Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Computational Prediction of High Methane Storage Capacity in V-MOF-74

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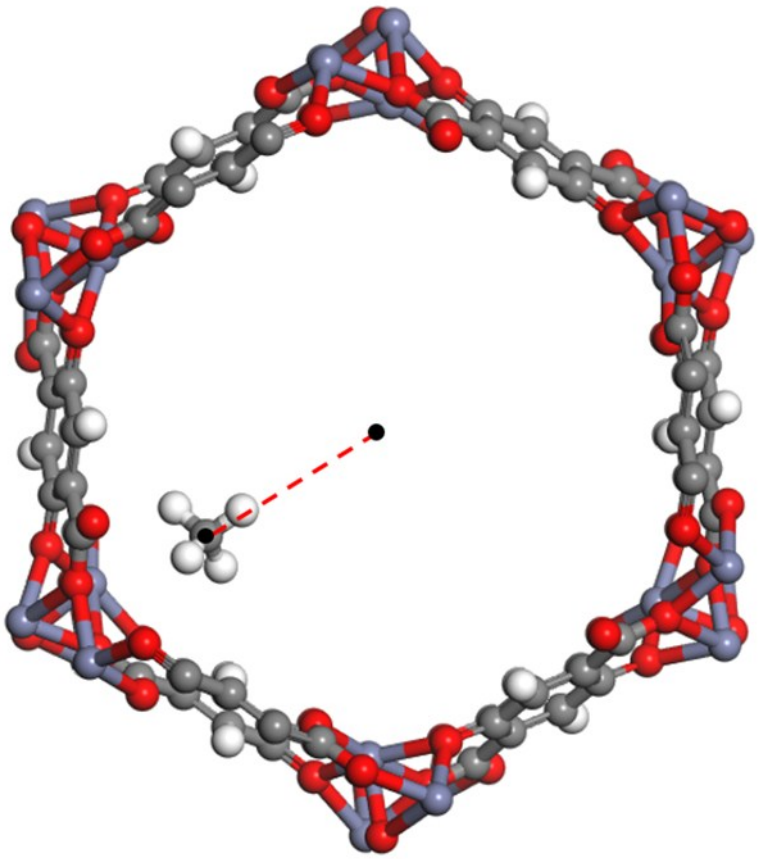

Figure S1. The figure represents the path of the sampled methane molecules along the dashed red line.

Table S1. Force Field Parameters for Each of Three Materials (vdW-DF, vdW-DF2, PBE+D2) for Co-MOF-74.

Functional	Atom type	ϵ (K)	σ (Å)
vdW-DF	Co	5064.13880	2.72
	C	54.02741	3.40
	O	31.09691	3.12
vdW-DF2	Co	2940.01624	2.24
	C	57.92403	3.32
	O	35.70363	2.98
PBE+D2	Co	8603.92784	1.74
	C	58.84683	3.12
	O	40.39893	2.60

Table S2. Force Field Parameters for Each of Three Materials (vdW-DF, vdW-DF2, PBE+D2) for Mg-MOF-74.

Functional	Atom type	ϵ (K)	σ (Å)
vdW-DF	Mg	5963.87	2.50
	C	54.03	3.40
	O	37.83	2.50
vdW-DF2	Mg	4028.53	2.06
	C	58.95	3.24
	O	38.68	2.82
PBE+D2	Mg	16633.65	1.52
	C	57.71	2.92
	O	34.94	2.16

Table S3. Force Field Parameters for Each of Three Materials (vdW-DF, vdW-DF2, PBE+D2) for Ni-MOF-74.

Functional	Atom type	ϵ (K)	σ (Å)
vdW-DF	Ni	5714.75	2.64
	C	54.00	3.40
	O	32.31	3.10
vdW-DF2	Ni	4331.56	2.10
	C	57.83	3.30
	O	35.85	2.90
PBE+D2	Ni	11149.26	1.70
	C	61.75	3.06
	O	37.83	3.08

Table S4. Calculated Binding Energies Using Various Exchange Correlation Functionals of the Methane in the Ni-MOF-74.

Functional	Binding Energy (kJ/mol)
optB86b-vdW	-29.74
optB88-vdW	-28.61
optPBE-vdW	-31.54
PBE	-3.95
PBE+D2	-24.77
PBEsol	-7.62
vdW-DF	-26.03
vdW-DF2	-25.03

Table S5. Derived Force Field Parameters for 9 M-MOF-74 (M= Co, Cr, Cu, Mg, Mn, Ni, Ti, V, and Zn) from s_6 = 0.45 tuned PBE+D2 functional

Structure	Atom type	ϵ (K)	σ (Å)
Co-MOF-74	Co	408.51	1.72
	C	65.39	3.10
	O	45.39	2.50
Cr-MOF-74	Cr	191.49	1.90
	C	54.86	3.40
	O	38.41	2.66
Cu-MOF-74	Cu	582.56	1.94
	C	72.32	3.00
	O	94.39	1.78
Mg-MOF-74	Mg	1660.93	1.52
	C	65.58	2.96
	O	42.00	2.26
Mn-MOF-74	Mn	597.93	1.74
	C	65.65	3.12
	O	46.77	2.44
Ni-MOF-74	Ni	835.67	1.70
	C	65.69	3.06
	O	46.10	2.44

Ti-MOF-74	Ti	3947.88	1.56
	C	59.65	3.16
	O	39.06	2.44
V-MOF-74	V	7190.74	1.44
	C	35.33	2.40
	O	35.33	2.40
Zn-MOF-74	Zn	956.27	1.68
	C	69.18	2.74
	O	49.08	2.40

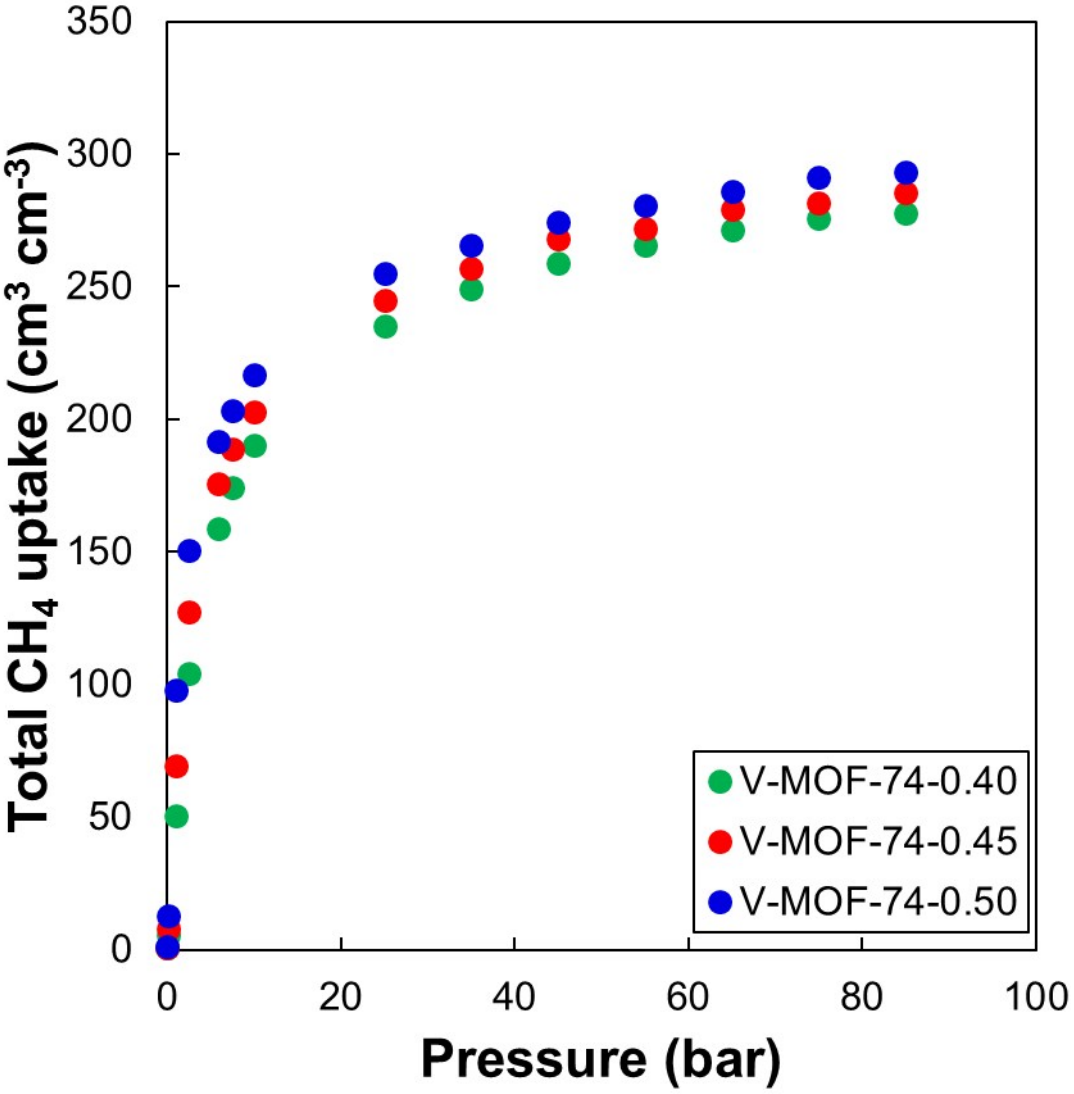

Figure S2. Predicted methane adsorption isotherm curves in V-MOF-74 with different force field parameters derived from various s6 parameters, 0.40 (green), 0.45 (red), and 0.50 (blue) at T = 298K.

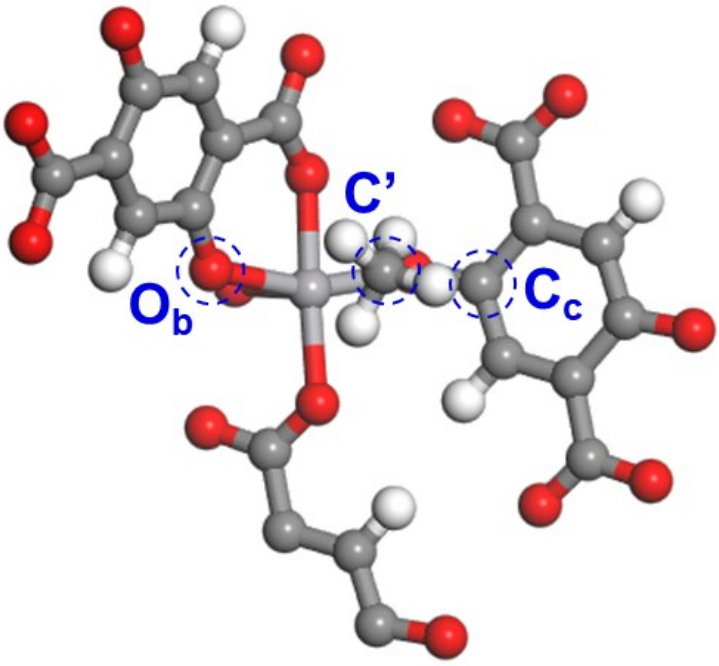

Figure S3. DFT optimized configuration of a single methane adsorbed inside V-MOF-74. The figure represents atoms as balls and sticks (gray, red, white, and silver for carbon, oxygen, hydrogen, and vanadium respectively).

Table S6. Comparison of Binding Geometries Calculated from DFT, and DFT-Derived Force Field.

Source	Distance (Å)		
	C'-V	C'-C_c	C'-O_b
DFT	2.88	3.57	3.47
DFT-derived force field	2.94	3.55	3.54

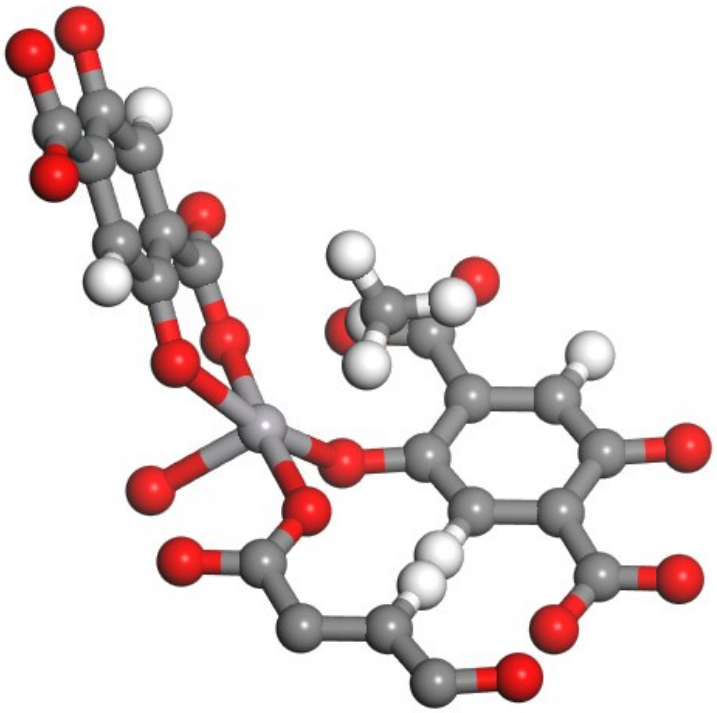

Figure S4. DFT optimized binding geometry for single CH_4 molecule in V-MOF-74.

Table S7. Comparison of Bond Length and Bend Angle for Adsorbed CH_4 with Free CH_4.

	Optimized	Reference value
C-H (Å)	1.097-1.103	1.087
H-C-H (°)	107.508-110.595	109.5

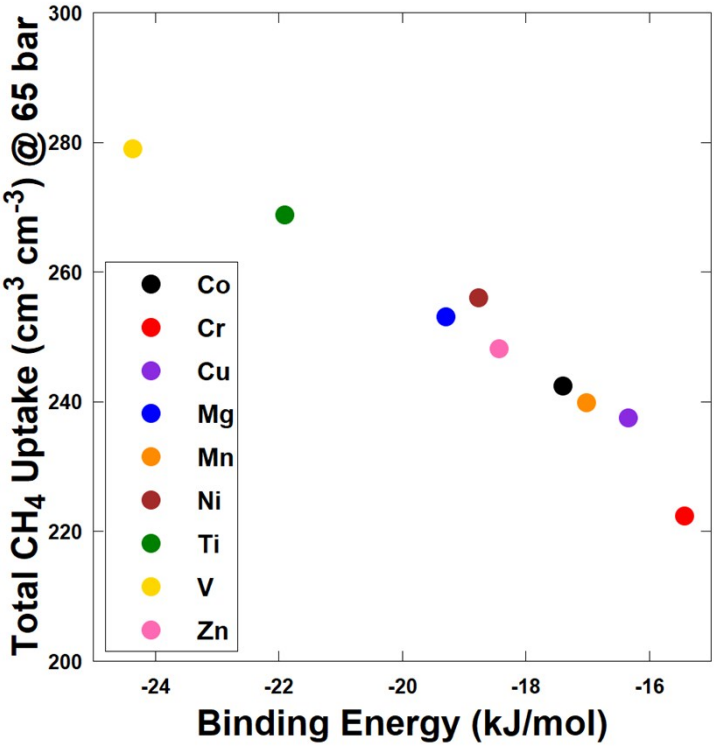

Figure S5. DFT (s_6 = 0.45) binding energy and total CH_4 uptake at 65 bar and 298 K.