

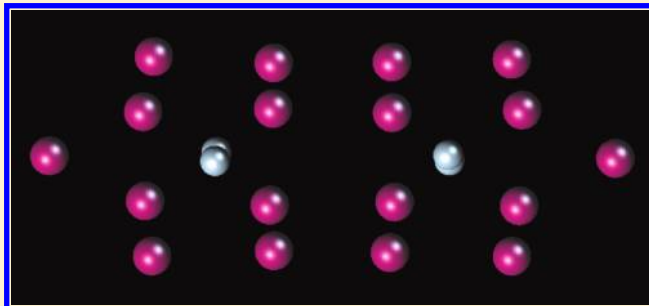
H₂ Molecules Encapsulated in Extended Be_n Cluster Cages: Toward Light-Metal Nanofoams for Hydrogen Storage

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ABSTRACT: Efficient storage of hydrogen is a bottleneck problem for hydrogen-based energy solutions. We demonstrate the feasibility of trapping a pair of hydrogen molecules in beryllium cluster cages. The systems are constructed by merging two smaller units with single molecules trapped, which are known to be stable in isolation. The resulting (H₂)₂@Be_n species can have hydrogen cores and beryllium shells of different shapes, and we report the calculated energy barriers for hydrogen exit from the cage. The relative stabilities are related to the molecular structure and charge distributions, and some initially counter-intuitive features are explained. Aspects of the release of hydrogen from such structures, and of possible scaling up to larger extended systems of fused cages, are discussed in terms of hydrogen storage. The predicted capacity could potentially be sufficient for practical usage.



1. INTRODUCTION

Hydrogen storage is a global issue at the heart of employing hydrogen for future energy needs. The ultimately small size of the molecule makes it extremely difficult to contain, other than in the form of atoms covalently bonded to a substrate (in larger molecules such as hydrocarbons, at surfaces of solids or clusters, etc.). However, strong bonds become an obstacle when hydrogen needs to be released for further usage, normally requiring excessively high temperatures. One apparent alternative is non-covalent bonding, but there is an operational lower bound to this interaction as well, with current estimates giving a value of about 0.5 eV.¹ Another possibility is to use a container to trap hydrogen molecules inside, which then releases them under appropriate conditions.

Among various possible containers at the molecular level that might provide sufficient storage capacity (currently required at least around 7 wt % of hydrogen), cluster cages of light atoms seem to merit further investigation. Carbon represents one well-known family of cluster cages, including fullerenes, nanotubes, etc. Similar structures can also be formed by boron. Hence, main group metals of the periodic table upper rows might offer another opportunity. Earlier theoretical work involved, in particular, a small B₁₂ cage, which appears unable to trap a single H atom,^{2,3} or small Mg_n and Ca_n ($n = 8-10$) cages, which can trap a single H₂ molecule.^{4,5} In a separate study we have investigated Be_n ($n = 8-14$) cages encapsulating one hydrogen molecule. In the present contribution, to improve the weight efficiency and, as a next stage, to introduce molecule–molecule interactions, we test Be_n ($n = 14-18$) cluster cages for endohedral containment of two H₂ molecules.

To eventually store a macroscopic amount of hydrogen in a mechanically stable container, many nanoscopic cages (with walls one atom thick in the above examples) would be required. When assembled together, and assuming their integrity preserved, the extended cages could be viewed as a metal “nanofoam” to be filled with hydrogen. Qualitatively similar aggregates, including nanoporous substances, of a single element composition, can be made experimentally using carbon⁶ and various transition metals (so far with much larger cages),⁷ and both types of system have been proposed for hydrogen storage. Although at present it seems difficult to create group IIA nanofoams, new procedures appear to show some progress, e.g., for Mg.⁸

In the present work we therefore attempt to merge the smallest H₂@Be_n species into larger systems of, to begin with, two such units. To increase the rather low storage capacity of single-molecule based species (about 2 wt % of hydrogen for H₂@Be₁₀), the clusters are merged by sharing facets. A related aim is to see if this procedure can preserve the structure of the units, including their empty cage Be_n counterparts with hydrogen released. Even though the empty cages may correspond to higher-energy isomers for larger cluster sizes, they may represent more likely kinetic products upon hydrogen removal, at least for some sizes, and could facilitate more efficient intake.

2. COMPUTATIONAL TOOLS AND METHODS

The NWChem ab initio package⁹ was used to perform calculations at the MP2 level of theory, which was chosen in

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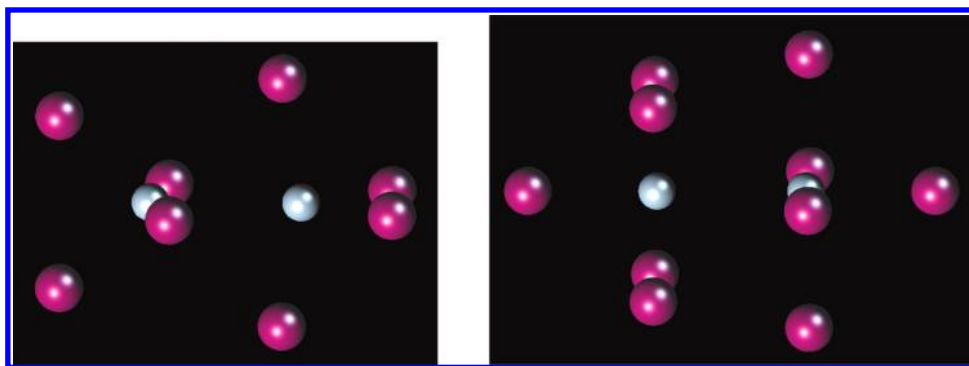


Figure 1. Optimized structures of $\text{H}_2@\text{Be}_8$ and $\text{H}_2@\text{Be}_{10}$.

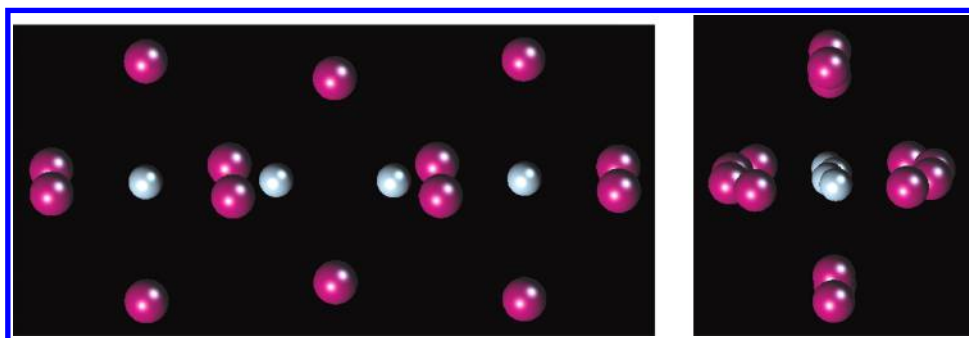


Figure 2. Optimized structures of $(\text{H}_2)_2@\text{Be}_{14}$, front and side views.

view of the noncovalent interactions and significant charge transfer in the systems in question. Geometries were optimized with aug-cc-pVDZ basis sets¹⁰ for Be and H, with all-atom optimizations carried out without symmetry constraints, and energy minima verified in terms of vibrational frequencies. The energies were then improved via single-point calculations using larger, aug-cc-pVTZ basis sets.¹⁰ Basis set superposition error corrections were applied using the standard counterpoise procedure.¹¹

The above approach, adopted to handle systems of larger size, is justified by its predictions for smaller structural counterparts, namely the building blocks of the systems under study, which were compared to complete optimizations using larger aug-cc-pVTZ basis sets. For $\text{H}_2@\text{Be}_8$ and $\text{H}_2@\text{Be}_{10}$ clusters of interest, the optimized geometries for the two basis sets differ by no more than 0.02 and 0.01 Å (about 1%) for the H–H and Be–H distances, respectively. The dissociation energies calculated with the larger basis set for the corresponding geometries differ by around 0.004 eV. The results for larger systems obtained using single-point calculations for aug-cc-pVTZ basis sets should therefore be comparable with the optimizations for smaller clusters that employ the larger basis set directly. Atomic charges were evaluated using charge distributions obtained within the standard natural bonding orbital (NBO) formalism.¹²

3. RESULTS AND DISCUSSION

The previously optimized structures of $\text{H}_2@\text{Be}_8$ and $\text{H}_2@\text{Be}_{10}$ mentioned above are shown in Figure 1 and are essentially the same as for the empty Be_8 and Be_{10} cages.¹³ A hydrogen molecule dissociates inside the cages due to strong electron-density transfer and a resulting Coulomb explosion of H_2 confined in the cage. A detailed study of these systems is reported

elsewhere, and some of their parameters are summarized for comparison below.

$(\text{H}_2)_2@\text{Be}_{14}$. This first system has two H_2 molecules bound noncovalently inside an elongated Be_{14} shell, which can be viewed as two axially fused Be_8 cages sharing a common Be_2 edge. Both H_2 molecules are dissociated, as for $\text{H}_2@\text{Be}_8$. The four H atoms form a slightly zigzagging chain, with two central atoms slightly closer to one another (by about 0.2 Å), flanked coaxially by four staggered rows of Be atoms, alternately slightly convex and slightly concave (Figure 2).

In the absence of the hydrogen chain, the corresponding empty beryllium cage retains its shape, producing a Be_{14} isomer about 2.5 eV higher in energy than the most stable geometry composed of three staggered Be_4 squares biccapped axially with atoms.¹³ For the latter isomer, however, our attempts to trap two H_2 molecules have so far been unsuccessful, the cage apparently being too tight. Indeed, the higher energy Be_{14} cage is about 0.4 Å longer due to its staggered arrangement of atoms, and has pairs of off-axis atoms at the ends rather than single-atom axial caps in the lower-energy isomer, thus providing more room to the outer H atoms in $(\text{H}_2)_2@\text{Be}_{14}$. Nevertheless, the H–H distances for this system are on average the shortest among all the species studied in this work (Table 1).

The encapsulated hydrogen molecules dissociate due to a strong charge transfer from the cage, resulting in more than one extra electron charge on each H atom (Table 2). This charge is slightly less than in $\text{H}_2@\text{Be}_8$ (−1.56 e), consistent with a smaller number of Be donors per H atom. The positive charges on the cage atoms monotonically increase from the middle to the ends of the cage (+0.15, +0.35, +0.41, and +0.45 e for subsequent staggered pairs of Be atoms), as expected, while the inner H atoms are marginally more negative.

Table 1. Equilibrium Parameters (in eV and Å) of (H₂)₂@Be_n

system	D_e^{total} per Be atom/ D_e^a	R_e (H–H)	R_e (Be–H)	R_e (Be–Be)
(H ₂) ₂ @Be ₁₄	2.11 (1.73)/ –3.74 (–4.25)	1.46 ^b , 1.63	1.39–1.72	1.95–2.58
(H ₂) ₂ @Be ₁₆	2.47 (2.08)/ –2.05 (–2.55)	1.70–2.68	1.48–1.91	1.96–2.27
(H ₂) ₂ @Be ₁₈	2.46 (2.08)/ –2.88 (–3.45)	1.80, 1.82 ^b	1.48–1.67	2.05–2.48
isomer II	2.52 (2.14)/ –1.85 (–2.36)	1.56	1.37–1.62	2.09–2.46
(H ₂) ₂ @Be ₁₇	2.52 (2.14)/ –1.19 (–1.71)	1.74–1.78 ^b	1.45–1.78	2.05–2.35

^a 2H₂ + nBe / 2H₂ + Be_n without (with) BSSE correction ^b Between inner H atoms.

Table 2. Atomic Charges and Dipole Moments (in *e* and *D*) of (H₂)₂@Be_n

system	$q(\text{H})$	$q(\text{Be})$	μ
(H ₂) ₂ @Be ₁₄	–1.27, –1.30 ^a	0.15–0.46 ^b	
(H ₂) ₂ @Be ₁₆	–1.14 ^a to –1.36	0.10–0.46 ^b	0.65
(H ₂) ₂ @Be ₁₈	–1.15 ^a , –1.23	0.04–0.38 ^b	0.18
II isomer	–1.22	0.05–0.43 ^b	
(H ₂) ₂ @Be ₁₇	–1.16 ^a , –1.20	0.09–0.45 ^c	0.25

^a Inner H atoms. ^b Outermost Be atoms. ^c Innermost shared Be atom.

The Coulomb repulsion of closely spaced hydrogen anions makes the system metastable (by a few electronvolts) relative to a separate Be₁₄ cage and H₂ molecules. The negative dissociation energy (Table 1) exceeds those of the other systems we consider here and is about three times that of H₂@Be₈, consistent with the H–H distances, which are significantly shorter than 1.71 Å in H₂@Be₈, and with three H–H contacts involved. Another consequence is that the cage is stretched axially by about 0.3 Å, while being inflated radially, mainly in the middle, by a similar amount.

The basis set superposition error correction slightly destabilizes the system by roughly the same amount (about 0.5 eV) for both dissociation channels (per Be atom for total dissociation). This result also holds for the other systems we consider below.

The (H₂)₂@Be₁₄ system therefore preserves integrity due to energy barriers that prevent hydrogen atoms escaping from inside the cage. The lowest such barrier of around 0.1 eV occurs for the outer H atoms moving radially (perpendicular to the cage axis), through the gap between Be atoms, and is about same as for H₂@Be₈. For a radial shift of the inner hydrogen atoms, or for pulling the outer ones axially, the barriers are slightly higher at around 0.2 eV. It is the higher axial barrier in H₂@Be₈ that enables two such species to be fused into (H₂)₂@Be₁₄ with hydrogen still trapped.

(H₂)₂@Be₁₆. Another system with two H₂ molecules encapsulated in a Be₁₆ cage can again be constructed by merging two H₂@Be₈ units, but with both their connecting Be₂ edges preserved and counter-shifted sideways to accommodate one another (Figure 3a). This arrangement leads to the hydrogen pairs turning away from an axial orientation, and to stretching in the middle of the cage. Now four atoms of the dissociated molecules form a planar asymmetric tetragon (distorted rhombus) inside a cage resembling that for Be₁₄ above but with two Be₂ dimers instead of single atoms in the middle of the shorter flanking rows. In contrast to H₂@Be₁₄, the asymmetry of the hydrogen core leads to a slight imperfection of the near-symmetric beryllium shell, and to a significant dipole moment (Table 2).

This arrangement increases the stability of the system to dissociation (Table 1) and decreases the energy relative to 2 H₂ + Be₁₆ by almost a half compared to the (H₂)₂@Be₁₄ case, the

D_e value being less than double that for H₂@Be₈. This stabilization is apparently due to significantly longer distances between the hydrogen anions, as a consequence of more space available inside the larger cage, consistent with larger Be–H separations. Another contributing factor is the lower average negative charge on the hydrogen atoms. Dissociation of (H₂)₂@Be₁₆ into two H₂@Be₈ units would require more than 10 eV.

As for the previous system, in (H₂)₂@Be₁₆ the inner H atoms are slightly more negative and the outermost Be atoms of the cage are most positive. However, unlike in (H₂)₂@Be₁₄ the charge first decreases (to +0.10–0.23 e per atom) and then increases again from the middle (+0.45 e per atom) to the ends (+0.42 e per atom) of the Be₁₆ cage.

The corresponding empty cage was obtained by relaxing the beryllium shell of (H₂)₂@Be₁₆ upon removing the hydrogen core. The shell reshapes into a “sandwich” structure of two near-planar Be₈ units (each consisting of hexagonal Be₇ plus a bridging atom at one side) in a staggered configuration (Figure 3b). The dissociation energy is reported relative to this isomer. Insertion of two H₂ molecules inside such a Be₁₆ cluster thus significantly alters its geometry via symmetrization as well as stretching in the plane of the H₄ core and shrinking perpendicular to it.

The minimal energy barrier preventing H atoms from exiting the cage has been evaluated as about 0.2 eV. It was obtained by gradually pulling the H atom nearest to the cluster surface out through a gap between Be atoms, with all other atoms' positions sequentially reoptimized.

(H₂)₂@Be₁₈. The next system can be obtained by inserting two H₂ molecules inside a Be₁₈ cage formed by axially merging two Be₁₀ cages and removing two axial atoms between them (Figure 4a). As a result, two dissociated hydrogen molecules are trapped inside an elongated Be₁₈ cage composed of four staggered near-square units plus axial capping atoms. The four H atoms near centers of the Be₄ units form a slightly zigzagging almost equidistant chain, with longer H–H separations compared to those in (H₂)₂@Be₁₄ (Table 1) and H₂@Be₁₀ (1.70 Å).

Without hydrogen inside, the relaxed cage mostly preserves its shape while recovering precise symmetry for the square units, and corresponds to a stable Be₁₈ isomer. The (H₂)₂@Be₁₈ system has the same total dissociation energy per Be atom as (H₂)₂@Be₁₆, and is metastable relative to an empty cage plus two free hydrogen molecules, lying about halfway between (H₂)₂@Be₁₄ and (H₂)₂@Be₁₆ in terms of dissociation energy (Table 1). The beryllium shell in (H₂)₂@Be₁₈ is stretched axially by about 0.3 Å relative to its length without the molecules inside, while retaining its radial dimensions.

The system can also be viewed in terms of two staggered H₂@Be₉ (resembling H₂@Be₁₀ without one axial Be atom) with their protruding H atoms pushed deeper into the Be₉ cages. The (H₂)₂@Be₁₈ species is stable by about 3 eV relative to dissociation into these components, which is much smaller than in the

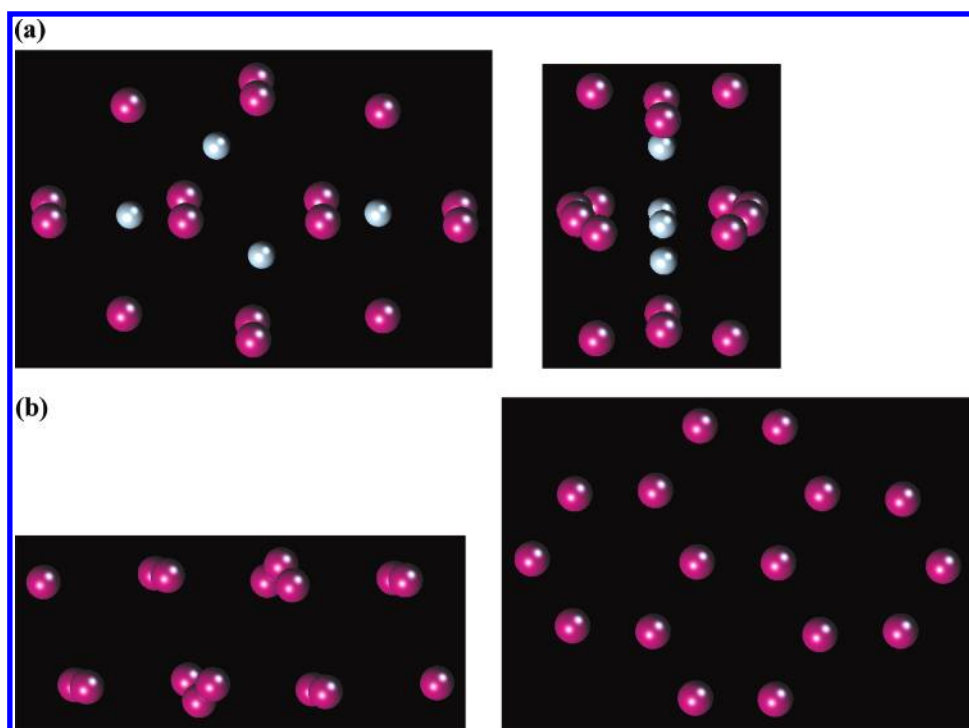


Figure 3. Optimized structures of $(\text{H}_2)_2@Be_{16}$, front and side views (a), and of Be_{16} cage relaxed from it, front and top views (b).

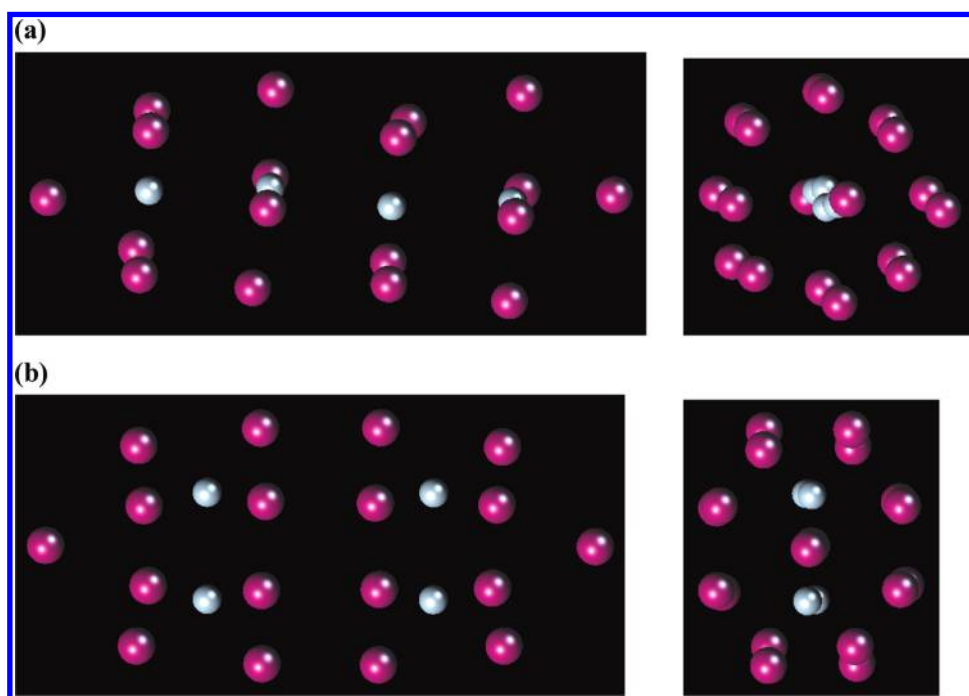


Figure 4. Optimized structures of $(\text{H}_2)_2@Be_{18}$ (a) and isomer II (b), front and side views.

$(\text{H}_2)_2@Be_{16}$ case due to much greater stability of $\text{H}_2@Be_9$ compared to $\text{H}_2@Be_8$.

The hydrogen atoms are slightly less negative in $(\text{H}_2)_2@Be_{18}$ compared to $(\text{H}_2)_2@Be_{14}$ (Table 2), contributing to a higher stability for the larger system. Unlike $(\text{H}_2)_2@Be_{14}$, this cluster exhibits a small dipole moment. The charges on the H atoms in $(\text{H}_2)_2@Be_{18}$ are also smaller than in $\text{H}_2@Be_{10}$ (-1.33 e), and

the H–H distances are longer, but the larger system's energy relative to $2\text{H}_2 + Be_{18}$ is more than twice that for $\text{H}_2@Be_{10}$ relative to $\text{H}_2 + Be_{10}$, consistent with three repelling H–H pairs in the larger system. In contrast to the situation for the previous two systems, the inner H atoms are slightly less negative, while the positive charge again concentrates at the ends of the cage, with the outer Be_4 unit carrying about twice the charge on the

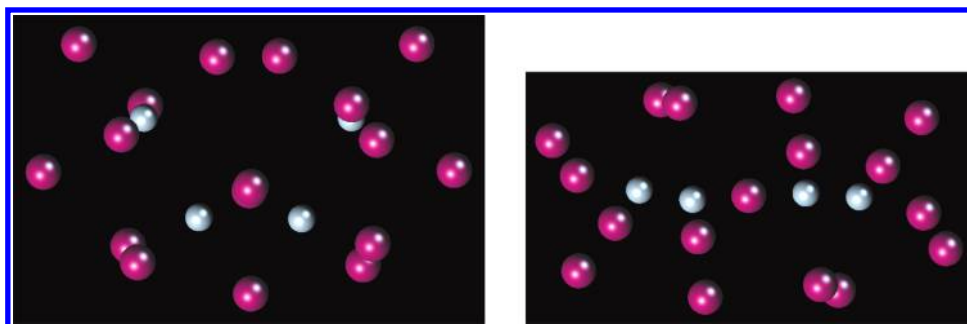


Figure 5. Optimized structures of $(\text{H}_2)_2@Be_{17}$ (corresponding to two facet-merged $\text{H}_2@Be_{10}$), front and top views.

inner Be_4 unit (1.37:0.62 e), and the outermost capping atoms being most charged.

Another isomer of $(\text{H}_2)_2@Be_{18}$ (denoted II) corresponds to near-parallel (dissociated) hydrogen molecules oriented perpendicular to the cage axis (Figure 4b), about 3.3 Å apart. This geometry can be built from two similarly merged higher-energy $\text{H}_2@Be_{10}$ isomers with perpendicularly oriented H_2 . It is interesting that other combinations of H_2 molecule orientations (one perpendicular to and one along the axis, or both perpendicular to axis and to one another) do not correspond to a stable endohedral isomer: instead the H atoms escape to the cage surface on relaxation. In particular, this makes it likely that, unlike $\text{H}_2@Be_{10}$, these two isomers cannot interconvert (over an energy barrier) endohedrally. For isomer II the Be_{18} cage with the H_2 molecules inside is stretched by up to 0.5 Å along their orientation.

The H_2 molecules perpendicular to the axis are squeezed by the shell to roughly 0.25 Å shorter H–H distances compared to the previous isomer (Table 1). Somewhat counterintuitively, while analogous compression makes the corresponding $\text{H}_2@Be_{10}$ isomer higher in energy, isomer II of $(\text{H}_2)_2@Be_{18}$ is more stable by about 1 eV for both dissociation channels considered, apparently due to the larger distance between the negatively charged H–H pairs. This isomer is also not as high in energy relative to $2\text{H}_2 + Be_{18}$ as the $(\text{H}_2)_2@Be_{14}$ and $(\text{H}_2)_2@Be_{16}$ clusters for the analogous dissociation products. However, the energy barrier for pulling a H atom out of the cage by further stretching the H–H distance in the dissociated molecule is only about 0.1 eV.

The charges on the H atoms and the charge distribution in the cage are similar for both isomers. However, the more symmetric isomer II has no dipole moment.

$(\text{H}_2)_2@Be_{17}$. A different system can be produced starting from two Be_{10} units merged at an angle (not axially as above) and sharing a Be_3 facet of the pyramidal ends of the units. This arrangement corresponds to a pair of dissociated H_2 molecules encapsulated separately in two Be_{10} -like half cages (Figure 5). On relaxation, the Be_{10} units twist to produce a staggered arrangement of their atoms and somewhat distort antisymmetrically but generally preserve their overall structure. As a result, the four H atoms form a bent (roughly C-shaped) near-equidistant chain inside a bent Be_{17} cage. This geometry is reflected in a small value of the dipole moment (Table 2), which is zero for the intact $\text{H}_2@Be_{10}$.

With hydrogen removed, the cage retains its shape, and, interestingly, has a significantly larger dipole moment of 0.90 D. Insertion of the H_2 molecules thus depolarizes this beryllium cage.

The charges on the H atoms are about the same for $(\text{H}_2)_2@Be_{17}$ and the $(\text{H}_2)_2@Be_{18}$ system with a near-linear hydrogen core. However, even though the H–H distances are longer for the $(\text{H}_2)_2@Be_{18}$ isomer, the $(\text{H}_2)_2@Be_{17}$ system is, counterintuitively,

considerably more stable relative to the empty cage plus two free molecules (Table 1). It is also significantly more stable in this regard compared to the lower-energy $(\text{H}_2)_2@Be_{18}$ isomer, while both systems have the same total dissociation energy per Be atom. Furthermore, the $(\text{H}_2)_2@Be_{17}$ species with three pairs of negative H atoms is slightly more stable than $\text{H}_2@Be_{10}$, which has only a marginally shorter distance between slightly more charged H atoms. A distinct feature of the system in question is the bent structure of the positively charged Be_{17} cage, with part of it located between two negatively charged H–H pairs. The resulting increased Coulomb interaction could be the origin of the above stabilization. Another possible contribution is the polarization of the outer Be atoms by a significant quadrupole moment originating from this negative–positive–negative charge alternation region in the inner part of the system.

As for $(\text{H}_2)_2@Be_{18}$, the inner H atoms are slightly less negative, and the outer atoms of the merged Be_{10} units in $(\text{H}_2)_2@Be_{17}$ are more positive. The shared innermost Be atom at the opposite (merged) ends of the units is, however, most charged.

Each inner H atom of the chain has two other hydrogen neighbors and thus experiences more repulsion than the outer atoms. These atoms can exit the Be_{17} cage over an energy barrier of around 0.3 eV, half the value for $\text{H}_2@Be_{10}$ (0.6 eV), apparently due to a stronger repulsion of a few H anions.

In contrast to $(\text{H}_2)_2@Be_{18}$, there appear to be no $(\text{H}_2)_2@Be_{17}$ isomers with the H–H pairs perpendicular to the axes of the Be_{10} units. One or both H–H pairs, if so oriented initially, recover their axial orientation upon relaxation, consistent with a small barrier (less than 0.1 eV) for such an endohedral rotation in $\text{H}_2@Be_{10}$, which probably disappears on distortion of the Be_{10} cage in the larger system.

Finally, within the size range considered ($n = 14, 16–18$), the stability of $(\text{H}_2)_2@Be_n$ in terms of the total dissociation energy does not exhibit a pronounced odd–even variation (Table 1), one possible reason being the closed-shell electronic structure of the Be atom, and hence no spin-pairing. The same is true for the corresponding empty beryllium cages, with $D_e^{\text{total}} = 2.38$ (2.03), 2.60 (2.24), 2.59 (2.24), and 2.62 (2.27) eV per atom without (with) the BSSE correction, consistent with previous results for Be_n including other values of n ,¹³ even though the most stable isomers are not cages for $n = 16–18$.

4. CONCLUSIONS

A series of beryllium cluster cages built of two merged Be_8 and Be_{10} units are found to accommodate a pair of hydrogen molecules dissociating via a (confined) Coulomb explosion due to a strong electron donation from the cage. These core–shell systems are

thus stabilized overall by a strong charge transfer. While the positive charge on the beryllium shell tends to concentrate at opposite ends, as expected, the negative charge on the hydrogen core is distributed more uniformly, with a preference for the H–H pairs spaced more closely.

The interaction between the H₂ molecules (or their atoms) is an important factor in the relative stabilities of the systems and their isomers. An isomer of the system built of two higher-energy isomers of units can be more stable, or vice versa, due to the interplay between the molecule–molecule and molecule–cage interactions, as for (H₂)₂@Be₁₈ and H₂@Be₁₀.

The shapes and sizes of different cages can be weakly or significantly modified when hydrogen is added endohedrally. The (H₂)₂@Be_{*n*} (*n* = 14, 16–18) species considered here are metastable with respect to dissociation into an empty cage plus free hydrogen molecules, and in most cases the associated barriers are low (0.1–0.3 eV). This result suggests that low temperature conditions will be needed to preserve such species, with a relatively easy release of hydrogen upon moderate heating (or rather “unfreezing”), possibly even at room temperature or below. Moreover, the metastability itself could perhaps be harnessed as a device for directly storing extra energy, with a capacity of between about 0.5 and 2 eV per H₂ molecule in the clusters considered in the present work.

It appears likely that larger counterparts could also be constructed, with more units merged together, scaling up to a beryllium “nanofoam” with cluster-cage “nanobubbles” each filled with hydrogen, starting from a molecule or two. Such an aggregation of cluster cages could significantly improve the storage capacity due to sharing cage walls. For instance, further linear structural extensions of the Be₁₈ and Be₁₄ cages described in the present work to longer beryllium “nanotubes” might bring the hydrogen storage capacity up to around 3 to 4 wt %, respectively. The Be₁₇ cage built of two facet-sharing Be₁₀ units suggests the possibility of merging cluster units in 2D and 3D, which we will consider further in future work. In particular, assuming possible sharing of Be₃ facets on both ends of the Be₁₀ units, we could ideally expect between 5 (with half of end facets used in 2D) and 8 wt % (all end facets used in 3D) of hydrogen. The latter value, if achieved, has the potential to provide useful hydrogen storage.

In addition, the observed increased stabilization of (H₂)₂@Be₁₇ highlights the importance of the cage shape and may be related to the electrostatic and polarization interactions associated with its 2D design. This result could imply a further increase of stability in larger 3D counterparts (up to a nanofoam) assembled from more H₂@Be₁₀ units similarly merged. This possibility will also be considered in future work.

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