THE JOURNAL OF PHYSICAL CHEMISTRY Letters

LETTER

pubs.acs.org/JPCL

An Inexpensive, Widely Available Material for 4 wt % Reversible Hydrogen Storage Near Room Temperature

Tod A. Pascal,[†,‡] Christopher Boxe,[§] and William A Goddard, III[*,†,‡]

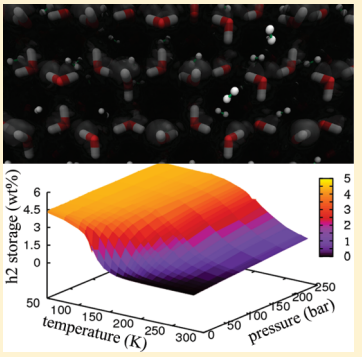
[†]Material and Process Simulation Center, California Institute of Technology, Pasadena, California 911205, United States

[‡]Graduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology, Daejeon, Korea

[§]Earth and Planetary Science Division, NASA Jet Propulsion Laboratories, Pasadena, California 91109, United States

Supporting Information

ABSTRACT: The search for cheap, renewable energy sources to replace fossil fuels has identified hydrogen gas (H_2) as the most promising, particularly for transportation. However, despite intense research efforts to find reliable storage materials, current practical technologies store only 1.3 wt % H_2 at 270 K, far short of the U.S. DOE targets. We report that hexagonal ice, the ordinary form of ice in snow, may be an efficient hydrogen storage material, achieving 3.8 wt % H_2 storage and 42 g L^{-1} at 150K and that after loading at 150 K, the 3.8 wt % H_2 can be kept at 270 K and then released upon heating by a few degrees Kelvin. This leads us to propose the ice-fixed melt-triggered (IFMT) strategy for hydrogen storage and utilization with ice as the median.



SECTION: Energy Conversion and Storage

Hydrogen has been identified as a most promising fuel for meeting our future energy needs; however, there are difficulties in storage and retrieving the hydrogen once stored.[2] Metal-based and chemical storage systems are capable of storing sufficient H_2 to meet the US DOE goals for transportation;[3] however, they involve H−H bond breaking and formation processes that lead to rates that are far too slow for modern applications. Systems based on physisorption of the H_2 molecules have sufficient rates, but the adsorption energies are low, so that the best-performing such material, MOF-177, stores only 1.3% wt H_2 at 270 K.[4]

Hexagonal ice (ice Ih) is the natural form of ice in snow and the upper atmosphere, and is the thermodynamically favored ice phase from 180 to 273 K and 0 to 1 GPa (10 000 bar ≈ 10 000 atm). It has an unusually low packing fraction (0.43) and density (0.92 g/mL). The internal pore diameter is small (≈ 0.23 nm) but we find that it can accommodate dihydrogen (H_2) molecule. Indeed using quasielastic neutron scattering experiments, Strauss et al.[5] showed that H_2 has a remarkably high diffusion constant in hexagonal D_2O at low temperatures (60 K), $D = 9.5 \times 10^{-5}$ cm^2/s, comparable to the diffusion constant of H_2 in liquid hydrogen ($D = 14 \times 10^{-5}$ cm^2/s at 25 K). Some reports indicate that little dihydrogen dissolves in ice near freezing at low pressures (100 bar),[6,7] but it is known that H_2 is 25% more soluble in ice than water.[8]

There is some evidence that hydrogen can form stable solutions with ice-like motifs at ambient pressures.[9] Thus Mao and Mao[10] found 5.3 wt % storage in hydrogen clathrate hydrate at 77 K and 2 kbar while Lee and co-workers[11] reported ∼4 wt % hydrogen storage in THF-containing binary-clathrate hydrates at freezing temperature and around 120 bar. Additionally, Dyadin and co-workers[12] showed that significant amounts of H_2 and at least 10 wt % He dissolve in ice Ih (D_2O) at 2−3 kbar, increasing the melting temperature by at least 10 K relative to perfect ice crystals. Also Londono and co-workers[13] showed experimentally that helium dissolves in ice II at 2.8 kbar to form stable He_x-$(D_2O)_6$ structures.

In this letter, we report the hydrogen storage capability of ice Ih using first-principles-based computer simulations (with interaction potentials based on accurate quantum mechanics). In order to accurately describe the interactions of H_2 with H_2O for large scale molecular dynamics (MD) and Monte Carlo (MC) simulations, we developed a classical force field (FF) fitted to potential energy surfaces of H_2−H_2O[14] and the H_2 dimer[15] derived from accurate quantum mechanics (QM) calculations, in conjunction with the empirical TIP4P/ice water potential[1] (Table 1 and Figure S1 (Supporting Information)). This approximation of rigid H_2 and rigid porous framework is validated by the good agreement with experiment for H_2/MOF and H_2/COF systems (see ref 21) and by the good agreement with

- the experimental H_2 dimer equation of state (EOS)[16] from 100 −270 K and 0−250 bar (Figure S2),
- the self-diffusion constant of H_2 in ice Ih at 60 K[5] (Figure S3), and
- the shift in melting temperature of hydrogen loaded ice Ih under pressure[12] (Table S2),

Received: April 4, 2011
Accepted: May 24, 2011
Published: May 24, 2011

Table 1. Short-Range van der Waals (vdW) and Hydrogen-Bonding (HB) Interaction Parameters for H_2-H_2O Used in This Study[a]

Interaction pair		vdW				Dreiding H-bond[a]		
		Type[b]	De (kcal/mol)	Re (Å)	ξ	De (kcal/mol)	Re (Å)	p
Ow	Ow	LJ12−6	0.2110	3.5546	n/a	n/a		
Ow	H_	Exp-6	0.1349	3.1932	11.44	n/a		
Hw	H_	Exp-6	0.0011	3.4061	14.88	n/a		
H_	H_	Exp-6	0.0209	3.1596	11.44	n/a		
Hm[c]	Ow[d]	n/a				0.0174	3.5827	1

[a] $E_{hbond} = D_e\{5\rho^{-12} - 6\rho^{-10}\}\cos^p(\theta)$, $\rho = (R_e)/(R)$ [b] $E_{vdw}^{LJ12-6} = D_e\{\rho^{-12} - 2\rho^{-6}\}$, $E_{vdw}^{Exp-6} = (D_e)/((\xi-6))\{6e^{\xi(1-\rho)} - \xi\rho^{-6}\}$ [c] donor [d] acceptor
[a] The H_2-H_2O and H_2-H_2 interactions are obtained from fitting the ab initio potential energy surfaces obtained at the CC or MP2 level needed to accurate predict London dispersion (vdW attraction). The water molecules are modeled using the rigid TIP4P-ice[1] FF. The atom types are: Ow (oxygen on water), Hw (hydrogen on water), H_ (hydrogen on H_2), Hm (pseudo-atom at the H_2 bond midpoint). Interactions not shown are zero. Our model includes Coulombic interactions based on the following fixed point charges (in electron units): Ow (−1.1794 displaced from atom center by 0.1577 Å), Hw (+0.5897), H_ (+0.36535) and Hm (−0.7307).

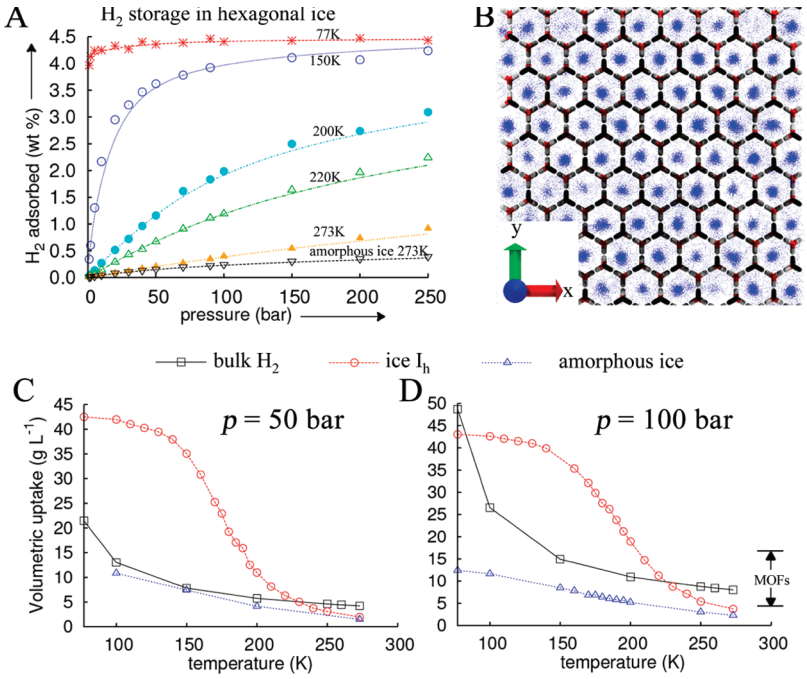


Figure 1. (A) Average loading of H_2 molecules in ice Ih predicted from GCMC simulations from 1 to 250 bar at 77 K (red stars), 150 K (blue circles), 200 K (cyan filled circles), 220 K (green upward triangles), 273 K (orange upward triangles) compared to amorphous ice at 273 K (black downward triangles). (B) Two dimensional plot of the H_2 density profile in the ice Ih channels at 150 K and 100 bar projected along the z axis. The H_2 molecules are at the center of the hexagonal channel with ∼1 molecule per fundamental unit cell (12 water molecules). (C) Volumetric loading curve at 40 bar for H_2 in ice Ih (red circles), amorphous ice (blue triangles) compared to an open tank (black squares). (D) Volumetric 100 bar loading curve for H_2. The range of values for MOFs at 300 K is shown as a reference.

suggesting that our FF and simulation methodology is accurate.

Using this QM derived FF, we used grand canonical Monte Carlo (GCMC) simulations[17,18] to predict the loading of H_2 in ice Ih crystal.[19,20] We showed previously that this GCMC methodology successfully predicts the hydrogen uptake in metal organic frameworks (MOFs) in excellent agreement with experiment.[21]

Figure 1a shows the gravimetric hydrogen uptake percent of ice Ih from 77 to 273 K and 1 to 250 bar. We find 3.96 wt % at 77 K and 1 bar, which is 75% larger than MOF-200 (using similar calculations) and twice that measured and calculated for MOF-177. Among the plethora of ice structures available in nature, ice Ih seems to be best suited for hydrogen storage since it has the lowest density and largest pore size. Indeed the GCMC density profiles (Figure 1b and Figures S4 and S5) show that most H_2 molecules occupy interstitial sites, preferentially located in the center of the hexagonal channels. In contrast, we find that amorphous ice stores only 1/4 as much H_2 at 77 K and 1 bar. The 77 K isotherm for ice Ih saturates to 4.4 wt % at 40 bar, which can be compared to 7.5 wt % and 70 bar for MOF-177 and 8.7 wt % and 60 bar for MOF-200. The relatively fast saturation of ice Ih is due to the small pore sizes; at saturation, where three H_2 molecules are stored in each fundamental unit cell (12 molecules), occupying 55% of the available volume.

dx.doi.org/10.1021/jz200453u |J. Phys. Chem. Lett. 2011, 2, 1417–1420

We calculate the H_2−ice Ih binding energy to be 12.8 ± 0.02 kJ/mol at 77K and 40 bar, significantly larger than the 3−4 kJ/mol of materials relying on physisorption with weak vdW interactions.[22] The quadrupole (H_2)−dipole (H_2O) interaction helps stabilize the H_2−ice structures, accounting for all of the binding, with the vdW forces always repulsive to act as a counter-balance to the favorable electrostatic forces. This calculated binding energy is about half the value 22−25 kJ/mol suggested for optimal storage near room temperature,[23] which explains the reduction in the storage capacity at 100 bar and 150 K (4.1 wt %), 175 K (3.1 wt %), 200 K (1.98%). At the ice melting temperature of 270 K and 100 bar, we calculate 0.4 wt % H_2 uptake by ice Ih, 3 times the capacity of carbon nanotubes and porous carbon materials, but comparable to the 1.0 wt % for MOF-177 and 1.25% for MOF-200.[21]

Figure 1c shows the volumetric uptake (density) of H_2 stored in ice Ih, amorphous ice, and in a hydrogen tank. At a constant pressure of 50 bar and 77K, we find that ice Ih stores twice the amount of hydrogen as the hydrogen tank, while at 100 K ice stores 3 times as much and at 150 K, 4 times as much. Beyond 150 K, the relative storage capacity of H_2 in ice Ih is significantly reduced as the thermal energy of the system overcomes the H_2−H_2O binding energy. Of note is that below 150 K and every pressure considered here, ice Ih stores 3−5 times more H_2 than amorphous ice, illustrating the uniqueness of the hexagonal channels for H_2 storage.

To investigate the process of loading, we carried out MD simulations of a 1 nm thick ice Ih slab (0.35 × 0.38 nm^2 surface area) exposed to H_2 gas (Figure 2a). Here ice Ih was loaded with H_2 obtained from GCMC calculations at 100 bar and 150 K, using an outside gas pressure of 150 bar. This system achieved thermal and mass balance after 23 ns, storing 3.98 wt % H_2 (which leads to an internal gas pressure of 130 ± 25 bar). The 3.98 wt % at 100 bar and 150 K from our MD simulations agrees with the 4.07 wt % we calculate using GCMC. Under these conditions, we observe a sustained exchange rate of 2 H_2 molecules/ns in and out of the ice surface (Figure 2b), which decreases to 1.7 molecules/ns after 62 ns due to distortion of the surface layers obstructing exit from the hexagonal channels. This surface disorder extends two layers into the crystal (Figure 2d). Similar simulations at 100 K and 40 bar (the saturation pressure) show little distortion of the ice Ih surface on the same time scale, most likely due to the lower energy of the H_2 molecules. Since the surface atoms of ice Ih have 1 fewer hydrogen bonds than the bulk, they would "melt" at a lower temperature, leading to a "Tammann temperature" for ice Ih of 180 to 200 K.[24−26] The disordered layer we observe in the MD at 150 K likely results from collisions with the high pressure (150 bar) external gas, but it may also reflect a limitation of the TIP4P-ice water model, which was not parametrized to describe free surfaces. Thus, the lack of polarization in this model may destabilize the surface layer, leading to a decreased Tammann temperature. This MD treats the vibrational energy states of water and H_2 as classical, whereas they should be in the lowest quantized vibrational level. We expect this to lead to negligible error in the loading curves.

To investigate the effect of a disordered surface layer on the H_2 storage ability of ice Ih, we equilibrated the 4.07 wt % GCMC structure, capped with a 0.5 nm thick amorphous ice layer. We

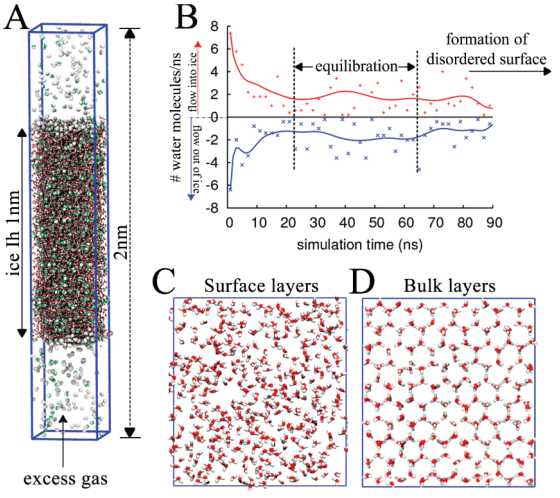


Figure 2. (A) Schematic of simulation cell used for MD simulations of the loading process. A 1 nm deep ice Ih slab is first loaded with H_2 at 100 bar and 150 K using our GCMC procedure. It is then immersed in a pre-equilibrated box of H_2 molecules at 150 bar, removing any overlapping H_2 molecules. (B) The flow rate of H_2 molecules into the ice structure (red crosses) and out of the ice (blue stars) as a function of time. The solid lines are best fits based on the cubic Bezier function approximations. There is a net flow of H_2 molecules into the ice until 23 ns when the system reaches thermodynamic equilibrium. After 62 ns, the surface layers start becoming disordered due to molecular vibrations and collisions with the outside H_2 molecules. (C) Snapshot of the ice surface after 90 ns of simulation, showing the formation of an amorphous layer ~0.8 nm thick. (D) Comparative snapshot of the middle ice layer, showing that the integrity of the hexagonal framework is maintained.

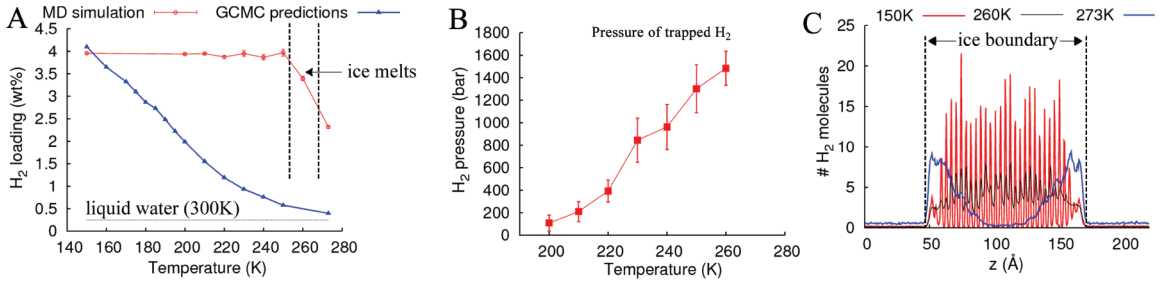


Figure 3. (A) Comparison of H_2 uptake as a function of temperature. The initial MD system consists of the GCMC optimized structure at 150 K and 100 bar (4.07 wt % H_2) with a 0.2 nm amorphous ice layer capping each end surrounded by a vacuum. The structure is stable up to 265−270 K, when the ice melts abruptly. (B) The pressure that the trapped H_2 gas exerts on the ice framework. Before melting, the H_2 exerts 1562 bar of pressure on the ice. (C) Average H_2 density along the direction normal to the capped ice surface at 150 K (red line), 260 K (black line), and 273 K (blue line). The ice extends from 5 to 15 nm on the *x* axis. The H_2 did not completely diffuse out of the water slab on the 50 ns time scale of our simulations; however, the shape and nonuniformity of the distribution indicates a gradual process of segregation.

dx.doi.org/10.1021/jz200453u |*J. Phys. Chem. Lett.* 2011, 2, 1417–1420

find the capped nanocube is stable on our entire simulation time scale (90 ns) at 150 K, with no exchange of H_2 out of the ice. Indeed, the system is thermodynamically stable up to 265 K (Figure 3a), even though the internal H_2 pressure rises to 1582 ± 204 bar by 265 K (Figure 3b). Between 265 and 270 K, the ice melts, causing 93.9% of the stored H_2 to evolve from the ice (because of the low solubility of H_2 in liquid water).

These results lead us to propose the ice-fixed melt-triggered (IFMT) strategy for hydrogen storage and utilization with ice as the median:

- load the H_2 at 100 K and 40 bar in crystalline ice Ih,
- seal the surfaces at 150 K and 250 bar external H_2 pressure,
- store between 150 and 265 K in low pressure gas until needed, and
- trigger evolution of the stored H_2 by changing the temperature slightly to just above melting, releasing 94% of the stored H_2.

On the time scale of our simulations, our results indicate that neglecting any contributions due to the small capping layer, this process would lead to 4.07 × 0.94 = 3.8 wt % usable H_2 storage and 42 g L^{-1} at 265 K, within range of the US DOE 2010 requirements for transportation: 6.0 wt % and 45 g L−1 at 243−358 K.[3] Of course there are many practical problems of forming high surface area crystals of ice quickly, sealing the surface, and then storing the system after loading the H_2, maybe in dry ice. However the enormous advantages of extremely low cost and wide availability of the storage material and the greenness in producing, using and disposing of the storage provides significant advantages that make the IFMT strategy worthy of additional study. Moreover, the IFMT mechanism presents a new paradigm for hydrogen storage that might produce even more efficient hydrogen storage materials.

■ ASSOCIATED CONTENT

Supporting Information. Computational methods, Table S1, Figures S1−S5 and references. This material is available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENT

The authors thank Jose Mendoza (Caltech) and Sang Soo Han (KRISS, Korea) for providing data on H_2 storage in MOFs prior to-publication. This project was partially supported by grants to Caltech from the Department of Energy (DE-PS36-08GO 98004P). It was also supported by the WCU program (31-2008-000-10055-0) through the National Research Foundation of Korea with the generous allocation of computing time from the KISTI supercomputing center. T.A.P. thanks the U.S. Department of Energy CSGF and the National Science Foundation for graduate fellowships.

■ REFERENCES

(1) Abascal, J.; Sanz, E.; Fernandez, R.; Vega, C. A Potential Model for the Study of Ices and Amorphous Water: Tip4p/Ice. *J. Chem. Phys.* **2005**, *122*, 234511.

(2) Schlapbach, L.; Zuttel, A. Hydrogen-Storage Materials for Mobile Applications. *Nature* **2001**, *414*, 353–358.

(3) Satyapal, S.; Petrovic, J.; Read, C.; Thomas, G.; Ordaz, G. The U.S. Department of Energy's National Hydrogen Storage Project: Progress Towards Meeting Hydrogen-Powered Vehicle Requirements. *Catal. Today* **2007**, *120*, 246–256.

(4) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. Exceptional H_2 Saturation Uptake in Microporous Metal−Organic Frameworks. *J. Am. Chem. Soc.* **2006**, *128*, 3494–3495.

(5) Strauss, H. L.; Chen, Z.; Loong, C. K. The Diffusion of H_2 in Hexagonal Ice at Low Temperatures. *J. Chem. Phys.* **1994**, *101*, 7177–7180.

(6) van der Waals, J. H.; Platteeuw, J. C. *Clathrate Solutions*; John Wiley & Sons, Inc.: New York, 1959.

(7) Franks, F. *Water. A Comprehensive Treatise. 2. Water in Crystalline Hydrates, Aqueous Solutions of Simple Nonelectrolytes*; Plenum Press: New-York/London, 1973.

(8) Landolt, B.; Schäfer, K.; Lax, E. *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. Band 2, Teil 2, Bandteil B, Eigenschaften der Materie in Ihren Aggregatzuständen. Gleichgewichte Ausser Schmelzgleichgewichten. Lösungsgleichgewichte I*; Springer: Berlin, 1962.

(9) Mao, W. L.; Mao, H. K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q. Z.; Hu, J. Z.; Shu, J. F.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. S. Hydrogen Clusters in Clathrate Hydrate. *Science* **2002**, *297*, 2247–2249.

(10) Mao, W. L.; Mao, H. K. Hydrogen Storage in Molecular Compounds. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 708–710.

(11) Lee, H.; Lee, J.-w.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. Tuning Clathrate Hydrates for Hydrogen Storage. *Nature* **2005**, *434*, 743–746.

(12) Dyadin, Y. A.; Aladko, E. Y.; Udachin, K. A.; Tkacz, M. The Solubility of Helium and Hydrogen in Ice Ih at High-Pressures. *Polym. J. Chem.* **1994**, *68*, 343–348.

(13) Londono, D.; Kuhs, W. F.; Finney, J. L. Enclathration of Helium in Ice-Ii - The 1st Helium Hydrate. *Nature* **1988**, *332*, 141–142.

(14) Phillips, T. R.; Maluendes, S.; Mclean, A. D.; Green, S. Anisotropic Rigid Rotor Potential-Energy Function for H_2O-H_2. *J. Chem. Phys.* **1994**, *101*, 5824–5830.

(15) Patkowski, K.; Cencek, W.; Jankowski, P.; Szalewicz, K.; Mehl, J. B.; Garberoglio, G.; Harvey, A. H. Potential Energy Surface for Interactions between Two Hydrogen Molecules. *J. Chem. Phys.* **2008**, *129*, 094304.

(16) Leachman, J. W.; Jacobsen, R. T.; Penoncello, S. G.; Lemmon, E. W. Fundamental Equations of State for Parahydrogen, Normal Hydrogen, and Orthohydrogen. *J. Phys. Chem. Ref. Data* **2009**, *38*, 721–748.

(17) The GCMC simulations reported here used the sorption module of Cerius2 (Accelrys, San Diego) with our ab initio FF. The results reported herein are for excess H_2 uptake as in ref 20.

(18) Garberoglio, G.; Skoulidas, A. I.; Johnson, J. K. Adsorption of Gases in Metal Organic Materials: Comparison of Simulations and Experiments. *J. Phys. Chem. B* **2005**, *109*, 13094–13103.

(19) Barnes, W. H. The Crystal Structure of Ice between 0 °C and −183 °C. *Proc. R. Soc. London, Ser. A* **1929**, *125*, 670–693.

(20) Bernal, J. D.; Fowler, R. H. A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions. *J. Chem. Phys.* **1933**, *1*, 515–548.

(21) Han, S. S.; Deng, W. Q.; Goddard, W. A. Improved Designs of Metal−Organic Frameworks for Hydrogen Storage. *Angew. Chem., Int. Ed.* **2007**, *46*, 6289–6292.

(22) Murray, L. J.; Dinca, M.; Long, J. R. Hydrogen Storage in Metal−Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.

(23) Garrone, E.; Bonelli, B.; Otero Areán, C. Enthalpy−Entropy Correlation for Hydrogen Adsorption on Zeolites. *Chem. Phys. Lett.* **2008**, *456*, 68–70.

(24) Golecki, I.; Jaccard, C. Intrinsic Surface Disorder in Ice near the Melting Point. *J. Phys. C: Solid State Phys.* **1978**, *11*, 4229.

(25) Suter, M. T.; Andersson, P. U.; Pettersson, J. B. C. Surface Properties of Water Ice at 150−191 K Studied by Elastic Helium Scattering. *J. Chem. Phys.* **2006**, *125*, 174704–174706.

(26) Wei, X.; Miranda, P. B.; Zhang, C.; Shen, Y. R. Sum-Frequency Spectroscopic Studies of Ice Interfaces. *Phys. Rev. B* **2002**, *66*, 085401.