near zero (< 0.2-0.6 cm-1) frequencies, that corresponds to rigid translational modes and should be zero by symmetry, indicates that our calculations are well converged. Therefore we concluded that all the structures are stable. Full phonon band dispersion along the high symmetry lines in the first Brillouin zone are given in Figure 2S.

Figure 2S. The phonon band structures of extDIA, extDIA-Si, extDIA-Ge, extDIA-Si-BN, and extDIA-BN. Imaginary frequencies are plotted along the negative frequency axis.



1.3 Comment on performance of semi-empirical PM6 method

We would like to comment on the performance of the semi-empirical PM6 method which is a significantly less computationally expensive alternative to DFT, and for which attempts have been made to utilize it for investigation of structures of porous materials (*J. Phys. Chem. C*, 2013, 117, 12159–12167). The results of PM6 characterization are collected in Table S-1. In general, for most of the considered structures, the PM6 method tends to predict structures with smaller unit cells, smaller pores and higher density. In the case of extDIA, for which we investigated many density functionals, the comparison suggests that PM6 results are within the range predicted by DFT, and are most similar to results with the LDA and PW92 functionals. In the case of other structures, we observe that differences between parameters calculated with DFT-PBE and PM6 are within 2.5% of each other. A larger difference between DFT-PBE and PM6 is observed for extDIA-Ge, where a much smaller unit cell is predicted with PM6. The unit cell volume reduction by 7% is also reflected in smaller pore diameters (by up to 5.2%) and higher density (7.5%). The only system for which PM6 predicts a larger unit cell (by 2.5%) than DFT-PBE is extDIA-Si-BN. However, both D_i and D_f are ca 0.1 Å smaller in the case of the PM6 structures suggesting slight deformation of the unit cell.

Table S-1. Geometrical parameters describing the unit cells of the extended diamond structures and their void space obtained with the semi-empirical PM6 method: the lattice parameters, the unit cell volume (UCV, in Å^3), helium accessible volume fraction (VF); largest included sphere diameter (D_i, in Å); largest free sphere diameter (D_f, in Å), and the corresponding materials' crystal density (d, in gcm^{-3}). The results obtained with the DFT are also listed to facilitate comparison. The structures were obtained using different DFT exchange-correlation functionals or a semiempirical method as indicated, and the software packages utilized (VASP, Quantum Espresso(QE), Mopac(MPC)) are also indicated after "/" separators.

	a	b	c	α	β	γ	UCV	VF	Di	Df	d
extDIA/PBE/VASP	6.806	6.764	6.819	59.780	59.535	59.931	220.68	0.100	4.42	3.46	0.9038
extDIA/LDA/VASP	6.762	6.703	6.778	59.679	59.354	59.857	215.42	0.094	4.35	3.40	0.9259
extDIA/PW91/VASP	6.802	6.765	6.814	59.810	59.587	59.949	220.62	0.100	4.42	3.46	0.9040
extDIA/PBE/QE	6.806	6.764	6.819	59.780	59.535	59.931	221.06	0.100	4.43	3.48	0.9022
extDIA/LDA/QE	6.776	6.778	6.779	60.074	60.011	60.096	220.51	0.100	4.43	3.47	0.9045
extDIA/PW91/QE	6.789	6.790	6.790	60.079	60.012	60.104	221.68	0.101	4.44	3.48	0.8997
extDIA/PW92/QE	6.712	6.713	6.713	60.074	60.012	60.096	214.16	0.092	4.34	3.41	0.9313

extDIA/PM6 /MPC	6.797	6.712	6.839	59.364	58.979	59.364	216.80	0.095	4.35	3.38	0.9120
extDIA-Si/PBE/QE	7.932	7.944	7.936	59.938	59.946	59.961	353.13	0.226	5.53	4.61	0.7160
extDIA-Si/PM6 /MPC	7.940	7.816	7.991	60.238	59.106	60.982	351.31	0.224	5.51	4.53	0.7197
extDIA-Ge/PBE/QE	8.185	8.152	8.208	59.946	59.597	60.236	386.60	0.255	6.02	4.83	1.0365
extDIA-Ge/PM6/MPC	8.035	7.942	8.080	59.466	58.770	60.037	359.75	0.234	5.76	4.58	1.114
extDIA-Si-BN/PBE/QE[a]	7.996	8.068	8.077	59.418	60.331	60.362	368.69	0.170	5.58	4.07	0.7001
extDIA-Si-BN/PM6/MPC[a]	7.864	8.058	8.202	58.483	62.972	62.437	376.93	0.173	5.46	4.01	0.6848
extDIA-BN/PBE/QE[a]	6.861	6.853	6.859	60.120	59.911	60.062	228.20	0.053	4.31	2.95	0.8972
extDIA-BN/PM6/MPC[a]	6.898	6.778	6.871	60.034	59.356	59.874	225.91	0.051	4.24	2.91	0.9063

[a] highest symmetry isomer