

Pressure-driven confinement of hydrogen molecules between graphene sheets in the regime of van der Waals repulsion

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Molecular hydrogen is well-known for its weak van der Waals potential, and as a result, its compressibility, even in its liquid and solid state. This fact gives rise to a large $p\Delta V$ term, which under the right conditions can overcome unfavorable energy and entropy changes for the confinement of H_2 , as demonstrated for the confinement of H_2 in graphite. It produces a remarkable two dimensional array of H_2 with ordered orientation, as H_2 is forced into the narrow and seemingly inhospitable space sandwiched between two hexagonal carbon rings. H_2 is thus a unique case in host-guest interaction and in the storage and confinement of gases, as pressure in the gigapascal range provides a powerful variable to manipulate the interaction between H_2 and solid hosts.

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Storage of hydrogen in carbon materials,^{1,2} with its potential application in hydrogen-fueled transportation system, has attracted much attention recently, and there are growing interests in the interactions between H_2 and hosts in solid lattices,^{2,3} although mechanism for hydrogen storage in carbon materials remains unclear.² As a nonpolar molecule, H_2 has the shortest bond distance with only two electrons. The van der Waals potential of H_2 is very weak, since dispersive interaction is due to the instantaneous polarization of electron clouds, the spatial extent of which in H_2 is the smallest among molecules. The binding energy in the dimer $H_2 \cdots H_2$ is only ~ 0.003 eV.⁴ Physisorption of H_2 on graphite surface is characterized by a shallow well of ~ 0.08 eV, and an equilibrium distance between H_2 and the surface around 2.7 Å, according to density-functional theory calculations.⁵ Such a small adsorption energy poses a serious challenge for trapping hydrogen, which is governed by the free energy change $\Delta G = \Delta H - T\Delta S = \Delta E + p\Delta V - T\Delta S$. Under ambient conditions, the volume of the solid is much smaller than V_{H_2} , the volume of H_2 gas, and $p\Delta V$ can be approximated by $p\Delta V \simeq -pV_{H_2} = -nRT$. On the other hand, trapping H_2 results in a decrease in the entropy, which is again dominated by the entropy of hydrogen gas S_{H_2} , with $-T\Delta S \simeq TS_{H_2}$. Treating H_2 as an ideal monoatomic gas by the Sackur-Tetrode equation,⁶ the TS_{H_2} term is estimated to be $14.2nRT$ at 1 atm and 300 K. Thus the positive entropy term is an order of magnitude larger than the negative $p\Delta V$ term, and these two terms add an endothermic amount of ~ 0.21 eV at 200 K and ~ 0.34 eV at 300 K per molecule, which are considerably larger than the adsorption energy and make the storage process difficult. This is in agreement with the low uptake of hydrogen by carbon nanotubes as found in Monte Carlo calculations,^{7,8} and is likely to be a problem for physisorption based storage due to the typically weak H_2 adsorption energy.

However, there is another side to the weak van der Waals potential of H_2 . Typically, the repulsive region of a van der Waals potential is very stiff, with energy rising sharply as the

inter-molecular distance falls below the equilibrium distance. But for H_2 the repulsive region is considerably less stiff than typical, again due to its weak van der Waals potential. As a result, solid hydrogen is known to be remarkably compressible, with density ranging from 0.04 to 0.48 mol/cm³ depending on external pressure.⁹ For the purpose of storage and confinement, it means that the term $-pV_{H_2}$ can be more favorable at higher pressure, when H_2 is in the liquid or solid state, rather than an ideal gas. In fact, we will show that at gigapascal pressures it is large enough to compensate both the ΔE and $T\Delta S$ terms and makes it thermodynamically favorable, upon compression, to confine H_2 in graphite within the narrow space sandwiched between two carbon hexagonal rings, producing a two-dimensional array of H_2 with ordered orientation. It marks H_2 as a unique case in host-guest interaction and in the storage and confinement of gases, as the pV term could be a much more important factor than the adsorption energy and provide a powerful variable to manipulate the interaction between H_2 and solid hosts.

Graphite is built by stacking up graphene sheets, each of which is a two-dimensional extension of hexagonal carbon rings. It is well known that atoms and molecules can be inserted between the graphene layers to form intercalation compounds.^{10,11} The space sandwiched between two carbon hexagonal rings can be considered as a cage, as shown in Fig. 1, except that its volume is small, with the diagonal C-C distance at only ~ 2.8 Å, which at first glance is too small even for H_2 , as the inter-molecular distance in the $H_2 \cdots H_2$ dimer is 3.3 Å.

To evaluate the energetics for the confinement process shown in Fig. 1, both first principles calculations and the experimental equation of state for H_2 are used. The structure and energy change under external pressure are calculated by the Vienna *Ab initio* Simulation Package,^{12,13} in which the local density functional (LDA) theory is implemented using a planewave basis set and pseudopotentials for the atomic core regions.¹⁴ The planewave cut-off energy is 928.1 eV, with pseudopotentials generated by the projector augmented

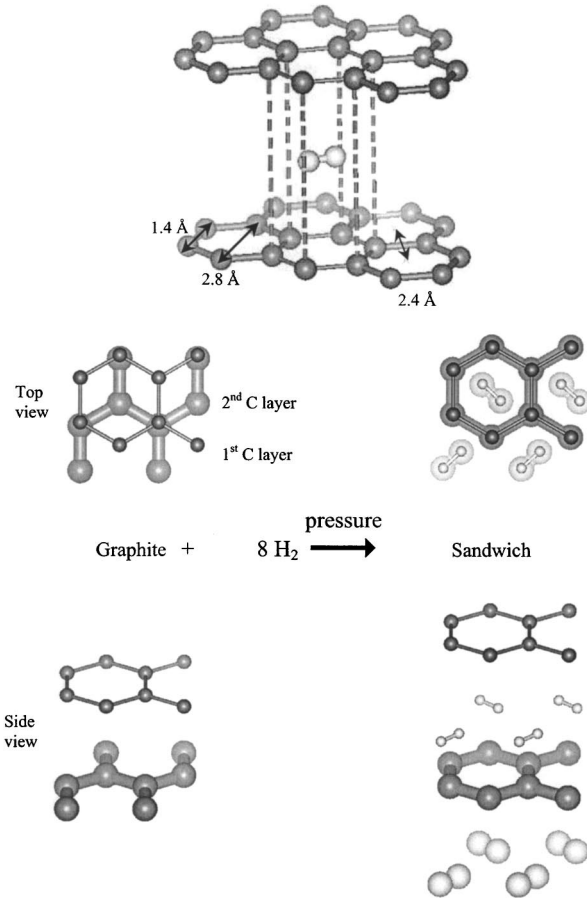


FIG. 1. Trapping of H_2 molecules as modeled by two graphene layers and 8 H_2 molecules in the unit cell. The structures shown are obtained by density-functional theory calculations. Top: the molecular dimensions for the space sandwiched between two hexagonal carbon rings in graphite; Bottom: The top and side views of the unit cell used in the modeling of graphite and the sandwich structure with H_2 confinement.

wave (PAW) method.¹⁵ The graphite is modeled by a rectangular supercell, containing two graphene layers, and a total of 16 carbon atoms, shown in Fig. 1. With one H_2 molecule between two hexagonal rings, the number of H_2 molecules is eight. With such a unit cell, the k -space sampling with a mesh of 12 points produces excellent convergence in the total energy. Both atomic positions and lattice constants are optimized, with the external pressure set at a constant value. A simplified model is used to evaluate the internal energy for H_2 under high pressure. The total energy of a supercell with 32 H_2 molecules is minimized at a constant pressure, and then averaged to obtain the energy for one H_2 . The internal energy E_{H_2} is thus obtained at zero temperature and should be slightly lower than the real value at 100 and 200 K.

The hexagonal graphite has *ABAB...* stacking of graphene layers, as shown in Fig. 1, which is also found to be the energy minimum in our calculations. The optimized C–C distance at zero pressure is 1.412 Å, and interlayer distance 3.268 Å, compared to the experimental values of 1.421 and 3.354 Å, respectively.¹⁶ Upon compression to 2 GPa, the C–C distance is shortened to 1.410 Å and interlayer distance to 3.124 Å, compared to the experimental values of 1.418

and 3.223 Å.¹⁶ When H_2 molecules are inserted between the graphene layers, the hexagonal rings become aligned after structural optimization. At zero pressure, the interlayer distance increases to 5.432 Å, from 3.268 Å in graphite. The energy change is actually endothermic, by a small value of ~ 0.14 eV, which is mainly due to the fact that the distance between the centers of H_2 molecules is shortened to ~ 2.44 Å, in the region of repulsive van der Waals interaction. As pressure increases, the absolute value of ΔE decreases to ~ 0.05 eV at 2 GPa, as shown in Table I and Fig. 2. Thus the energy change does not favor the confinement, although its absolute value is small.

The $p\Delta V$ term can be divided into two parts. The first part, $p(V_s - V_g)$, where V_s is the volume of the sandwich structure, and V_g the volume of graphite, is directly obtained from the unit cell volume in our calculations. As both are solids, the volumes change only slightly as the pressure is increased. On the other hand, the volume of H_2 must be estimated by experimental data, due to its diffusive nature. The equation of state for H_2 has been well-known, and using the fit for $n\text{--H}_2$ in the range of $0.2 < P < 2$ GPa and $75 < T < 307$ K, the volume is calculated by

$$V = (36.716 + 0.003\,300\,3T - 22.479T^{-1/2})P^{-1/3} \\ + (-17.174 - 0.021\,393T)P^{-2/3} \\ + (-8.9886 + 0.110\,01T + 69.233T^{-1/2} \\ - 31.395T^{-1})P^{-1},$$

with T in K, pressure in kbar, and volume in cm^3/mole , which has an estimated error less than 0.5%.¹⁷ As listed in Table I, the value of $8V_{\text{H}_2}$ is larger than the $(V_s - V_g)$ term, and mainly due to its contribution through $p\Delta V = p(V_s - V_g) - 8pV_{\text{H}_2}$, the enthalpy change is exothermic, with a value of -0.74 eV at 2 GPa and 200 K, for the unit cell under consideration.

Trapping H_2 between graphene layers is a condensation process, and entropy is the other very importance factor. Here again, an evaluation can be obtained from experiment for the entropy of H_2 , while the entropy difference between graphite and the sandwich structure can be approximated as zero. The $-T\Delta S$ term is then approximated by $8TS_{\text{H}_2}$, using the data tabulated by Hemmes, Driessen, and Griessen.¹⁸ At 200 K, the calculated free energy change ΔG is positive at low pressure, and decreases with increasing pressure, as shown in Fig. 2. It becomes negative at ~ 1.5 GPa, and reaches a value of -0.15 eV at 2 GPa. When temperature is lowered to 100 K, the volume of H_2 decreases by $\sim 10\%$, and the process becomes slightly less exothermic in the enthalpy value of -0.61 eV. On the other hand, the $T\Delta S$ value is also reduced due to a significant decrease in both T and S_{H_2} ,¹⁸ making the corresponding ΔG more negative at -0.55 eV.

As mentioned above, we made two approximations in our estimate. First, the internal energy of H_2 is obtained by the potential energy of a model “ H_2 solid,” and the actual internal energy should be slightly higher. Second, the entropy for the trapped H_2 , as included in the term S_s , the entropy for

TABLE I. Thermodynamic quantities as a function of pressure, calculated by density-functional theory with PAW potentials and the experimental equation of state.

Pressure (GPa)	ΔE (eV)	$V_S - V_G$ (Å)	$8V_{H_2}$ (Å)	$p\Delta V$ (eV)	ΔH (eV) = $\Delta E + p\Delta V$	$-T\Delta S$ (eV)	ΔG (eV) = $\Delta H - T\Delta S$
200 K							
0.000	0.136						
0.250	0.134	90.58	289.89	-0.311	-0.177	0.879	0.702
0.500	0.121	89.98	227.72	-0.430	-0.309	0.782	0.474
0.750	0.113	88.74	199.93	-0.520	-0.407	0.728	0.321
1.000	0.104	87.47	182.85	-0.595	-0.491	0.685	0.194
1.250	0.086	86.52	170.80	-0.657	-0.571	0.652	0.080
1.500	0.057	86.22	161.63	-0.706	-0.649	0.628	-0.021
1.750	0.053	85.22	154.31	-0.755	-0.701	0.604	-0.098
2.000	0.045	85.73	148.25	-0.780	-0.736	0.582	-0.153
100 K ^a							
1.000	0.104	87.47	162.73	-0.470	-0.365	0.092	-0.274
2.000	0.045	85.73	138.29	-0.656	-0.611	0.063	-0.549

^aThe values of V and S for H_2 at 100 K are from H. Hemmes *et al.*, J. Phys. C: Solid State Phys. **19**, 3571 (1986).

the sandwich structure, is taken as zero, while the actual value should also be slightly higher. Corrections to both approximations would add negative values to the estimated ΔG , and the actual value of ΔG should thus be slightly more exothermic than our estimate.

The realization of such a trapping process would require the opening up of the interlayer distance in graphite, which is probably easier in graphite nanofibers than in a perfect graphite crystal with infinitely stacked graphene layers. The interlayer distance at ~ 5.4 Å is similar to the potassium intercalation compound, and over the years, many techniques have been developed to vary the interlayer distance, up to 9 Å, and to change the intercalate concentration.¹⁰ Furthermore, for an intercalated graphite, the volume difference $V_S - V_G$ would be reduced to almost zero, and correspondingly the ΔG value is determined by $-8pV_{H_2} + 8TS_{H_2}$, if ΔE remains small. In that case, confinement of H_2 becomes easier and can be achieved at 100 K with a reduced pressure of ~ 0.2 GPa.¹⁸

Assuming that a graphite with the right interlayer distance exists, we also examined the barrier for the diffusion of H_2 through the space between graphene layers. For that purpose, the number of H_2 in the upper layer is reduced to one, corresponding to 1/4 coverage, with the length of c maintained at the 2 GPa value. The barrier for moving this H_2 to a neighboring empty site is 0.1 eV, as calculated by the nudged elastic band method.^{19,20} It indicates the presence of a potential well for H_2 , with the bottom at the center and the barrier at the edge of the hexagonal ring. The confined structure is thus a metastable state in terms of energy, but a minimum in terms of enthalpy and free energy under sufficient external pressure. When one more H_2 is present in the upper level, corresponding to 1/2 coverage, the barrier height increases to 0.3 eV, due to the van der Waals repulsion between the two H_2 molecules. Once the interlayer distance is opened up by the initial trapping of a few H_2 molecules or other intercalates, diffusion of H_2 through the lattice is still possible, while in the process more and more H_2 are trapped in the hexagonal potential well.

It is worthwhile to note that the distances in the confined structure are in the van der Waals repulsive region. The H_2 to

graphene plane distance is 2.592 Å at 2 GPa, while the equilibrium distance of a physisorbed H_2 in such a configuration is 2.69 Å.⁵ Similarly on the H_2 plane, the distance between the centers of H_2 in neighboring sites is around 2.44 Å,

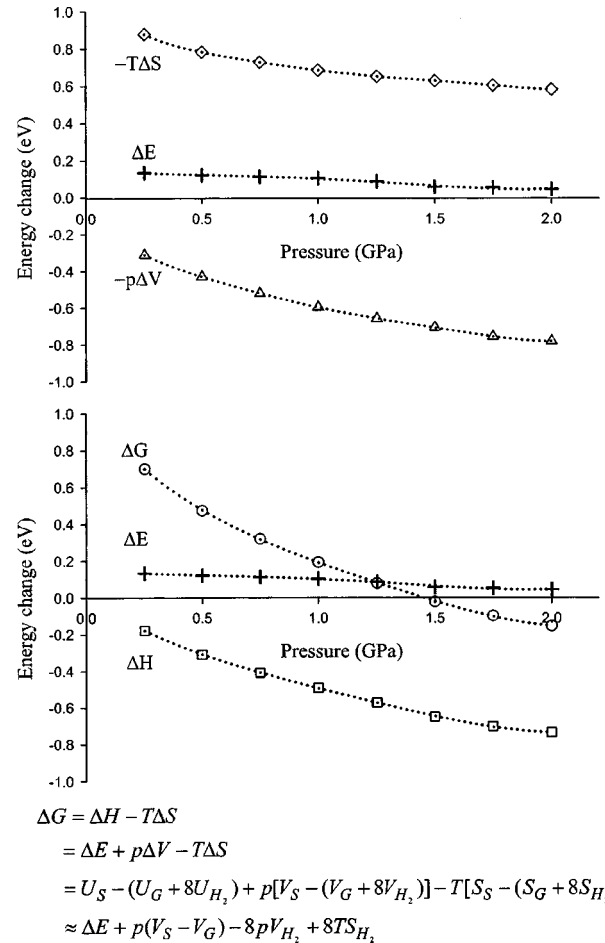


FIG. 2. The thermodynamic data for the trapping process as a function of pressure at 200 K, estimated by density-functional theory calculation and experimental equation of state for H_2 . Bottom: The approximate expression of the Gibbs free energy for the confinement process illustrated in Fig. 1.

which is substantially lower than the distance of ~ 3.3 Å in $\text{H}_2 \cdots \text{H}_2$ dimer,⁴ although the repulsive energy at 2.44 Å is only around 0.08 eV.^{4,21}

Dresselhaus and co-workers noted before that a H_2 molecule can be approximately treated as a sphere, and the lattice of solid hydrogen bears some resemblance to the graphite lattice in that it has a hexagonal close-packed structure, except that its lattice parameter is incommensurate with graphite lattice.² Specifically, the value of a , which is just the distance between the centers of two neighboring hexagonal rings and the distance between two neighboring H_2 discussed above, is 3.76 Å for solid hydrogen at 4.2 K, in contrast to the value of 2.46 Å in graphite. Our results indicate that mutual adaption between H_2 and graphite can be induced, with molecular hydrogen forced to fit its packing according to the graphite lattice, and at the same time the interlayer distance between graphite expanded, as the repulsion is overpowered by external compression.

However, it is not a simple matter of pressure. When p is increased from 1 to 2 GPa to ~ 20 GPa, V_{H_2} would be halved,¹⁸ making the $p\Delta V$ in Table I positive and the confinement unfavorable, as the term $V_s - V_g$ would not change much. The gigapascal and 100–200 K region of the H_2 phase diagram is special because the V_{H_2} term is large, even though H_2 is already in the condensed state. It is significantly larger than the expansion of the host lattice after the trapping of the guest (comparing the $8V_{\text{H}_2}$ and $V_s - V_g$ terms in Table I), and produces a $p\Delta V$ term strong enough to overcome both unfavorable energy and entropy changes. As the two important factors, volume and entropy, are intrinsic H_2 properties, H_2 is thus unique among gases in that the pressure could offer a powerful push for confinement. The study of H_2 as a guest in other types of host lattices should be very interesting, since it could be forced into narrow spaces upon compression and serve as an agent to induce structural changes in the host system.

Currently much attention has been given to the design of microporous crystals for hydrogen storage,³ by varying the chemical compositions, changing the pore sizes and increas-

ing surface areas. With the limited extent of electron cloud on H_2 , it is unlikely that there could be a significant increase in the energy gain for the physisorption of H_2 . However, pressure could add a new dimension in such efforts. For the process shown in Fig. 1, the storage capacity reaches an impressive value of 7.7% by weight, with a mole ratio of 1 between H and C atoms, for seemingly narrow and inhospitable cages sandwiched between two hexagonal carbon rings. With its impressive compressibility, H_2 should be quite adaptable to pore sizes and structures. But for practical applications, there must be a mechanism to lock the H_2 molecules in the cage before pressure and temperature are relaxed to ambient conditions.

The solid of H_2 is the archetypal quantum solid and an important model system in condensed matter physics.^{4,9} The two-dimensional array of H_2 confined between graphenes stands out in one important aspect: The orientation of H_2 is ordered. With all other carbon and hydrogen atoms fixed, the barrier for rotating one H_2 is calculated to be around 0.05 eV. In solid hydrogen, the orientation of H_2 in the hexagonal close-packed lattice is disordered, and a gradual transition to orientational order is completed only at a pressure of 140 GPa,²² the study of which has attracted much attention due to its fundamental importance.⁹ The confined H_2 in graphite should provide an interesting system for future spectroscopic studies.

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