

Supplemental materials for “Benzene adsorbed on Si(001): The Role of Electron Correlation and Finite Temperature”

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A. Detailed Calculation Results

TABLE I: Calculated adsorption energies (in eV) of the BF and TB structures as a function of coverage or cluster size, in comparison with previous PBE and vdW-DF calculations. The coverage of 0.125 ML, 0.25 ML, and 0.5 ML represents the 4×4 , 2×4 , and 2×2 unit cells, respectively.

		BF	TB
PBE [1]	0.25 ML	0.84	0.91
	0.5 ML	0.82	1.05
PBE [2]	0.125 ML	0.96	1.24
	0.25 ML	0.93	1.16
	0.5 ML	0.89	1.16
PBE (This work)	0.125 ML	0.91	1.01
	0.25 ML	0.92	1.01
	0.5 ML	0.85	1.06
	Si ₃₁ H ₂₈	1.09	1.50
PBE0 (This work)	Si ₄₅ H ₃₆	0.91	1.29
	Si ₅₉ H ₄₄	0.95	1.13
	Si ₃₁ H ₂₈	1.42	2.06
	Si ₅₉ H ₄₄	1.31	1.61
MP2 [3]	Si ₃₁ H ₂₈	1.26	1.16
vdW-DF [2]	0.125 ML	0.84	0.82
	0.25 ML	0.82	0.74
	0.5 ML	0.82	0.77
PBE+vdW (This work)	0.125 ML	1.29	1.37
	0.25 ML	1.47	1.54
	0.5 ML	1.46	1.62
	Si ₃₁ H ₂₈	1.67	2.11
	Si ₄₅ H ₃₆	1.62	1.98
	Si ₅₉ H ₄₄	1.70	1.88
PBE0+vdW (This work)	Si ₃₁ H ₂₈	2.05	2.67
	Si ₅₉ H ₄₄	2.15	2.49
EX+cRPA (This work)	Si ₃₁ H ₂₈	1.47	2.41
	Si ₄₅ H ₃₆	1.31	1.88
	Si ₅₉ H ₄₄	1.43	1.65

[1] J.-Y. Lee and J.-H. Cho, Phys. Rev. B **72**, 235317 (2005).

[2] K. Johnston, J. Kleis, B. I. Lundqvist, and R. M. Nieminen, Phys. Rev. B **77**, R121404 (2008).

[3] Y. Jung, and M. S. Gordon, J. Am. Chem. Soc. **127**, 3131 (2005).

TABLE II: Calculated bond lengths (\AA) of adsorbed benzene on Si(001) within the BF and TB structures using the PBE functional. The results obtained using PBE+vdW are also given in parentheses. The top view of each structure is displayed.

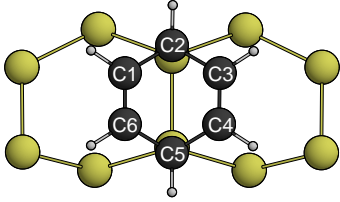
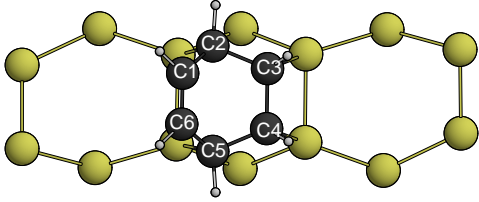
			
		BF	TB
PBE (PBE+vdW)	$d_{C_1-C_2}$	1.501 (1.501)	1.498 (1.498)
	$d_{C_2-C_3}$	1.501 (1.501)	1.572 (1.574)
	$d_{C_3-C_4}$	1.347 (1.347)	1.575 (1.575)
	$d_{C_4-C_5}$	1.500 (1.500)	1.573 (1.574)
	$d_{C_5-C_6}$	1.500 (1.500)	1.499 (1.498)
	$d_{C_6-C_1}$	1.347 (1.347)	1.347 (1.347)
	d_{C_2-Si}	1.969 (1.963)	1.986 (1.988)
	d_{C_5-Si}	1.987 (1.983)	1.998 (1.200)
		d_{C_3-Si}	
	d_{C_4-Si}		2.006 (2.006)

TABLE III: Calculated energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the BF and TB structures. All values are given in eV.

cluster		BF	TB
$Si_{31}H_{28}$	PBE	1.17	2.34
	PBE+vdW	1.10	2.31
	PBE0	2.44	3.85
	PBE0+vdW	2.36	3.83
$Si_{59}H_{44}$	PBE	0.86	1.14
	PBE+vdW	0.78	1.10
	PBE0	2.07	2.37
	PBE0+vdW	1.98	2.32

TABLE IV: Energy decomposition for benzene adsorption on Si(001). *ECMD* denotes the energy cost for molecular deformation, calculated by the energy difference between the isolated benzene molecule (fixed in the optimized structure of the adsorbed benzene/Si(001) system) and the free benzene molecule. *ECSD* denotes the energy cost for surface deformation, calculated by the energy difference between the isolated Si(001) surface (fixed in the optimized structure of the adsorbed benzene/Si(001) system) and the clean Si(001) surface. *EGBF* denotes the energy gain for bond formation between the isolated benzene layer and the isolated Si(001) surface, calculated by the energy difference of the benzene/Si(001) system relative to the isolated benzene layer and the isolated Si(001) surface. The values represent the results for the BF structure, while those in parentheses represent the results for the TB structure. All values are given in eV.

		PBE	PBE+vdW	EX+cRPA
<i>ECMD</i>	Si ₃₁ H ₂₈	-2.26 (-6.13)	-2.25 (-6.15)	-2.29 (-6.14)
	Si ₄₅ H ₃₆	-2.26 (-6.13)	-2.25 (-6.15)	-2.29 (-6.14)
	Si ₅₉ H ₄₄	-2.26 (-6.13)	-2.25 (-6.15)	-2.29 (-6.14)
	0.25 ML	-2.25 (-6.12)	-2.25 (-6.15)	
<i>ECSD</i>	Si ₃₁ H ₂₈	-0.27 (-1.22)	-0.13 (-1.02)	-0.09 (-0.36)
	Si ₄₅ H ₃₆	-0.44 (-1.41)	-0.26 (-1.16)	-0.23 (-0.82)
	Si ₅₉ H ₄₄	-0.42 (-1.60)	-0.20 (-1.32)	-0.13 (-0.86)
	0.25 ML	-0.40 (-1.52)	-0.37 (-1.43)	
<i>EGBF</i>	Si ₃₁ H ₂₈	3.62 (8.85)	4.05 (9.27)	3.85 (8.91)
	Si ₄₅ H ₃₆	3.62 (8.94)	8.94 (9.28)	3.83 (8.84)
	Si ₅₉ H ₄₄	3.63 (8.85)	4.15 (9.35)	3.85 (8.64)
	0.25 ML	3.57 (8.65)	4.09 (9.12)	
<i>E_{ads}</i>	Si ₃₁ H ₂₈	1.09 (1.50)	1.67 (2.11)	1.47 (2.41)
	Si ₄₅ H ₃₆	0.91 (1.29)	1.62 (1.98)	1.31 (1.88)
	Si ₅₉ H ₄₄	0.95 (1.13)	1.70 (1.88)	1.43 (1.65)
	0.25 ML	0.92 (1.01)	1.47 (1.54)	

B. Decomposition of Vibrational Free Energy

In order to calculate the free energy $F = U - TS$, one needs to evaluate the internal energy U and the entropy S . The internal energy U can be written as

$$U = E_{\text{total}} + U_{\text{vib}}, \quad (1)$$

where E_{total} is the static or the total energy. The vibrational contribution to the internal energy is given by

$$U_{\text{vib}} = \sum_i \left[\frac{\hbar\omega_i}{\exp(\frac{\hbar\omega_i}{k_B T}) - 1} + \frac{1}{2}\hbar\omega_i \right], \quad (2)$$

where the energies $\hbar\omega_i$ are the normal vibrational modes. Figure 1 shows the vibrational density of states calculated for the BF and Tb structures. The vibrational entropy energy S can be written as

$$S = k_B \sum_i \left[\frac{\hbar\omega_i/k_B T}{\exp(\frac{\hbar\omega_i}{k_B T}) - 1} - \ln(1 - \exp(\frac{-\hbar\omega_i}{k_B T})) \right]. \quad (3)$$

Thus, the vibrational free energy difference between the BF and TB structures can be evaluated by

$$\Delta F = \Delta E_{\text{total}} + \Delta U_{\text{vib}} - T\Delta S. \quad (4)$$

Figure 2 shows the decomposition of the vibrational free energy contributions to the vibrational energy and entropy.

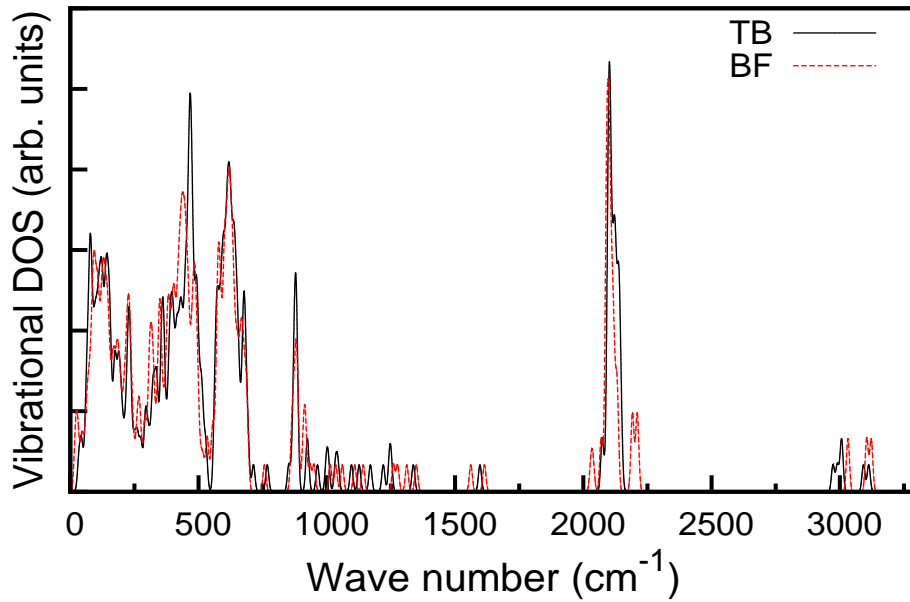


FIG. 1: (color online) Vibrational density of states (DOS) calculated for the BF and TB structures on the $\text{Si}_{59}\text{H}_{44}$ cluster. Both are convoluted with a Gaussian broadening function with 6 cm^{-1} width.

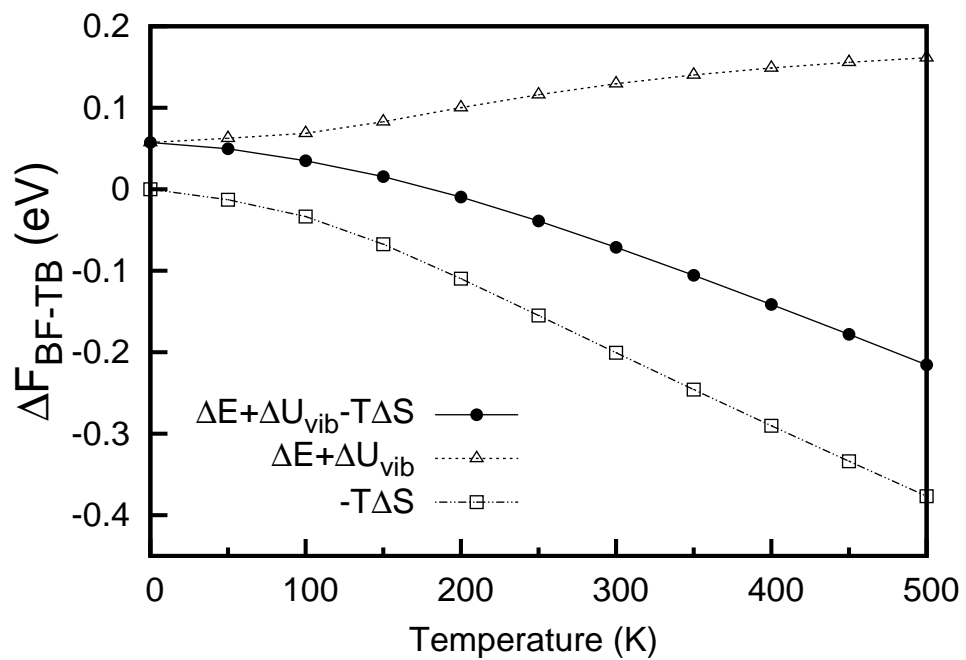


FIG. 2: Calculated free energy difference $\Delta F_{\text{BF-TB}}$ between the BF and TB structures. The components of $\Delta F_{\text{BF-TB}}$ contributed by the vibrational energy and entropy are also plotted.