H4-Alkanes: A new class of hydrogen storage material?

D. Harrison, E. Welchman, and T. Thonhauser

Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA.

(Dated: 31 December 2017)

The methane-based material (H2)nCH4, also called H4M for short, is in essence a methane molecule with 4 physisorbed H2 molecules. While H4M has exceptionally high hydrogen storage densities when it forms a molecular solid, unfortunately, this solid is only stable at impractically high pressures and/or low temperatures. To overcome this limitation, we show through simulations that longer alkanes (methane is the shortest alkane) also form stable structures that still physisorb 4 H2 molecules per carbon atom; we call those structures H4-alkanes. We further show via molecular dynamics simulations that the stability field of molecular solids formed from H4-alkanes increases remarkably with chain length compared to H4M, just as it does for regular alkanes. From our simulations of H4-alkanes with lengths 1, 4, 10, and 20, we see that e.g. for the 20-carbon stability field is doubled at higher pressures. While even longer chains show only insignificant improvements, we discuss various other options to stabilize H4-alkanes more. Our proof-of-principle results lay the groundwork to show that H4-alkanes can become viable hydrogen storage materials.

I. INTRODUCTION

In the search for a clean and renewable replacement for fossil fuels, using hydrogen as an energy carrier represents the ideal solution. Unfortunately, hydrogen is not practical for mobile applications in its natural state because of its low volumetric density. Many potential approaches and materials for solving this problem have been explored but (H2)4CH4—also known as H4M—demonstrates the largest volumetric and gravimetric densities of any known hydrogen storage material its 50.2 mass% (33.3 mass% without the hydrogen in CH4) and 0.15 kg H2/L far exceed the ultimate gravimetric and volumetric density targets for hydrogen storage materials set by the Department of Energy (DOE). H4M was first discovered almost two decades ago and contains four H2 molecules bound to a CH4 methane molecule by van der Waals interactions, see Fig. 1. Unfortunately, H4M requires extreme conditions to remain stable (65 K at ambient pressure or 5–6 GPa at ambient temperature) and despite its great promise has seen little study beyond property characterization. Due to the narrow stability range of H4M, any attempt to harness its high storage densities requires further stabilization. To this end, previous work has attempted to use external agents such as metal organic frameworks, carbon nanotubes, boron nitride nanotubes, graphite, or hexagonal boron nitride. Although relatively little work has been done on H4M specifically, other relevant works include investigations of high-pressure systems and the extensive work done on clathrates, a class of materials to which H4M is related.

Rather than try to improve the stability of H4M directly, we instead use H4M as the inspiration to study a new class of materials. Alkanes are hydrocarbon chains of the form CnH2n+2. Of particular interest is their increase in melting and boiling point with chain length n, as seen in Fig. 2. For example, as chain length increases from n = 1 to n = 6, the melting and boiling temperatures increase by over 100 and 200 °C, respectively. This increase in the melting/boiling temperatures is due to the additional long-range interactions among the longer chains. Because H4M is essentially an alkane chain with n = 1 (i.e. methane) and 4 physisorbed H2 molecules, we hypothesize that if we physisorb 4 H2 per carbon atom to a longer alkane chain, it would form a stable compound with a higher melting point than H4M. This results in a new class of materials of the form (H2)nCnH2n+2, which we call H4-alkanes. In the following, we show that such materials can be stable and that the stability of these materials increases with chain length, analogous to how the stability of regular alkane chains increases with length. To this end, we calculate the phase diagrams of several H4-alkanes of various lengths. In particular, we determine the melting temperatures of chains with lengths n = 1, 4, 10, and 20 for pressures ranging from 0 GPa to 6 GPa in increments of 1 GPa. These chain lengths were chosen because they are representatives of gaseous...
(n = 4), liquid (n = 10), and solid alkanes (n = 20) under ambient conditions; even chain lengths n were chosen because they show a larger increase of stability going from n − 1 to n compared to odd ones (see e.g. the step-structure in the blue line in Fig. 2). We will refer to H4-alkanes of length n as “n-carbon,” except for the case of n = 1, which we will continue to call H4M.

II. COMPUTATIONAL DETAILS

A. Structure Searches

Structure searches for the various H4-alkanes with n = 1, 4, 10, and 20 were performed with the structure search program Universal Structure Predictor: Evolutionary Xtallography (USPEX) in conjunction with the program Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The potential used was the Adaptive Internmolecular Reactive Empirical Bond Order (AIREBO) potential, which is specifically parameterized for hydrocarbons; a value of 3.0 was used for the Lennard-Jones sigma scale factor. Note that the AIREBO potential does not include three-body dispersive interactions. We found this criteria to agree very well with the loss of long-range order in the alkane-alkane center-of-mass radial distribution plots for all of our H4-alkanes. An example, the standard deviations of (α, β, γ) in degrees for the 4-carbon at 6 GPa and 230 K and 240 K (with radial distribution functions shown in Fig. 3) were (0.295, 0.306, 0.236) and (12.280, 14.325, 16.223), respectively. Compared to Fig. 3 we can see that the loss of structure going from 230 K to 240 K corresponds very well with a sharp increase in the variance of the lattice angles. We explicitly show how the lattice angle behavior changes upon melting in Fig. 3 where we plot γ over the full MD run. We see this same degree of correspondence between radial distribution function and angle variance at all of the pressures we have studied (0 to 6 GPa). For a few selected cases we have also studied the energy vs. temperature behavior and saw ‘jumps’ at the phase transitions. However, the melting temperatures derived from this approach coincide exactly with the temperatures found by our method of analyzing the deviation in lattice angles.

B. Molecular Dynamics Modeling

The best (i.e. lowest energy) structures obtained from the structure search were then used as the starting structure for our MD simulations, again using LAMMPS in conjunction with the AIREBO potential. A time-step of 0.5 fs was used. For each H4-alkane, a supercell was created such that the length of each unit cell vector was at least 19 Å, resulting in at least 2200 atoms per unit cell. Many MD simulations were then performed on the system at a variety of temperatures and pressures, with pressure ranging from 1 atm to 60,000 atm in increments of 10,000 atm (i.e., ~0 GPa to 6 GPa in increments of 1 GPa) and temperatures being probed in increments of 10 K until a clear criteria of melting was fulfilled. Every simulation was run for a total of 11 ns, with the first nanosecond being used for equilibration and the remaining 10 for analyzing melting criteria.

C. Criteria for Melting

Rather than using the radial distribution function—a standard method for identifying melting in a material—we designed a simple, non-graphical order parameter to streamline the process of identifying melting in a large number of simulations. We used the following criteria: if the standard deviation in any of the lattice angles α, β, or γ was greater than 5° (with data taken over the last 10 nanoseconds of our MD run), it was considered to be a liquid. The justification for this criteria is that liquids have zero shear modulus, and the shear modulus is essentially a shear stress divided by the resultant change in angle, so we expect a large increase in the standard deviation of the lattice angles after the material melts. We found this criteria to agree very well with the loss of long-range order in the alkane-alkane center-of-mass radial distribution plots for all of our H4-alkanes. As an example, the standard deviations of (α, β, γ) in degrees for the 4-carbon at 6 GPa and 230 K and 240 K (with radial distribution functions shown in Fig. 3) were (0.295, 0.306, 0.236) and (12.280, 14.325, 16.223), respectively. Compared to Fig. 3 we can see that the loss of structure going from 230 K to 240 K corresponds very well with a sharp increase in the variance of the lattice angles. We explicitly show how the lattice angle behavior changes upon melting in Fig. 3 where we plot γ over the full MD run. We see this same degree of correspondence between radial distribution function and angle variance at all of the pressures we have studied (0 to 6 GPa). For a few selected cases we have also studied the energy vs. temperature behavior and saw ‘jumps’ at the phase transitions. However, the melting temperatures derived from this approach coincide exactly with the temperatures found by our method of analyzing the deviation in lattice angles,
III. RESULTS AND DISCUSSION

A. H4-Alkane Structures

Our goal in performing a structure search for H4M or any of the other H4-alkanes was not foremost to find the true ground-state structures and global minimum, but to have a consistent method for generating a reasonable starting structure for our MD simulations. Nonetheless, we briefly discuss here the structures found for H4M and the other H4-alkanes, shown in Fig. 5. Note that simply putting H4-alkanes more or less arbitrarily into a large unit cell results in a lot of chain-breaking, which the structure search avoids.

Although the true structure of H4M remains unknown, previous investigations have suggested highly ordered structures (e.g. body-centered tetragonal or body-centered orthogonal). In contrast, although we find an approximately orthorhombic unit cell, it is not body-centered. Note that Ref. [30] screened many different randomly generated structures using classical force fields, whereas Ref. [7] did not generate random structures, but instead compared several high-symmetry structures using DFT. In contrast, we used an evolutionary random structure search algorithm in conjunction with LAMMPS. Comparing the energy of our H4M structure to a body-centered orthogonal structure (such as suggested by Ref. [30]) at a pressure of 6 GPa upon relaxation using LAMMPS, we find the structures to be nearly isoenergetic, with an energy difference of less than 4 meV/atom.

For the other H4-alkanes we find that, as the chain length increases, there is more order among the chains. The 4-carbon structures seem to have aligned alkane slabs with alternating tilt, whereas in the 10-carbon structure the alkane chains are pointed in the same direction, although with an offset to one another. The 20-carbon structure is most ordered, with the alkane chains mostly in alignment with one another, forming a rhombus.

B. Comparison with Experiment

To test our approach, we first perform a structure search and MD simulations for H4M to find its phase diagram, which can be compared with experiment. In Fig. 6, we find near exact agreement of the phase diagram for lower pressures, although our results increasingly under-predict the melting temperature compared to experiment as the pressure increases. This error is likely due to the AIREBO potential being optimized for lower pressures. Even so, the error is still very reasonable for melting temperatures calculated with empirical force fields, especially considering we are more interested in trends, i.e. differences, in melting temperatures as chain length increases, rather than their absolute values.
FIG. 5. Structures found for a) H4M, b) 4-carbon, c) 10-carbon, and d) 20-carbon. Certain carbon atoms have been color-coded so that it is clear which chains are distinct and which are periodic images.

FIG. 6. Calculated phase diagram for H4M compared to experimental data taken from Mao et al.\textsuperscript{12,13} The experimental melting curve is defined by the points where H4M solidified upon temperature decrease.

C. Phase Diagram of H4-Alkanes

The most pertinent results of our study are collected in Fig. 7, where we depict the phase diagrams for the various H4-alkanes. We do see a clear trend of increasing phase stability and melting temperature as chain length increases. For the 20-carbon at 6 GPa the increase is over 200 K (relative to H4M), i.e. a doubling of the stability field. From comparing the melting temperatures at lower pressures to those at higher pressures, we see that, although there is a significant increase in melting temperature compared to H4M for the longer chains at higher pressures (i.e. 2–6 GPa), there is almost no difference or even a decrease in melting temperature at lower pressures. To verify that this decrease is not merely an artifact of the AIREBO potential used, we also calculated the melting temperatures for pure butane ($n = 4$) and octane ($n = 8$) at ambient pressures after performing an abbreviated structure search, finding melting temperatures of 190 K and 290 K. Although these values are ~60 K above the experimental values (see Fig. 2), they still show a consistent stabilization with chain length. The most reasonable explanation for the decrease in stability at ambient pressure is that there are competing interactions between the increased stability seen in the longer chains when they are aligned properly and the decreased stability from H$_2$ molecules serving as a barrier to intra-chain interactions. In order to benefit from the intra-chain interactions for the longer chains, they need to be oriented in a specific manner (i.e. aligned with each other as seen in Fig. 5d). To maintain this orientation requires higher pressures, which is perhaps why
these longer chains are less stable at ambient pressure. This case differs from that of regular alkanes due to the hydrogen molecules between the chains, which function as a barrier to intra-chain interactions.

As a side note, a 60-carbon structure was also studied, although due to its size it was necessary to generate the structure randomly with PACKMOL.\cite{14} No significant improvement was found over the 20-carbon; analysis of the 60-carbon structures near the end of the molecular dynamics simulations showed significant chain breaking. It is possible that there is little improvement in H4-alkane stability after a certain chain length due to chain breaking. Also note that in Fig. 7, except for H4M, there are no data points at 1 GPa. This is because for all of the structures other than H4M we could not obtain complete and reliable MD trajectories. This most likely signifies an instability of the structures at that particular pressure and possibly suggests a more complicated phase transition.

Despite the significant improvement we see for the longer chains at high pressures, the lack of stabilization at ambient pressures makes H4-alkanes still not practical for automotive applications of hydrogen storage, where even high-pressure tanks are typically limited to no more than 0.1 GPa. Nonetheless, we see our work as a proof-of-principle that longer chains significantly increase the stability field of H4-alkanes and almost double it for the 20-carbon. Another point of importance is that certain nonlinear alkane isomers, such as the cycloalkanes, have higher melting temperatures than the straight alkanes. It is possible that when H4-alkanes are created from these nonlinear alkanes, they would have higher melting temperatures. However, for simplicity, as the number of possible isomers tremendously grows with chain length, in this work we restricted ourselves to linear alkane chains. Furthermore, an almost limitless number of structures exist with only slightly higher energy, which show intermingling of the chains, which would further significantly increase the melting temperature, but are unfortunately difficult to produce with a structure search algorithm.

Several other unexplored avenues also provide hope for hydrogen storage applications of H4-alkanes (or derivative materials). The simplest is modifying the H4-alkanes via adding stabilizing molecules or doping it. Another possibility is removing hydrogen from the system, which has exceptional hydrogen content anyway and would not drastically suffer from some hydrogen reduction. As hydrogen is removed, H4-alkanes must approach the higher stability of pure alkanes (similarly, we would expect the structures to become increasingly less stable as more than 4 H2 molecules are added per carbon atom). Assuming the transition from the stability of H4-alkanes to regular alkanes increases monotonically, it is likely that a class of materials such as H2-alkanes (with 2 H2 per carbon) would have significantly increased stability. It is also worth mentioning that hydrogen can also be produced through decomposing alkanes themselves. Finally, the overall phase diagram of the binary molecular system H2 + CH4 is very interesting, but also highly complex—see Fig. 1 in Ref. [11]. It is thus conceivable that other hydrogen-rich phases exist that may have more favorable stability than H4-alkanes.

IV. CONCLUSIONS

The material H4M has exceptional hydrogen storage density, but unfortunately requires very high pressures and/or low temperature to be stable. To overcome this shortcoming, we use the H4M structure and the increasing stability of regular alkane chains as inspiration and predict the possible formation of structures known as H4-alkanes (i.e. alkane chains with 4 physisorbed H2 molecules per carbon atom). We use a structure search methodology to find candidate structures for H4-alkanes of length 1, 4, 10, and 20 and our MD simulations show a significant increase in stability for the longer chains at higher pressures. We see our work as proof-of-principle that encourages further research to stabilize H4-alkanes even more and thus realize their potential for practical hydrogen storage applications.

ACKNOWLEDGMENTS

This work was supported in full by NSF Grant No. DMR-1145968.

1. M. Kimowsky, J. P. Marco-Lózar, and A. Linares-Solano, J. Renew. Energy 2013, 1 (2013)
2. D. Durbín and C. Malardier-Jugroot, Int. J. Hydrogen Energy 38, 14595 (2013)
3. G. W. Crabtree, M. S. Dresselhaus, and M. V. Buchanan, Phys. Today 57, 39 (2004)
4. J. Graetz, Chem. Soc. Rev. 38, 73 (2009)
5. D. Harrison, E. Welchman, Y. J. Chabal, and T. Thonhauser, in Vol. 5 Energy Storage, Handbook of Clean Energy Systems edited by J. Yan (Wiley, Hoboken, NJ, 2015) pp. 2665–2683.
W. L. Mao, C. A. Koh, and E. D. Sloan, Phys. Today **60**, 42 (2007).

Q. Li and T. Thonhauser, J. Phys. Condens. Matter **24**, 424204 (2012).

J. Yang, A. Sudik, C. Wolverton, and D. J. Siegel, Chem. Soc. Rev. **39**, 656 (2010).

DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles, retrieved from [http://energy.gov/sites/prod/files/2014/03/f12/targets_onboard_hydro_storage.pdf](http://energy.gov/sites/prod/files/2014/03/f12/targets_onboard_hydro_storage.pdf) (US Department of Energy, 2009) – for a good side-by-side comparison between the old and new DOE targets see Ref. [8].

R. K. Ahluwalia, J.-K. Peng, and T. Q. Hua, Int. J. Hydrogen Energy **40**, 6373 (2015).

M. S. Somayazulu, L. W. Finger, R. J. Hemley, and H. K. Mao, Science **271**, 1400 (1996).

W. L. Mao, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, Chem. Phys. Lett. **402**, 66 (2005).

M. Wang, X. Cheng, D. Ren, H. Zhang, and T. Yongjian, Mod. Phys. Lett. B **29**, 1550062 (2015).

R. J. Hemley, Annu. Rev. Phys. Chem. **51**, 763 (2000).

Y. Song, Phys. Chem. Chem. Phys. **15**, 14524 (2013).

H. Lee, J.-W. Lee, D.-Y. Kim, J. Park, Y.-T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, and J. A. Ripmeester, Nature **434**, 743 (2005).

L. J. Florusse, C. J. Peters, J. Schoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, and E. D. Sloan, Science **306**, 469 (2004).

S. Wang, H.-k. Mao, X.-J. Chen, and W. L. Mao, Proc. Natl. Acad. Sci. USA **106**, 14763 (2009).

A. Gupta, J. Lachance, E. D. Sloan, and C. A. Koh, Chem. Eng. Sci. **63**, 5848 (2008).

M. D. Loudon, *Organic Chemistry*, 3rd ed. (Benjamin/Cummings, Redwood City, CA, 1995).

A. R. Oganov and C. W. Glass, J. Chem. Phys. **124**, 244704 (2006).

A. R. Oganov, A. O. Lyakhov, and M. Valle, Acc. Chem. Res. **44**, 227 (2011).

A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, Comput. Phys. Commun. **184**, 1172 (2013).

Q. Zhu, A. R. Oganov, C. W. Glass, and H. T. Stokes, Acta Crystallogr. Sect. B Struct. Sci. **68**, 215 (2012).

S. Plimpton, J. Comput. Phys. **117**, 1 (1995).

D. W. Brenner, O. a. Shenderova, J. a. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, J. Phys. Condens. Matter **14**, 789 (2002).

S. Stuart, A. Tutein, and J. Harrison, J. Chem. Phys. **112**, 6472 (2000).

O. Anatole von Lilienfeld and A. Tkatchenko, J. Chem. Phys. **132**, 234109 (2010).

M. Kroon, W. Mao, P. Cummings, C. Peters, G.-J. Witkamp, and H. Docherty, *High capacity molecular hydrogen storage in novel crystalline solids*, retrieved from [https://gcep.stanford.edu/pdfs/CTlSZRP4nww_77Shjd-A2g/WendyMao_Symposium2009.pdf](https://gcep.stanford.edu/pdfs/CTlSZRP4nww_77Shjd-A2g/WendyMao_Symposium2009.pdf) (2009).

L. Martínez, R. Andrade, E. G. Birgin, and J. M. Martínez, J. Comput. Chem. **30**, 2157 (2009).

K. Osuka, Y. Shigeta, and S. Takenaka, Int. J. Hydrogen Energy **27**, 11 (2002).

N. Shah, S. Ma, Y. Wang, and G. P. Huffman, Int. J. Hydrogen Energy **32**, 3315 (2007).