

Molecular Mechanisms of Hydrogen-Loaded β -Hydroquinone ClathrateJohn L. Daschbach, Tsun-Mei Chang,[†] L. René Corrales,* Liem X. Dang, and Pete McGrail*Pacific Northwest National Laboratory, Richland, Washington 99352, and University of Wisconsin - Parkside, Kenosha, Wisconsin 53141**Received: May 2, 2006*

Molecular dynamics simulations are used to investigate the molecular interactions of hydrogen-loaded β -hydroquinone clathrate. It is found that, at lower temperatures, higher loadings are more stable, whereas at higher temperatures, lower loadings are more stable. Attractive forces between the guest and host molecules lead to a stabilized minimum-energy configuration at low temperatures. At higher temperatures, greater displacements take the system away from the shallow energy minimum, and the trend reverses. The nature of the cavity structure is nearly spherical for a loading of one, leads to preferential occupation near the hydroxyl ring crowns of the cavity with a loading of two, and at higher loadings, leads to occupation of the interstitial sites (the hydroxyl rings) between cages by a single H₂ molecule with the remaining molecules occupying the equatorial plane of the cavity. Occupation of the interstitial positions of the cavities leads to facile diffusion.

Introduction

The ability to store and release hydrogen safely under ambient conditions is a prerequisite for its widespread use as an energy source.¹ There are also energy density, total system mass, and cost criteria issues that must be satisfied to make hydrogen a viable option. There are currently many approaches being developed that include adsorption in nanostructured materials and storage in metal hydride compounds.¹ Clathrate materials are one attractive class of compounds that possess both nanoscale structure and a high degree of order. Organic clathrates often form stable compounds from a wide variety of precursors below their melting temperature at atmospheric pressure for many different guest atoms and molecules.^{2,3} A suitable organic clathrate for hydrogen storage would probably require multiple H₂ occupancy per cage, would need to be stable over a wide range of loading, and have a modest molecular weight. The H₂ guest occupancy will be a function of temperature and pressure, and with a combination of overpressure and temperature, the organic clathrate might be cycled between loading and discharge repeatedly. If a clathrate with H₂ as the guest was found with the correct properties, and it had facile transport characteristics, it would be a strong candidate as a hydrogen storage system. The potential to tailor the clathrate properties through synthesis or crystal engineering is an attractive asset for organic systems that can be assisted by molecular-level characterization obtainable from molecular dynamics simulations.

In this work, β -hydroquinone is used as a prototypical material for H₂ storage, where the effects of both multiple loading and intercage transport are studied. Previous theoretical studies of this system have validated the use of the empirical force field model used in this study.^{4,5} We note that H₂ enclathration in β -hydroquinone has not been demonstrated.

Using van der Waals statistical mechanical treatment of β -hydroquinone clathrates⁶ and a recent calculation of its formation energy with H₂ as the guest,⁴ we estimate the dissociation pressure at 298 K to be ~ 600 atm. Nonetheless, molecular dynamics (MD) simulations are not constrained by limitations in creating the clathrate structure with the chosen guest.

The first clathrate structural determination was by Palin and Powel in 1947 for the SO₂-containing β -hydroquinone structure,⁷ although the first use of the term “clathrate” followed shortly thereafter.⁸ In the β -hydroquinone clathrate, a cage is composed of six hydroquinone molecules in a roughly spherical shape with a radius of ~ 4 Å. The cages are terminated at the top and bottom by a ring of six hydroxyl groups, forming a crown. The cages are stacked, forming a channel, where a hydroquinone contributes only one hydroxyl to a crown between two cages. The other hydroxyl is part of a crown in a different channel. The resulting ratio of hydroquinone to cages is 3:1. The known β -hydroquinone clathrates have at most one guest molecule per cage that stabilizes the clathrate structure.³ In contrast, at room temperature, the empty β -hydroquinone structure is on the order of 0.2 kcal mol⁻¹ higher in energy than the more stable non-clathrate α -crystalline structure.⁹

Contributions of molecular motion, particularly molecular rotations or librations, to the thermodynamics of the system have been studied for the guest molecule in the β -hydroquinone clathrate.^{6,10,11} For small diatomic guests, the system behaves similarly to solvation in a nonpolar solvent,¹² with hindered rotational motion and constrained translational motion or “rattling” within a cage.¹¹ The energy of inclusion is on the order of 5 (O₂)¹³ to 15 (SO₂) kcal mol⁻¹.¹² The IR and Raman spectra of some linear triatomic guests have been interpreted as arising from nonrotating guests,¹⁴ but in contrast, heat capacity measurements indicate nearly free rotation in the clathrate cavity.¹⁵ For nonpolar molecules, guest–guest interac-

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tions are small, but there is evidence for nearest-neighbor interactions for hindered rotation of O₂ at low temperature.¹⁶

Theoretical classical statistical mechanical^{6,13} and quantum mechanical^{17–19} studies using rigid lattices and more recently using a flexible lattice employing empirical force field techniques^{5,10,20} were carried out to obtain thermodynamic properties. Formation energies, guest molecule minimum-energy positions, and lattice deformations for a wide number of guest molecules have been computed using the AMBER model potential functions.^{4,5,21} It was found that small guest molecules give rise to very small changes in the clathrate structure relative to the empty clathrate. Somewhat larger molecules generate small decreases in the cage size along the channel with the lattice being stabilized by the host–guest interaction. Larger guest molecules lead to lattice parameters very close to the empty reference structure, while even larger molecules expand the lattice along the channel. Molecular dynamics techniques have been used to study the clathrate hydrates with more than one guest, H₂ or N₂, per cage,^{22–26} but similar studies with organic clathrates have not been carried out. In the present study, we investigate the dynamics of the β -hydroquinone clathrate loaded with one to four H₂ molecules per cage.

Methods

The simulations were carried out using *AMBER 7* with the 99EP force field parameters.²⁷ The interactions between the hydrogen molecule and the hydroquinone molecule were of the Lennard-Jones form with parameters obtained from the literature.²⁸ The calculations were performed using the NPT ensemble with a step size of 2 fs and the SHAKE algorithm. Coulombic interactions were treated with particle mesh ewald with a real space cutoff of 11 Å.

The periodic system consists of 180 hydroquinone molecules in the β -hydroquinone clathrate structure in a rectangular supercell with initial cell dimensions of $x = 28.80$ Å, $y = 32.25$ Å, and $z = 27.52$ Å, consistent with the crystal unit cell determined from X-ray diffraction of the H₂S filled structure.²⁹ In the supercell structure, there are 12 channels with 5 cages per channel.

Each cage was initially loaded with identical configurations of one, two, three, or four H₂ molecules. The system loaded with one H₂ had the molecule at the center of the cage, whereas at higher loading, the molecules were placed on a ring with a 1 Å radius parallel to the cage equator. During the initial simulation consisting of a 400 ps dynamics run at 100 K, the H₂ molecules rapidly rearranged to their optimal configuration at that temperature. The output from the 100 K run was used as the initial configuration for other temperatures. Each system was equilibrated for 500 ps at the specified temperature followed by a sampling run of 1000 ps. In all cases, the systems were found to converge in energy and temperature in <50 ps. The energy convergence at 20 K was found to be better than 0.1% for all loadings.

Results

Table 1 lists the potential energy difference $\Delta E(n)$ per cage where n is the number of guest molecules and the energy difference is between the H₂-loaded clathrate and the metastable empty clathrate, where the isolated H₂ potential energy is zero.⁴ The four H₂ system at 300 K underwent a structural change during the last 400 ps, and thus for this system, the reported energy was averaged over a portion of the equilibration run and the early part of the sampling run prior to the catastrophe. For

TABLE 1: Potential Energy Differences $\Delta E(n)$ (kcal/mol-cage) between H₂ Loaded β -Hydroquinone and the Metastable Empty Clathrate Structure with $n = (1-4)$

temperature (K)	$\Delta E(1)$	$\Delta E(2)$	$\Delta E(3)$	$\Delta E(4)$
20	−2.5	−4.2	−4.7	−4.7
50	−2.5	−3.9	−4.3	−4.0
100	−2.4	−3.5	−3.4	−2.7
160	−2.4	−3.0	−2.4	−1.4
200	−2.3	−2.7	−1.7	−0.4
300	−2.2	−1.9	−0.2	2.3

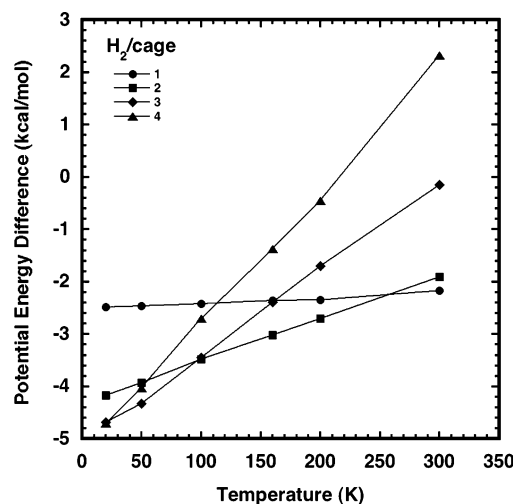


Figure 1. The potential energy difference between the metastable empty β -hydroquinone and occupied systems for different initial H₂ loadings per cage. The energy is per cage or three hydroquinone molecules.

all loadings and temperatures, with the exception of the metastable system at 300 K, the insertion energy is favorable.

The energy change of the singly occupied system at 20 K is lower than a previously reported value of -1.5 kcal mol^{−1} from an optimization calculation.⁴ This difference is attributed to refinements in the potentials²⁷ introduced after the earlier publication.⁵ The computed insertion energy for the singly loaded system is in accord with calculations for the heat of adsorption of H₂ into carbon slit pores, carbon nanotubes, or silica pores that range from 0.9 to 2.66 kcal mol^{−1} at 300 K.³⁰ The larger (more favorable) energies were obtained for materials with pore sizes between 6.5 and 7.6 Å, with the energies decreasing with increasing pore size, where the tighter pores lead to more favorable accommodation. The cage structure of β -hydroquinone with a diameter of ~ 8 Å is expected to enhance the interaction energy because the clathrate cavity provides a more confining structure as compared to a nanotube.

These data suggest β -hydroquinone could be loaded with multiple H₂ molecules at low temperature, although the decrease in energy is sublinear with load, a result of H₂–H₂ repulsive interactions. Achieving multiple loading is at first surprising because close-packed clusters of H₂ have volumes of 50.8, 63.5, and 69.8 cm³ mol^{−1} for two, three, and four molecules, respectively;³¹ whereas the computed ideal guest size in β -hydroquinone is 27 cm³ mol^{−1}, and the estimated maximum size is 46 cm³ mol^{−1}.⁴ In fact, the more open structure of the β -hydroquinone structure along the channel will not behave as a spherical cavity upon loading with multiple H₂. At loadings greater than one, the H₂ intermolecular repulsion necessarily moves the molecules away from each other and into closer proximity to the cage walls. The increase in the dispersion interaction with the cage therefore compensates for the repulsion, as has been noted for the H₂ clathrate hydrate system.³² An ab

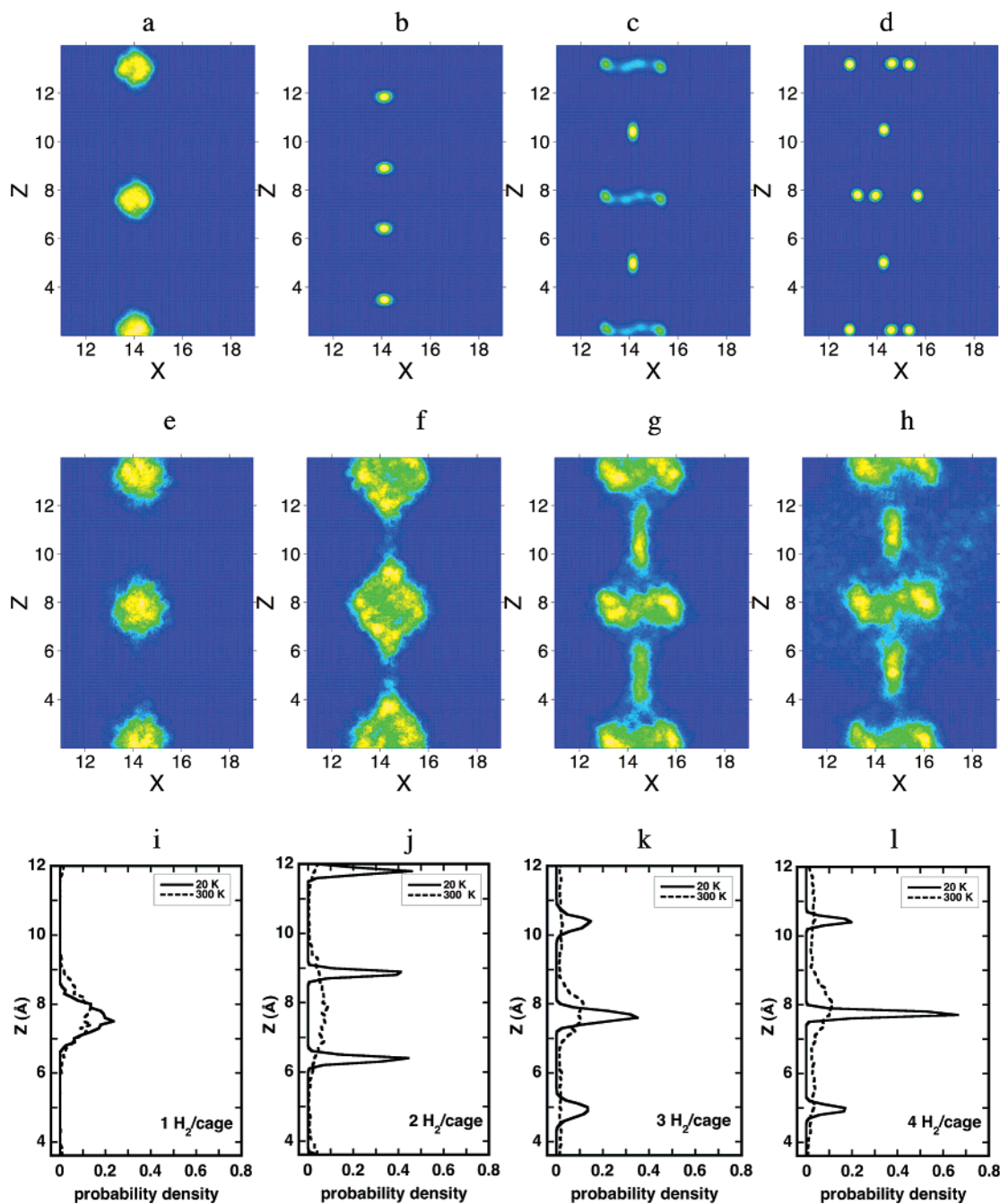


Figure 2. Two- and one-dimensional occupation cross sections are shown for the H_2 center of mass in a β -hydroquinone clathrate. The figures are for initial loadings of one (a, e, i), two (b, f, j), three (c, g, k), and four H_2 (d, h, l) molecules per cage where (a–d) are at 20 K, (e–h) are at 300 K, and (i–l) show both temperatures. The data are cage-centered along the z -axis (the channel) with a portion of the adjacent cages also shown, where the lower panels have a slightly narrower range along the z -axis.

initio study of hydrogen physisorption on graphene calculates that the center-of-mass H_2 –carbon interaction is attractive for $2.3 \text{ \AA} < R(\text{graphene}-\text{H}_2) < 5 \text{ \AA}$, repulsive for $R(\text{H}_2-\text{H}_2) < 3.4 \text{ \AA}$, and very weakly attractive at larger separation.³³ Therefore, within the β -hydroquinone, 8- \AA -diameter cage regions exist where H_2 –cage attractive forces are dominant.

Figure 1 illustrates the change in $\Delta E(n)$ with temperature where the rate of change is an increasing function of the H_2 loading. As the temperature is increased, the guest molecules are displaced away from their minimum-energy configuration. In contrast, in the single occupied cavity, the H_2 molecule effectively remains away from the repulsive regions of the cage.

Figure 2 shows false color representations of two-dimensional histograms of the position of the H_2 center of mass at 1-ps increments for a single clathrate channel projected onto the XZ

plane, as a function of H_2 loading at 20 K (a–d) and 300 K (e–h). Figure 2i–l shows the same data for the H_2 center of mass projected onto the z -axis for a single cage at 20 and 300 K for the same loadings.

At 20 K with a single H_2 molecule per cage, the data in Figure 2a and i show a nearly spherical distribution, consistent with the general treatment of the cavity as spherical.^{6,18} The width of the distribution is about 1 \AA , while at 300 K, the distribution broadens to about 1.5 \AA but retains the spherical form with a very slight elongation along the channel. The apparent shift of the distribution along the channel with increasing temperature is a result of expansion of the clathrate lattice.

The distribution differs with two H_2 per cage at 20 K where the H_2 molecules are displaced along the channel in tightly confined regions $\sim 2.5 \text{ \AA}$ apart. The H_2 intermolecular repulsion

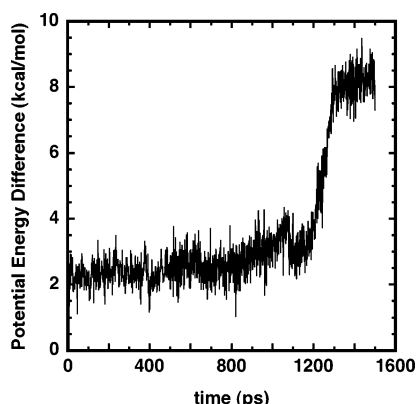


Figure 3. The potential energy difference at 300 K for a system loaded with four H₂ per cage relative to the empty structure at the same temperature.

at this distance is small, ~ 0.5 kcal mol⁻¹,³³ but considerably larger than kT (0.04 kcal mol⁻¹) and sufficient to localize the H₂ at opposite ends of the cage. At 300 K, the H₂ occupy a substantially larger region of space, as expected with the repulsion energy on the order of kT , and with considerable density at the cage center. At 300 K, a slight H₂ occupation density in the vicinity of the interstitial positions between cages is evidence for intercage diffusion. The diffusive motion is expected to be collective, proceeding via a flipping mechanism where a cage rapidly exchanges an encompassed H₂ for one at the interstitial position, keeping the cage occupation constant. Inspection of multiple trajectories indicates the average cage occupancy is always close to two with the flipping mechanism preferred.

For three H₂ at 20 K, the cage interstitial position has a high occupation density, with two H₂ occupying sites near the cage equator. There are six energetically equivalent sites around the equator due to the slightly puckered arrangement of the hydroquinones that make up the cage walls. Projections taken onto the *XY* plane, not shown, show that the occupancy is confined to the equatorial annulus, with a preference for the six sites. At 300 K, the distributions expand near the cage center and the interstitial sites. Trajectories confirm exchange between the equatorial and interstitial positions with enhanced diffusion between cages.

The configuration distributions are similar for the three and four H₂ per cage loadings, but the interstitial distribution is tighter for the latter along the *z*-axis as a result of having three H₂ in the vicinity of the equator. Projections onto the *XY* plane confirm that the three H₂ in a single cage are localized close to one or the other threefold symmetric selections from the six energetically equivalent sites. Heating the system to 300 K shows significant broadening of the distribution but less than that seen in the system of three H₂ per cage. There is occupation outside the cage regions, a consequence of the metastable nature of the system at 300 K, where a bubble or fracture in the crystal has developed into which H₂ can diffuse.

Figure 3 shows the trajectory of $\Delta E(4)$ at 300 K where the data starts 10 ps after increasing the temperature to 300 from 100 K. Between 10 and 800 ps, the $\Delta E(4)$ increases gradually from 2.27 to 2.55 kcal mol⁻¹, followed over the next 200 ps by a moderate fluctuation in energy. From 1100 to 1300 ps, $\Delta E(4)$ increases from 3 to 8 kcal mol⁻¹ and then appears to stabilize. Snapshots along the trajectory show a fracture forming along an *XY* plane with H₂ diffusing through the fracture where the remainder of the system retains the clathrate structure.

A system loaded with a single H₂ per cage behaves like a molecule solvated in a nonpolar solvent¹² interacting weakly with the cages structure as a nearly spherical potential. However, with increased loading, the asymmetrical nature of the cage is revealed where the H₂-H₂ repulsion is sufficient to localize the H₂ positions at low temperature. At high loadings of three and four H₂ per cage, there is a preference of having one H₂ located at the interstitial position. The presence of binding sites along the equator of the cage leads to a corrugation that is observed for high loadings of three and four H₂ per cage at 20 K H₂. Finally, it is found that diffusive transport along the channel generally proceeds via a flipping, or swapping, mechanism that involves the interstitial position composed of the hydroxyl hydrogen-bonded ring. In the three and four H₂ per cage systems, a molecule in the interstitial position is always present resulting in enhanced diffusion.

Molecular dynamics simulations suggest that it should be possible to load H₂ into the β -hydroquinone clathrate structure, possibly by loading the metastable empty structure at low temperature. The channel structure of the β -hydroquinone clathrate results in facile diffusion along one axis at sufficiently high temperature. This channeled structure, a feature of many organic clathrates,³ is attractive for a material used to reversibly store H₂. It is reasonable to think that with the ability to design organic clathrates with chemical constituents other than aromatic carbon³⁴ systems may be found which provide reversible H₂ storage under mild conditions.

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