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Ab initio calculations predicting the existence of an oxidized calcium dihydrogen complex to store molecular hydrogen in densities up to 100 g/L

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We propose a system that can store molecular hydrogen in densities up to ~100 g/L. Our *ab initio* calculations predict the existence of an oxidized calcium dihydrogen complex, which holds up to *eight* H_2, i.e., Ca(ion)$(H_2)_8$. The dihydrogen binding to the Ca is via a weak electron-donation mechanism from the occupied H_2 σ orbital to the unoccupied, but bound, Ca 3*d* orbitals. Because of the high concentration of the hydrogen in such complexes, even in calcium-intercalated pillared graphite, one can obtain reversible hydrogen storage denser than that of liquid hydrogen, 70 g/L.

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The most practical high-pressure tank can store up to 39 g/L of hydrogen gas at room temperature and 700 bar.[1] In comparison, at the extremely low temperature of 20 K, liquid hydrogen can be as dense as 70 g/L. The U.S. Department of Energy (DOE) year 2015 system target for volumetric density is 81 g/L for competitive consumer vehicles that use hydrogen as the fuel.[2] Such a target raises an important fundamental question: *Can we store hydrogen more densely than that in its liquid form?*

If hydrogen is stored in its atomic form, the above target can be readily met. For example, CH_4 has 105 g/L hydrogen. However, atomic H is not a fuel in itself; most hydrogen fuel-cell or internal-combustion engines need molecular hydrogen to generate power. To be useful, atomic hydrogen must be reformed into H_2. This extra reforming process may introduce serious problems that must be resolved onboard, such as heat transfer, operating temperature, fueling time, and energy efficiency. Alternatively, one can directly store molecular H_2 on adsorbents to avoid such complications. The specific density of an adsorbed H_2 monolayer on porous single-wall carbon nanotubes has been estimated at 64 g/L (Ref. 3) at its maximum, which is noticeably less than that of liquid hydrogen and the DOE target.

In this paper, we propose, based on *ab initio* calculations, a system that can store molecular H_2 in densities up to ~100 g/L, which is significantly higher than the DOE target. We predict that when calcium is oxidized and hydrogenated, a stable calcium dihydrogen complex exists that holds as many as eight hydrogen molecules. The resulting Ca(ion)-$(H_2)_8$ cluster has a record-high theoretical hydrogen content compared to other hydrogen-metal clusters such as WH_{12} and MoH_{12}.[4] For practical hydrogen storage, we propose calcium-intercalated nanoporous materials. Density-functional theory (DFT) calculations show that calcium-intercalated pillared graphite can hold reversibly more than 70 g/L of molecular hydrogen.

Because our new results are considerably higher than previous estimates,[3] it is important to understand the assumptions in Ref. 3 that do not apply to the current system. In Ref 3, intermolecular distances were assumed to be van der Waalsian. Because the heat of vaporization of liquid hydrogen at 20 K is small [only 0.2 kJ/mol-H_2 (Ref. 3)], the packing density of H_2 in liquid hydrogen is understandably modest. The H_2 physisorption energy on carbon-based materials or coordinatively saturated metal-organic frameworks is higher, but still only about 5 kJ/mol-H_2.[5] Thus, when taking into account the space occupied by adsorbents, it is not surprising that volumetric density in such pure physisorption systems still cannot exceed that of liquid hydrogen.

Recently, several theory groups[4,6–11] have predicted enhanced dihydrogen interaction at the exposed metal sites in a number of carbon-based systems, as well as coordinatively unsaturated metal-organic frameworks. Such a nonclassical binding has been attributed to (1) electron donation from the occupied H_2 σ orbital to the empty metal *p* or *d* orbitals and/or (2) electron back donation from the occupied *d* orbitals to the empty H_2 σ^* orbital.[12] Interestingly, while the adsorbed H_2 is nearly intact except for a modest elongation of its H-H bond by up to 10%, the metal-H_2 distance decreases considerably, down to ~2 Å, due to the enhanced binding. Equally important, a transition-metal (TM) atom on a substrate can hold not one but several H_2—up to five in the case of Sc.[6] Taken together, these facts suggest new opportunities to pack H_2 more densely than ever before. Until now, however, the highest theoretical volumetric density estimated for these systems was only 63 g/L in Ti-decorated polymers,[11] with the assumption of van der Waals packing.

The experimental demonstration of nonclassical dihydrogen binding can be traced back to the so-called Kubas molecules (or complexes) such as $W(CO)_2(PR_3)_2(H_2)$.[13,14] Here, it has been suggested that the dihydrogen binding is stabilized by the "unique" back-donation mechanism of TM. For hydrogen storage purposes, however, theory has shown that the donation mechanism may allow for a larger hydrogen packing density as in Ref. 6, which reveals that the number of adsorbed H_2 is proportional to the number of empty *d* orbitals. Moreover, if back donation is involved, the binding strength is typically greater than 60 kJ/mol-H_2.[6,13] Therefore, an optimized high-volumetric storage system should be donation dominated with as many *empty d* orbitals as possible. The problem with the donation-dominated TM systems is, however, the strong clustering tendency of the TM atoms due to their large cohesive energies, 4–5 eV. This may be avoidable if we use earlier alkaline or alkali-earth atoms of smaller cohesive energies, typically 1–2 eV.[15] Recently a Ca ion adsorbed on to fullerenes[16] or covalent organic frameworks[17] has been suggested to hold four or five hydrogen molecules with enhanced physisorption energies of greater than 0.2 eV per H_2.

Our study contains two parts: (1) To understand the fundamental mechanism of molecular H_2 binding to various metal atoms and ions, we perform DFT calculations with B3LYP exchange-correlation (xc) functional and high-level quantum chemistry calculations, including the Moller-Plesset perturbation theory of second order (MP2) and coupled cluster with single and double excitations (CCSD) using the GAUSSIAN03 package with the 6−311++G(d,p) basis set.[18] The analyses on Mulliken population and orbital energies are done with the GAUSSIAN03 at the B3LYP level. (2) To design more practical high-volumetric-density systems, we perform DFT calculations using the Vienna *ab initio* simulation package (VASP) with projector augmented-wave (PAW) potentials[19,20] within the local-density approximation (LDA).[21] For a comparative study, we also perform the same VASP calculations based on the generalized gradient approximation (GGA).[22] The GGA results systematically underestimate the LDA results as in Refs. 7 and 23, but exhibit the same trend; thus, we only present the LDA results here. A plane-wave kinetic-energy cutoff of 500 eV was used and the Brillouin zone integration was done with $(8\times8\times6)$, $(6\times6\times6)$, $(4\times4\times6)$, $(4\times4\times6)$, and $(3\times3\times6)$ **k**-points meshes for the $\sqrt{3}\times\sqrt{3}$, 2×2, $\sqrt{7}\times\sqrt{7}$, 3×3, and 4×4 supercells, respectively.

Charge-neutral alkaline and alkali-earth elements do not bind any H_2 beyond that of physisorption, as their diffusive *s* electrons form a repulsive shell that prevents H_2 from getting closer than the van der Waals distance. Because of their small electronegativities ranging from 0.8 to 1.2, however, Ca, K, Mg, Na, and Li can be easily oxidized (or ionized). When oxidized, they form a complex with multidihydrogen.

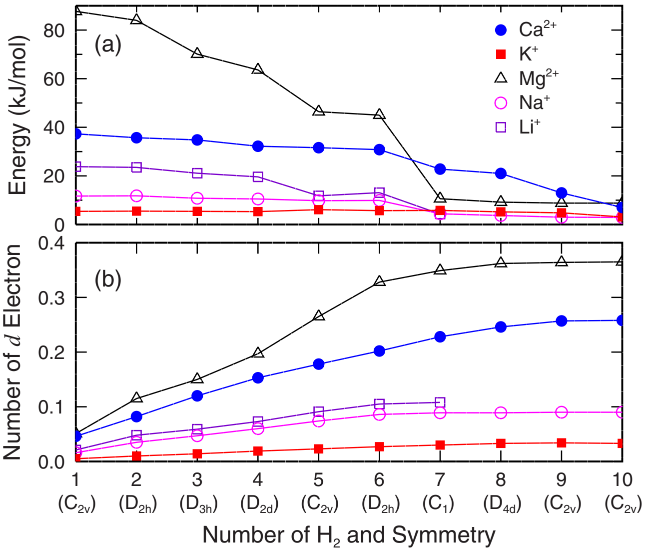

FIG. 1. (Color online) (a) Successive dihydrogen adsorption energies from Gaussian-MP2 and (b) donated *d* electrons on alkaline and alkali-earth ions from Gaussian-B3LYP. The symmetry of each ion-dihydrogen lowest-energy complex is denoted.

TABLE I. Selected orbital energy levels (in units of eV) of Ca, K, Mg, Na, and Li in various oxidation states, obtained from the Gaussian-B3LYP calculation. Energy zero here corresponds to the vacuum level. The orbital degeneracy is 1 for *s*, 3 for *p*, and 5 for *d*. The occupation of the *s* orbital has been bracket (or color) coded: [red]=2, {blue}=1, (black)=0. On the other hand, all the *p* and *d* orbitals are empty. For spin-polarized systems, only the levels for spin-up states are shown.

	4*s*	4*p*	3*d*
Ca	[−4.20]	−1.03	0.06
Ca^+	{−9.88}	−5.81	−6.70
Ca^{2+}	(−14.15)	−10.35	−14.25
K	{−2.90}	−0.65	3.92
K^+	(−5.94)	−3.69	−1.90
	3*s*	3*p*	3*d*
Mg	[−5.29]	−0.92	7.93
Mg^+	{−12.62}	−6.95	0.84
Mg^{2+}	(−18.12)	−12.97	−5.33
Na	{−3.48}	−0.57	9.04
Na^+	(−7.10)	−4.10	3.59
	2*s*	2*p*	3*d*
Li	{−3.65}	−0.87	11.58
Li^+	(−6.95)	−4.94	6.55

For Ca^{2+}, the binding energy to the first H_2 is 44.7, 37.3, and 36.7 kJ/mol-H_2 as calculated from B3LYP, MP2, and CCSD, respectively, whereas for K^+, it is 5.4, 5.4, and 5.2 kJ/mol-H_2, respectively, which agrees well with the experimental value of 6.1 kJ/mol-H_2 (Ref. 24). Mg^{2+}, Na^+, and Li^+ bind a H_2 with 87.7, 11.7, and 23.8 kJ/mol-H_2, respectively, as from MP2. Figure 1(a) shows all successive MP2 adsorption energies of dihydrogen on all the ions listed above. For the Ca ion, the H_2 adsorption energy gradually

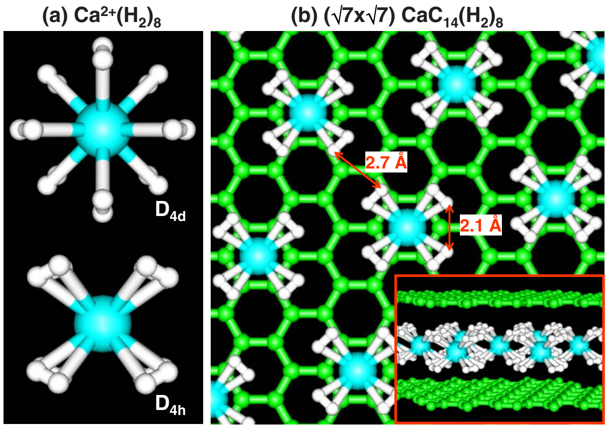

FIG. 2. (Color online) Atomic structures of (a) H_2-loaded $Ca(H_2)_8$ complexes with the D_{4d} and D_{4h} symmetries, and (b) $Ca(H_2)_8$-intercalated graphite in a $\sqrt{7}\times\sqrt{7}$ pattern. Inset shows the side view. Green (mid-size), blue (large-size), and white (small-size) atoms are C, Ca, and H, respectively.

decreases to 21 kJ/mol-H_2 up to the eighth H_2, and the d electrons donated from H_2 σ orbitals steadily accumulate as shown in Fig. 1(b). For other ions, the adsorption energy suddenly drops below 10 kJ/mol-H_2 after the sixth H_2, and the d electron accumulation stops. This observation is consistent with the previous study of MH_{12}.[25] Thus, only Ca^{2+} can accommodate up to eight H_2 molecules with adsorption energies greater than 15 kJ/mol-H_2, and the steady donation from the H_2 σ orbitals to Ca d orbitals is responsible for the increased binding. Interestingly, even if the numbers of d electrons are similar both in Na and Li ion, the dihydrogen binding in Li^+ is twice as strong as in Na^+. This can be attributed to stronger donation coupling of H_2 with localized Li's $2p$ orbital as opposed to Na's $3p$ or K's $4p$.[7]

To understand why Ca is unique, we compared atomic-orbital energies of Ca, K, Mg, Na, and Li atoms and ions (see Table I). As a charge-neutral atom, none of the elements has bound $3d$ levels below the vacuum, although the d levels for Ca are considerably lower than for the others—only 0.06 eV above the vacuum level. When the Ca is oxidized (even if only slightly), its $3d$ levels already become bound and hence localized. Localized states are necessary for dihydrogen binding,[6–8] which explains why a strong binding between oxidized Ca^{2+} and molecular H_2 can exist.

The above finding on the $Ca^{2+}(H_2)_n$ complexes lays the groundwork for more practical designs of high-density hydrogen storage systems by using them as a building block. The reduced H_2-H_2 distance (as low as 2.7 Å compared to 4 Å in liquid hydrogen) and the record-high content of dihydrogen are ideally fit to high volumetric-density storage. Figure 2(a) shows two Ca^{2+}-dihydrogen complexes loaded with eight H_2; both are highly symmetric with the point-group symmetries of D_{4d} and D_{4h}. On average, dihydrogen binding energies in MP2 are 30.5 and 28.9 kJ/mol-H_2, respectively.

Such complexes could be easily incorporated into existing porous materials such as metal-organic frameworks,[26] carbon nanotubes, or graphite. The same is true for calcium. Recent experiments[27] showed that a bulk quantity of Ca-intercalated graphite can be fabricated in the form of CaC_6. Calcium inside the graphite will be oxidized or positively charged, but the degree of oxidation depends on the distance between the Ca ion and graphene planes, as is clearly shown in Fig. 3. Once oxidized, the Ca will acquire the power to adsorb H_2 to form $Ca(ion)(H_2)_8$ complexes, as we demonstrated in the study of Ca^{2+}.

The Ca-intercalated graphites at their equilibrium layer-layer spacing (4.4 Å), however, cannot be used for hydrogen storage because there is no available space for adsorbing H_2 gas. In order to store hydrogen, we need to make them porous by dilating the layer-layer distances between the graphene planes. The dilating the interlayer spacing to ~7.5 Å requires about 250 kJ/mol-Ca, as shown in Fig. 3. This value is too high for hydrogen alone to initiate the dilation by adsorption energy gains. So, in practice it needs to be dilated externally, and it has been reported that graphite can be pillared with organic linkers for dilation.[28] Hence, we first assumed that the porous graphite is engineered via pillaring; based on this assumption, we estimated the maximum theoretical storage capacities and average hydrogen adsorption energies depending on Ca loading into the graphite systems—from CaC_6 ($\sqrt{3}\times\sqrt{3}$) to CaC_{32} (4×4).

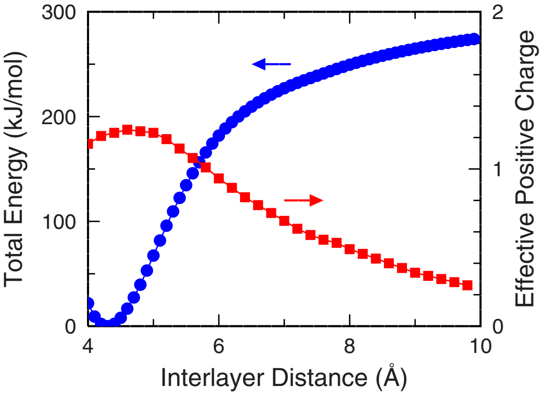

FIG. 3. (Color online) VASP-LDA total energy and effective positive charge of Ca in Ca-intercalated graphite $\sqrt{7}\times\sqrt{7}$, depending on interlayer distance, obtained from Bader analysis (Ref. 29).

Table II summarizes the LDA-calculated results and estimates when we intercalated the D_{4h} Ca-dihydrogen complex into porous graphites. In the porous graphites, a Ca atom is attached to a nearby graphene plane. The Ca binding energy, however, is relatively small—around 50–90 kJ/mol-Ca depending on Ca coverage. So the Ca can be easily liberated to the porous space if two or three hydrogen molecules are adsorbed, and thus can continue adsorbing hydrogen up to eight molecules. In the case of a high packing density such as $\sqrt{3}\times\sqrt{3}$ or 2×2, we found that the $Ca(H_2)_8$ are too close to each other, which makes them in the repulsive van der Waals hard-wall region, as shown in Fig. 4. The $\sqrt{7}\times\sqrt{7}$ packing [shown in Fig. 2(b)] appears to be best with an average adsorption energy of ~30 kJ/mol-H_2 and a volumetric density=95 g/L. Lowering the packing density to 3×3 or 4×4 has little effect on the adsorption energy, because the $Ca(H_2)_8$ complexes are already far enough apart, but it does result in loss of storage capacity.

Figure 4 shows LDA van der Waals interaction energy of $Ca(H_2)_8$ complexes that are packed in a hexagonal close-

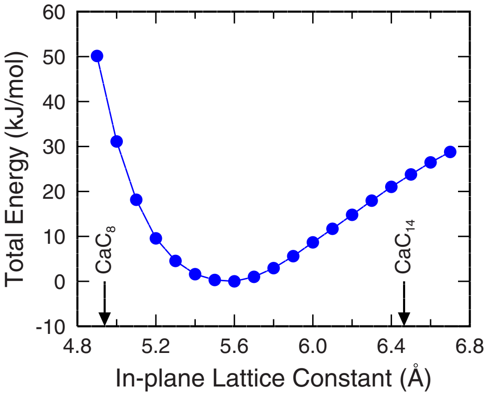

FIG. 4. (Color online) VASP-LDA total energy of the $Ca(H_2)_8$ cluster, packed in a hexagonal close-packed lattice with the fixed interlayer distance d=7.8 Å and varying in-plane lattice constant, a. The energy minimum takes place at a=5.5–5.6 Å, corresponding to $CaC_{10.5}$.

TABLE II. VASP-LDA equilibrium lattice constants (*a*: in-plane, *d*: interlayer) of $Ca(H_2)_8$-intercalated graphites in various $Ca(H_2)_8$ coverage from $\sqrt{3}\times\sqrt{3}$ to 4×4. At each fixed *a* and *d* (assuming pillared graphites), we calculated Ca binding energy ($\Delta E_{\text{C-Ca}}$) to the nearby graphene plane with reference to the middle of the interlayer space, average hydrogen adsorption energy ($\Delta E_{\text{Ca-H2}}$) when $Ca(H_2)_8$ is formed, and corresponding volumetric and gravimetric densities based on the supercell volume and elements. The average H_2 adsorption energy is defined as $\Delta E_{\text{Ca-H2}}=-\{E[Ca(H_2)_8]-E[Ca]-8E[H_2]\}/8$, where $E[Ca(H_2)_8]$, $E[Ca]$, and $E[H_2]$ are total energies of fully equilibrated $Ca(H_2)_8$-intercalated graphite, Ca-intercalated pillared graphite, and H_2 in vacuum, respectively. Assuming LDA van der Waals interactions between $Ca(H_2)_8$ complexes (Fig. 4), we estimate the *optimized* H_2 packing density to be around $CaC_{10.5}(H_2)_8$. The volumetric and gravimetric contributions of pillars are neglected in the estimate, and the listed values will serve for theoretical maximums when the systems are fully loaded by H_2.

	a (Å)	*d* (Å)	$\Delta E_{\text{C-Ca}}$ (kJ/mol-Ca)	$\Delta E_{\text{Ca-H2}}$ (kJ/mol-H_2)	Volume (g/L)	Weight (%)
$CaC_6(H_2)_8$						
$\sqrt{3}\times\sqrt{3}$	4.312	8.851	85.9	−4.0	179	12.6
$CaC_8(H_2)_8$						
2×2	4.939	8.707	84.9	19.2	146	10.6
$CaC_{10.5}(H_2)_8$	~5.5	~7.8	~87	~31	~127	~8.8
$CaC_{14}(H_2)_8$						
$\sqrt{7}\times\sqrt{7}$	6.465	7.761	65.6	30.7	95	7.2
$CaC_{18}(H_2)_8$						
3×3	7.341	7.732	64.7	29.7	74	5.9
$CaC_{32}(H_2)_8$						
4×4	9.789	7.669	50.5	31.6	42	3.7

packed lattice with the fixed interlayer distance of $d=7.8$ Å and varying in-plane lattice constant, *a*, but without any graphene network. The figure clearly shows that the van der Waals energy minimum is located at $a=5.5-5.6$ Å, which is in between the packing densities of CaC_8 and CaC_{14}. Therefore, the optimized packing in view of total energy is around $CaC_{10.5}$, representing a volumetric density of about 127 g/L when each Ca holds eight hydrogen molecules. Because this storage capacity well exceeds that of liquid hydrogen, our results imply that Ca-intercalated porous materials show viability as a path for high-volumetric hydrogen storage.

In conclusion, comprehensive and state-of-the-art, first-principles calculations reveal that oxidized calcium can be a good candidate for high-density, room-temperature reversible hydrogen storage. Even when intercalated into a nanostructured pillared graphite network, the fully H_2 loaded $Ca(H_2)_8$ complexes provide a volumetric capacity that exceeds those of liquid hydrogen and the DOE 2015 target and also have favorable binding energies.

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