Supporting Information

Toward Accurate and Efficient Predictions of Entropy and Gibbs Free Energy of Adsorption of High Nitrogen Compounds on Carbonaceous Materials

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This document includes Tables S1-S4, which present low vibrational harmonic and anharmonic frequencies for all calculated high nitrogen compounds (HNCs) carbon systems (Table S1), and for water dimer with available MP2, CCSD(T) and experimental data (Tables S2), the vibrational, rotational, translational and total entropy values calculated using the M06-2X optimized geometry and CCSD(T) and experimental vibrational frequencies for water dimer (Tables S3), and the energy barrier values to correct the rotational entropy term obtained at the M06-2X/6-31+G(d,p) level for all HNC-carbon systems (Table S4). Figures S1 and S2 illustrate the graphs from calculations of the energy barrier values to correct the rotational entropy term obtained at the M06-2X/6-31+G(d,p) level for all HNC-carbon systems. This information is available free of charge via the Internet at http://pubs.acs.org.

Supporting Information

Table S1: Low vibrational frequencies [cm-1] for adsorption of high nitrogen compounds on the modeled carbon surfaces from gas phase (M06-2X/6-31+G(d,p))

System	*Harmonic*	*Anharmonic*[a]
Pyridine_c	13, 29, 72, 80, 84, 93, 108, 151, 166	*13*, 11, 112, 52, 76, 96, 146, 128, 155
Pyrazine_c	38, 39, 39, 84, 91, 92, 107, 114, 164, 168	*38*, 30, 44, 133, 86, 75, 186, *114*, 138, 165
Pyrimidine_c	19, 29, 35, 72, 82, 91, 93, 94, 159, 165	*19*, 7, 26, 119, 94, 91, 80, 168, 181, 150
Pyridazine_c	15, 30, 38, 68, 86, 93, 95, 107, 165, 167	*15*, 26, 38, 29, 13, 83, *95*, 69, 64, 153
1,2,3-triazine_c	33, 37, 39, 79, 86, 93, 98, 102, 166, 167	*33*, 5, *39*, 36, 57, 91, 35, 23, 149, 110
1,2,4-trazine_c	3, 24, 37, 78, 83, 92, 97, 100, 158, 165	*3*, *24,* 49, 37, 62, 108, 176, 181, 198, 150
1,3,5-trazine_c	12, 26, 30, 80, 83, 89, 98, 104, 149, 169	29, *26*, 1, 117, 86, *89*, 147, *104*, 151, 167
1,2,3,4-tetrazine_c	28, 36, 80, 84, 93, 98, 102, 163, 165	16, 40, 35, 72, 91, *98*, 71, 173, 152
1,2,3,5-tetrazine_c	40, 41, 47, 86, 92, 97, 107, 117, 161, 167	29, *42*, *47*, 57, 56, 40, 61, 12, 129, 149
1,2,4,5-tetrazine_c	21, 35, 38, 82, 89, 91, 100, 107, 158, 167	*21*, 17, 19, 49, 58, 56, 98, 37, 140, 153
Pentazine_c	23, 33, 84, 88, 93, 105, 112, 158, 167	12, 21, 59, 56, 90, 75, 102, 153, 148
$(H_2O)_2$	153, 158, 168, 214	*153*, *158*, *168*, 9

[a] The values in itlalic are negative anharmonic frequencies (which are obtained in error during numerical differentiations) replaced by harmonic frequencies in the calculation of entropies.

Table S2: Low vibrational frequencies [cm-1] for water dimer from gas phase

	M06-2X/6-31+G(d,p)		*CCSD(T)/CBS*[b]		*Exp*[c]
System	***Harm***	***Anh***[a]	***Harm***	***Anh***	
$(H_2O)_2$	153, 158, 168, 214, 376	*153, 158, 168*, 9, 125	129,150, 156,188	85,127, 123,148	88, 103, 108, 143

[a] The values in italic are negative anharmonic frequencies (which are obtained in error during numerical differentiations) replaced by harmonic frequencies in the calculations of entropies.

[b] Kalescky, R.; Zou, W.; Kraka, E.; Cremer, D. Local vibrational modes of the water dimer-Comparison of theory and experiment. *Chem. Phys. Lett.* **2012**, *554*, 243–247.

[c] Braly, L. B.; Liu, K.; Brown, M. G.; Keutsch, F. N.; Fellers, R. S.; Saykally, R. J. Terahertz laser spectroscopy of the water dimer intermolecular vibrations. II.(HO). *J. Chem. Phys.* **2000**, *112,* 10314-10326.

[c] Keutsch, F. N.; Braly, L. B.; Brown, M. G.; Harker, H. A.; Petersen, P. B.; Leforestier, C.; Saykally, R. J. Water dimer hydrogen bond stretch, donor torsion overtone, and "in-plane bend" vibrations. *J. Chem. Phys.* **2003**, *119*, 8927-8937.

Table S3: Vibrational ($T*\Delta S_{vib}$), rotational ($T*\Delta S_{rot}$), translational ($T*\Delta S_{trans}$) and total ($T*\Delta S_{ads}$) values [kcal/mol] for water dimer calculated using the M06-2X/6-31G+(d,p)) optimized geometry, CCSD(T) and experimental harmonic and anharmonic frequencies

Method/System	M06-2X		M06-2X//CCSD(T)[a]		M06-2X //Exp[b]	Exp[c]
	Harm	**Anh**	**Harm**	**Anh**		
$T*\Delta S_{vib}$	3.30	5.6	3.60	3.11	4.51	
$T*\Delta S_{rot}$	0.04	0.04	0.04	0.04	0.04	
$T*\Delta S_{trans}$	-9.69	-9.69	-9.70	-9.70	-9.70	
$T*\Delta S_{ads}$	-6.35	-4.05	-6.06	-6.55	-5.15	-5.08-5.43 (353-393 K)

[a] Kalescky, R.; Zou, W.; Kraka, E.; Cremer, D. Local vibrational modes of the water dimer-Comparison of theory and experiment. *Chem. Phys. Lett.* **2012**, *554*, 243–247.

[b] Braly, L. B.; Liu, K.; Brown, M. G.; Keutsch, F. N.; Fellers, R. S.; Saykally, R. J. Terahertz laser spectroscopy of the water dimer intermolecular vibrations. II.(HO). *J. Chem. Phys.* **2000**, *112,* 10314-10326.

[b] Keutsch, F. N.; Braly, L. B.; Brown, M. G.; Harker, H. A.; Petersen, P. B.; Leforestier, C.; Saykally, R. J. Water dimer hydrogen bond stretch, donor torsion overtone, and "in-plane bend" vibrations. *J. Chem. Phys.* **2003**, *119*, 8927-8937.

[c] Curtiss, L. A.; Frutrip, D. J.; Blander, M. Studies of molecular association in H_2O and D_2O vapors by measurement of thermal conductivity. *J. Chem. Phys.* **1979**, *71*, 2703-2712.

Table S4: Energy barrier values [kcal/mol] for adsorption of high nitrogen compounds on the modeled carbon surface from the rotational entropy term calculations using OpenThermo from gas phase (M062X/6-31+G(d,p))

System	Small barrier (kcal/mol)
Pyridine_c	0.5
Pyrazine_c	0.04
Pyrimidine_c	0.5
Pyridazine_c	0.3
1,2,3-triazine_c	0.0001694
1,2,4-trazine_c	0.1
1,3,5-trazine_c	0.6
1,2,3,4-tetrazine_c	0.2
1,2,3,5-tetrazine_c	0.164
1,2,4,5-tetrazine_c	0.2
Pentazine_c	0.8

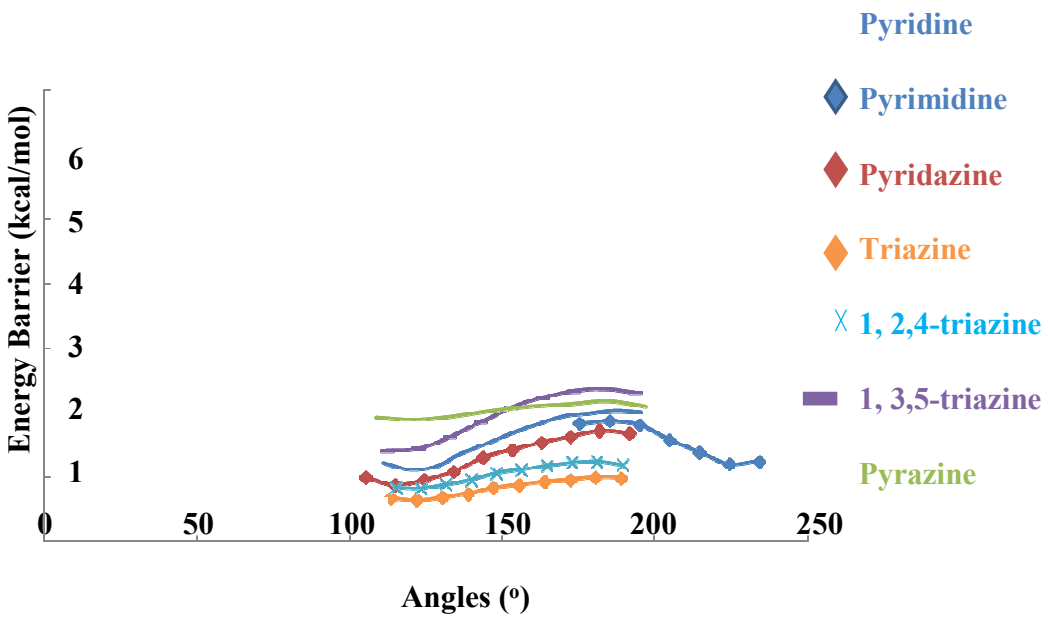
Energy Barrier (kcal/mol)
6
5
4
3
2
1
0
50
100
150
200
250
Angles (º)
Pyridine
Pyrimidine
Pyridazine
Triazine
1, 2,4-triazine
1, 3,5-triazine
Pyrazine

Figure S1.

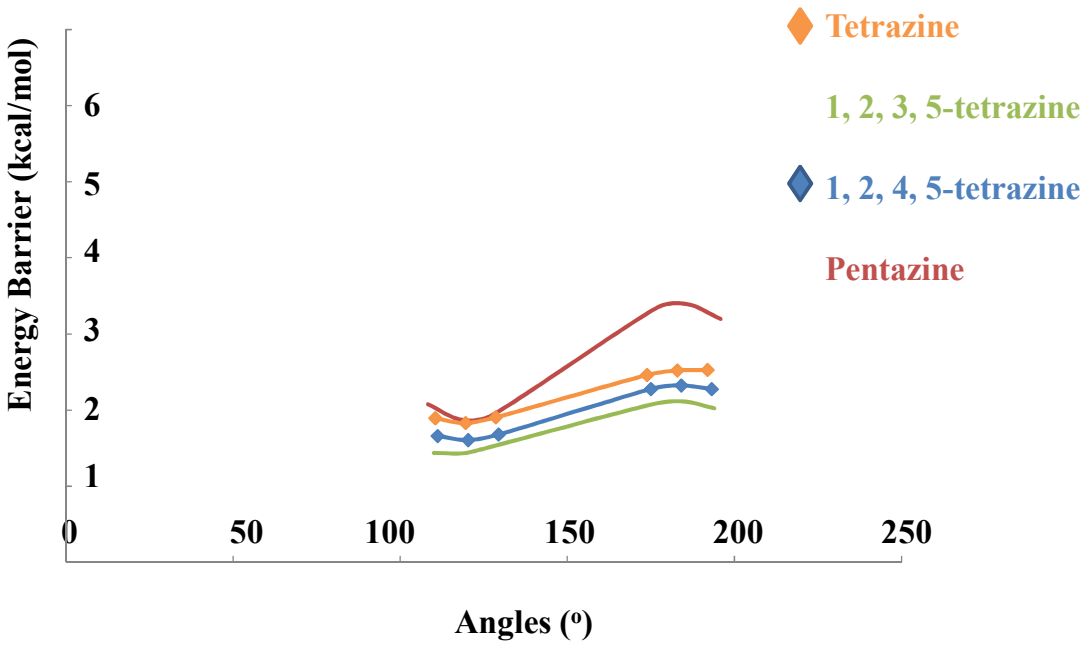
Energy Barrier (kcal/mol)
6
5
4
3
2
1
0
50
100
150
200
250
Angles (º)
Tetrazine
1, 2, 3, 5-tetrazine
1, 2, 4, 5-tetrazine
Pentazine

Figure S2.