Simulation of Capture and Release Processes of Hydrogen by $\beta$-Hydroquinone Clathrate

Martín Pérez-Rodríguez,* Javier Otero-Fernández, Antonio Comesañá, Ángel M. Fernández-Fernández, and Manuel M. Piñeiro*

Departamento de Física Aplicada, Universidade de Vigo, Campus Lagoas-Marcosende, E36310 Vigo, Spain

ABSTRACT: Using molecular simulation techniques, we investigate the storage capabilities of H$_2$ gas by the clathrate of hydroquinone (HQ). Quantum mechanics calculations have been used to assess structure and interactions at the atomic scale and molecular dynamics to model the HQ clathrate at successive equilibriums during the processes of capture and release of H$_2$, as well as the diffusion of H$_2$ inside the clathrate structure. The thermodynamic conditions of the simulations performed try to reproduce closely the corresponding experimental procedures, with results that are in good agreement with literature observed trends. The results obtained contribute to depict a more complete and better substantiated image of the mechanisms involved in stability and in the processes of capture and release of H$_2$ by the HQ clathrate.

1. INTRODUCTION

Hydrogen is undoubtedly an environmentally friendly source of energy because its oxidation product is water.\textsuperscript{1,2} Its high availability and almost zero emissions make H$_2$ one of the most desirable potential combustibles for the future. Nevertheless, its widespread use is still hindered by a number of challenging technical issues. Among them, the tremendous reactivity of H$_2$ with atmospheric oxygen must be outlined, limiting its implantation. Enhancing the safe storage, transport, and controlled release of H$_2$ represents then a crucial step to ensure its feasibility as combustible.\textsuperscript{3} Nowadays, there are three main methods implemented to store H$_2$. Gas compression at 300 bar and liquefaction at 20 K and 700 bar are the best two known ways. The problem with these strategies is that around 20 and 30–40% of the stored energy are lost during the condensation processes. In addition, these methods have an important associated risk because of the high pressures involved.\textsuperscript{4} The third method is the storage inside metal hydride matrices. The main issues involved here are the rather low mass storage ratio, about 2–5% (m/m), and the high cost of the metals used, such as La, Ti, Ni, or Pt. A feasible alternative, that a priori might combine safety and higher storing ratios, is the use of organic clathrates.\textsuperscript{5} See, for instance, the interesting review about hydrogen-storage materials by Schlapbach and Züttel.\textsuperscript{6}

Clathrates are nonstoichiometric inclusion compounds, with a solid crystalline lattice containing voids (cages) where small molecules can be trapped (enclathrated).\textsuperscript{7,8} The substance building up the solid lattice of the clathrate is called the host, and any substance trapped inside the voids of the lattice is denoted as guest. Usually, guests are not completely confined inside the cages, therefore the use of trapped term instead of confined, but have some spaces to move inside the host from one cage to another. Hosts can be of inorganic or organic nature. The best characterized family of clathrates is inorganic and corresponds to water. Water clathrates are commonly termed as hydrates,\textsuperscript{9} with the CH$_4$ hydrate being abundant in nature, appearing either along large areas below the seabed or as an important part of the soil in permafrost regions.\textsuperscript{10}

Among the organic substances able to form clathrates, the benzene-1,4-diol, commonly known as quinol or hydroquinone (HQ), is particularly interesting.\textsuperscript{11} From a theoretical perspective, this clathrate belongs to the category of H-bonded materials, and from a practical viewpoint, its high availability is a major competitive advantage. Nevertheless, the main reason supporting ongoing studies of HQ clathrates is their potential use as selective containers for substances of industrial or strategic interest. For example, the HQ clathrate could be used as a solid source of radioactive materials\textsuperscript{12} or for H$_2$ storage.\textsuperscript{13–16} The HQ clathrate with C60 as the guest was recently proposed for H$_2$ enhanced storage.\textsuperscript{17} Lee et al. have investigated the controlled separation of gas mixtures using clathrates,\textsuperscript{18–22} finding a remarkable selectivity of the HQ clathrate for CO$_2$ molecules. This fact suggests the application of HQ clathrates as CO$_2$ scrubbers\textsuperscript{23} for decarbonization-related processes. An extensive characterization, including structural and spectroscopic properties, phase equilibria, dynamics, occupation rate, and selectivity of CH$_4$ and CO$_2$ HQ clathrates, can be found in a dedicated series of works by Torrè et al.\textsuperscript{24–29}

The empirical formula for HQ clathrates in a unit cell is 3C$_6$H$_4$(OH)$_2$·G, where G is the guest molecule enclosed in...
the clathrate structure and $\theta$ the occupancy rate.\textsuperscript{25} HQ can occur at least in four known crystalline structures: $\alpha$-HQ is the stable form of pure HQ at ambient conditions;\textsuperscript{35} $\beta$-HQ is the structure of the lattice in clathrates,\textsuperscript{11,31} formed when HQ crystallizes in the presence of some potential guest; $\gamma$-HQ is metastable, and it is obtained by rapid evaporation in ether or sublimation;\textsuperscript{22,23} and finally, the $\delta$-HQ structure appears in pure HQ at high pressures.\textsuperscript{34}

As $\beta$-HQ is the structure of the stabilized clathrates, in the following we will concentrate in this structure containing H$_2$ as the guest molecule. More details related with the different forms of HQ and other guests, specially in the context of molecular simulation, can be found in a previous paper\textsuperscript{35} and the references therein. Although $\beta$-HQ is the clathrate structure, $\alpha$-HQ can also accommodate small guests as H$_2$, in a process called solubilization, with a maximum $N_{\text{guest}}/N_{\text{host}}$ molecule ratio of 1:18. The corresponding ratio for $\beta$-HQ with full single cage occupancy is 1:3. Three types of $\beta$-HQ have been investigated so far,$^{11,31,36,37}$ denoted, respectively, as $\beta$-HQ types I, II, and III. The type of structure depends to some extent on the process of formation, but it is mainly determined by the dimensions of the guest molecule, corresponding type I to the smaller guests, as is the H$_2$ case, and type III to the larger ones. Symmetry is reduced accordingly from rhombohedral R3 in type I to R3 in type II and P3 in type III. These structures are related by smooth transformations, and recrystallization is not required to transit from one type to another. If the guest is exchanged by another one with different dimensions, the lattice can adapt to the new molecules changing the type of structure, as discussed previously.$^{35}$

Classical molecular dynamics (MD) provides a theoretical framework for the study of thermophysical and phase equilibria phenomena and has been widely used in the investigation of some kinds of clathrates. In particular, there is extensive literature about clathrate hydrates (also called water clathrates), but this is not the case for HQ clathrates. For example, Burnham and English\textsuperscript{38} in a recent work use MD to benchmark several polarizable and nonpolarizable water models in the context of sI and sII type clathrate hydrates. Phase equilibria and stability have been determined using MD for methane\textsuperscript{39,40} or carbon dioxide\textsuperscript{41} hydrates. More extensive revisions of the field can be found in several reviews.\textsuperscript{42–44} There are many interesting research studies about hydrogen storage in type II clathrate hydrates using MD.\textsuperscript{45,46} Adding a promoter such as tetrahydrofuran was shown to improve the stability and the storage capacity of hydrates.\textsuperscript{47–50} Studies about calculations of the intercage hopping barriers of hydrogen molecules in clathrate hydrates were made using MD in combination with QM calculations.\textsuperscript{46,51,52} The first investigations that explored $\beta$-HQ thermodynamics with MD were published by Dang and Pettit,$^{53,54}$ followed by Santikary et al.\textsuperscript{55} These works considered noble gases enclathrated in a solid lattice of HQ. MD simulations of H$_2$ as the guest have also been published, and in particular, it is worth citing the work of Daschbach et al.\textsuperscript{56} More recently, quantum ab initio calculations have also been employed not only with small guests as H$_2$\textsuperscript{57} but also with Ne and HF.\textsuperscript{58}

The objective of the present work is to contribute to the understanding of the capture, storing, and release processes of H$_2$ in the $\beta$-HQ clathrate at the molecular scale. To this aim, electronic density functional theory (DFT) calculations, combined with the quantum theory of atoms in molecules (QTAIM) framework, have been applied to determine the paths for guest molecules to diffuse within the HQ lattice and the overall geometric structure. In addition, DFT will help us to calculate the charges and equilibrium geometric parameters of HQ\textsuperscript{35} and H$_2$ subsequently used in MD calculations. These MD calculations will be shown to describe adequately the dynamic processes of capturing and releasing the guest molecules and their internal diffusion. The simulations will follow closely the experimental setup whenever possible.

1.1. Nomenclature.
Clathrates are characterized by a crystal lattice with voids containing guests, as pointed out previously. Therefore, an intuitive way to name them is using the formula of the guest followed by the @ character and then the host formula. In this case, we will use H$_2$@HQ and will omit $\beta$ in the name of the structure because this is the stable form of HQ with H$_2$ as the guest at moderate conditions.

The geometry of the crystal voids in clathrates is well defined, and usually, some (or all) of them are communicated with others in their vicinity. Therefore, we will use the term void or cage interchangeably to express the space where the guest molecule gets trapped, and when a series of cages are connected in the same spatial direction, we will talk of a channel.

The spaces that the guest has to pass through when going from one cage to another are, in this case, very well delimited by a ring of OH groups forming a regular H-bonded hexagon (see Figure 1). Because of its similarity with a polygon, in addition to the name ring, we will also refer to it as face or hexagon.

The occupation can be described using several forms: the stoichiometric ratio ($N_{\text{guest}}/N_{\text{host}}$), mass ratio (w/w), or as we will prefer in the following, the number of guests by cage, $\theta$. The latter is perhaps the most intuitive and informative at the molecular scale because of the fact that a dissociated lattice will not conserve the cage structures but will have the same number of molecules and, therefore, the same corresponding mass.

Figure 1. Cross section of the $\beta$-HQ initial structure for our simulations, viewed along the z axis (lattice parameter $c$, perpendicular to the paper). Atoms are represented as spheres (C, black; O, red; and H gray) and H-bonds as dashed lines. Full molecules are included for better clarity. One individual unit cell is highlighted in the left bottom corner of the structure with crystal axes. Channels arrange in the z axis direction and are delimited by the OH hexagons connected by H-bonds. There are three channels per unit cell, shown with blue circles.
2. RESULTS AND DISCUSSION

2.1. QM Study of the Guest Channel. We carried out a QM study of the \( \beta \)-HQ channels, previous to MD simulations of release and capture processes. In this part, we calculated the overall geometry, the topology of the charge density, and the transition barriers between adjacent cages.

Initial coordinates for our simulations were taken from the crystallographic data of the \( \beta \)-HQ clathrate with CO\(_2\) as the guest, obtained experimentally by Torre et al.\(^{39}\) using X-ray diffraction. This structure pertains to the \( \text{R3} \) symmetry group, and its unit cell is characterized by the following parameters: \( a = b = 16.207 \pm 0.006 \text{ Å}, c = 5.780 \pm 0.002 \text{ Å} \). From the initial coordinates, we built up a convenient structure consisting of only one channel with four aligned cages. Two independent systems were actually built up, called, respectively, 1L and 2L. The first one is made of one layer of HQ molecules (338 atoms), and the second one consists of two concentric HQ layers (540 atoms). A representation of the 2L system is shown in Figure 2. The resulting structures were first optimized to obtain the optimal local geometry, fixing the position of the outer oxygen atoms. This way, it is possible to retain approximately the shape and volume of the crystal cells and to allow some degree of flexibility in the structure. This type of approximation was successfully applied to a system of two cages in the sI clathrate hydrate for studying the intercage transition of CH\(_4\) and CO\(_2\) in a previous work.\(^{60}\) Then, one of the central cages of 1L and 2L systems was filled with a single H\(_2\) molecule, with the aim to determine the optimal position of the guest. The resulting optimal geometry of just one occupied cage is illustrated in Figure 3.

After reoptimization, H\(_2\) is placed in the central part of the cage and the orientation of the molecule is not parallel to the channel axis, as it was observed with other similar systems, for example, CO\(_2\) in the water clathrate.\(^{61}\) The H\(_2\) center of mass is located at 212 pm from the OH ring planes and the H–H axis is tilted, oriented toward one of the O atoms in the ring, with about 47° of deviation from the channel axis. These results confirm that a non-negligible interaction between the guest and the host occurs, in addition to the dispersive one that maintains the guest trapped inside the cage. Orientation toward the O atom suggests that the cause of the interaction is the H\(_2\) multipole moment, as it was the case for CO\(_2\) in water.

With the aim of clarifying how this interaction affects the transition of a guest molecule from cage to cage, we studied the topology of the electronic density in the QTAIM framework and the energy barriers associated with the transition. The plane of the OH ring face was examined under the light of QTAIM, and critical points (CPs) and relevant paths were obtained. Results of our analysis are summarized in Figure 4.

Electronic density, \( \rho(x) \), is represented in sections along the plane of the OH ring for three systems: (a) without guest; (b) with an atom of H of the H\(_2\) molecule in the center of the ring; and (c) with the center of mass of H\(_2\) in the center of the ring. Conventional molecular models corresponding to these three situations are also represented in the upper right quadrant. CPs connected with the atomic nuclei (NCPs) are represented by bigger orange dots, with O nuclei in the vertex of the hexagon and H nuclei over the side between two oxygens. Smaller orange dots correspond to CPs connected with the center of a ring (RCPs). Blue dots represent the CPs connected with the central point of a bond (BCPs), the place in the bond path where the electronic density is a minimum, that is, the weaker part of the bond. Bond paths are depicted as bold brown lines. Contour lines of \( \rho(x) \) are in dark gray and gradient lines in light gray. It is clear from the figure that the transition of H\(_2\) produces a substantial modification of the electronic density distribution inside the ring, but the external part remains largely unaffected. Bond paths appear during the transition connecting O atoms in the ring with the H\(_2\) molecule. These paths, although not straight, are fully contained in the plane of the ring when an H atom is placed in the center (Figure 4b). In addition, even the part that corresponds to O atoms remains in that plane when the center of mass of H\(_2\) is placed in the center of the ring (Figure 4c). From the BCPs present in the figure, these bond paths continue above and below the plane of the paper toward each H nucleus in H\(_2\). These results confirm the existence of guest–host interaction and its nature. This interaction is internal to the cages and affects mainly the guest molecules, which was an expected result because of the relatively small mass of H\(_2\) compared with the mass of the cage and the small volume compared to the span of the hexagonal ring.

It is noteworthy that the departure from a straight line observed in the radial bond paths happens in the same direction for all oxygen atoms. It illustrates that the H nucleus of an OH group is not at the center of the bond path between two oxygens because of the H-bond. More interestingly, it also implies the coupling between all the OH groups forming the hexagonal ring, which is expected to enhance the stability of the structure. The turn orientation can be clockwise or anti-clockwise, and this fact cannot be determined a priori. Even

![Figure 2. Systems 1L and 2L used in DFT calculations shown along the z axis. C atoms are represented in black, O in red, and H atoms in gray. H-bonds are shown as red dashed lines. The O atoms fixed during geometry optimization are marked with a blue circle.](https://example.com/f2.png)

![Figure 3. One cage of the H\(_2\)@HQ clathrate structure, made up of 12 HQ molecules and 1 molecule of H\(_2\). C atoms are represented in black, O in red, and H in white. The guest molecule is represented as bigger white spheres. H-bonds are shown as red dashed lines. (A) Frontal view, approximately along the axis of the H\(_2\) bond axis, (B) lateral view.](https://example.com/f3.png)
both orientations can be interchanged directly by proton-transfer processes. Therefore, the use of some kind of chirality parameter in the description of these systems would be of interest. Using the same level of theory, we calculated the potential energy profiles for the transition of an H$_2$ molecule from cage to cage, following the path of minimal electronic density obtained from the previous QTAIM analysis. This path links the CPs connected with the center of a cage (CCPs) of adjacent cages, passing through the RCP of the OH ring in the middle of the cages, and results in an almost straight line in this case. Calculated values along the path of minimal density of charge are shown in Figure 5.

In the 1L system, the barriers obtained from the potential energy profiles are of the order of 0.1 eV for the H$_2$ most favorable orientation (normal to the ring plane) and of 0.12 eV for the less favorable one (H$_2$ parallel to the ring plane). In the 2L system, the values are higher, approximately 0.35 eV. The reason for this discrepancy is that in the 1L system, the fixed external O atoms restrict the mobility of all HQ molecules, but in the 2L system, because of the additional external layer, the molecules forming the channel do not have any atom fixed. This results in a slight contraction of the channel in the 2L system when compared with that in 1L.

Figure 4. Electronic density contour plot in the plane of the hexagonal face formed by the OH groups ring. Side views of the corresponding geometries are shown on the upper right quadrant of the figure. In the center of each one is the hexagonal face viewed laterally (red lines). Three systems are shown: (a) HQ without guest; (b) H$_2$ transiting across the ring, with one H atom in the same plane of the face; and (c) H$_2$ transiting, with the BCP of H$_2$ in the plane of the face.

Figure 5. Energy profiles, in electronvolt, of H$_2$ passing through the hexagonal OH ring in the 1L system, calculated at the PBE/6-31g* level. X axis is the position, in angstrom, normal to the plane of the ring. Hollow circles correspond to the H$_2$ molecule oriented perpendicularly to the ring plane, and solid circles correspond to H$_2$ oriented parallel to the ring plane.
To our knowledge, there is no previous literature in which the $\text{H}_2$ intercage transition was specifically calculated for $\text{H}_2@\text{HQ}$ systems using QM methods. Nevertheless, if we focus our attention on the particular subsystem implied in the barriers, we can put our results into perspective by comparing them with other theoretical calculations. The hexagonal face consists essentially of six OH groups linked with H-bonds. These H-bonds, as we have observed in previous paragraphs, are concerted, providing additional stability to the structure. The ideal OH hexamer defined in this way can be directly compared with the equivalent structure happening in the hexagonal face of a planar water hexamer. The water hexamers are well-known structures because of their ubiquity. For example, Hjertenæs et al. have recently studied the planar isolated water hexamer with the motivation of its application to clathrate hydrates. They use a post Hartree–Fock QM approximation: counterpoise-corrected coupled cluster including up to (perturbative) triple excitations CCSD(T) method in combination with the correlation consistent aug-cc-pVTZ basis set, which provides very accurate energy values. In addition, they benchmark several DFT popular functionals against their CCSD(T) reference values to assess the relative quality of them. Their reference value for the transition barrier of $\text{H}_2$ passing through the water hexamer is 18 kJ/mol (0.187 eV). Our values in the 1L system, from 0.1 to 0.12 eV, deviate between 46 and 36% from it, and our values for the 2L system (contracted channel) rise to about the double. This is a quite reasonable result, provided that among the other functionals in their study, for example, B3LYP presents an error in the transition barrier of 33.8%, BLYP-D2 of −22.2%, or M06-2X of −56.9%.

The planar isolated water hexamer is far from describing the complete structure of the channels in clathrates, though. In addition to it, we can also consider whole cages of clathrate hydrates, where we have a lattice structure, and about which the literature is abundant. As a reference, we can take the activation (transition) barrier of $3 \pm 1$ kJ/mol (0.3 eV) at 250 K, obtained experimentally by Okuchi et al. using the pulsed field gradient NMR technique. There are several computational studies reproducing this value, within the error margins. For example, Alavi et al. calculated $\text{H}_2$ cage-to-cage transitions through hexagonal faces (water hexamers) in rigid structures of sII clathrate hydrates obtaining transition barriers of $5−6$ kcal/mol (0.22–0.26 eV) using B3LYP and MP2 with 6-311++g(d,p) basis set. Román-Pérez et al. found a diffusion activation energy of 0.2 eV for $\text{H}_2$ using ab initio Van der Waals density functional formalism in equivalent systems. More recently, Trinh et al. obtained barriers of 10 kJ/mol (0.1 eV) with occupation $\theta = 1$ and 12 kJ/mol (0.12 eV) with occupation $\theta = 2$, using ab initio MD (BLYP with the local DZPM basis set) at 100 K and values of 22 kJ/mol (0.23 eV) and 29 kJ/mol (0.3 eV), respectively, at 0 K. Our values agree very well with all of those described for both 1L and 2L systems, although using a lower level of theory because of the big size of our systems. If we compare $\text{H}_2$ with larger guest molecules, the barriers obtained for CO$_2$ or CH$_4$ in clathrate hydrates were 0.59 and 1.16 eV, respectively, around an order of magnitude higher than the values discussed above.

2.2. MD Study of $\text{H}_2$ Release and Capture. For MD simulations, we started from the molecular model used in previous works to describe CO$_2$ and CH$_4$ HQ clathrate. This model uses OPLS-AA force field standard parameters but recalculates the equilibrium geometries of the molecules involved and their point atomic electric charges, as explained in more detail in Section 4.2. The $\beta$-HQ system used in simulations consists of $2 \times 2 \times 8$ crystalline unit cells, containing 12 channels of 8 voids long each, as shown in Figure 1. For modeling the bulk crystal, an infinite lattice was supposed using periodic boundary conditions (PBCs).

For simulating the release process with MD, a box was built by enlarging three times, with empty space, the HQ system box along the X coordinate (i.e., along the channels’ direction). This way, we are emulating the experimental vacuum applied to the clathrate samples for releasing guest gases. Our ideal vacuum would be equivalent to 0 bar in the initial state. The HQ inside the enlarged box was filled with $\text{H}_2$ molecules at a rate of one guest molecule per cavity. The resultant system was then allowed to evolve freely to simulate the migration of guests from inside the clathrate to the void portions of the simulation box at the chosen thermodynamic conditions, until the system reached the equilibrium. Following the experimental conditions for releasing, the simulations were performed at constant mole number, volume, and temperature (NVT or canonical ensemble) and within an interval of

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**Figure 6.** Three stages of the NVT simulations set corresponding to the $\text{H}_2$ release. The simulation box is represented by a blue rectangle and is viewed along the x axis (lattice parameter $a$). The clathrate is placed at the center of the box, surrounded laterally by empty spaces. From top to bottom: the starting clathrate structure completely filled at a rate of 1 guest per cage; system at 10 ns of simulation, where some molecules of gas left the clathrate; and end structure at 500 ns, where only a small percentage ($\approx 10\%$) of $\text{H}_2$ remains inside the $\beta$-HQ structure.
temperatures from 100 to 400 K. Successive equilibriums were initially spaced with a step of 10 K, and afterward, a denser mesh was applied, with a step of 5 K in the interval from 200 to 250 K to better describe the fastest part of the release process. In Figure 6, three stages of these simulations are represented, where the progressive migration of H₂ molecules is shown outside the β-HQ structure. Occupation rate values are represented in Figure 7 along with a fit to a logistic curve.

![Figure 7. Guest release process: occupancy rate (\(\theta\)) vs temperature (K). Points correspond to NVT simulations, and the solid line is a sigmoidal fit of them.](image)

The fitting serves both as a guide to the eye and as a mean to calculate the lower limit to occupation. The releasing process starts at about 170 K and stabilizes near 300 K, with a minimum occupancy rate of approximately \(\theta = 0.1\).

The capture process was modeled in a similar manner. In this case, it starts with an empty box of the HQ clathrate, in contact with a reservoir of H₂ gas molecules. We chose 96 molecules of gas to equate the number of crystal voids inside the HQ box. Following again the corresponding experimental procedure, simulations were performed at constant mole number, pressure (1 bar), and temperature (NPT or isothermal—isoobaric ensemble). The range of temperatures tested was from 100 to 300 K, and the simulation times were about 50 ns. Figure 8 shows the results of these simulations. As in the release process, the overall shape corresponds to a two-state system with a soft transition, reason why we fitted the data again to a logistic curve, also depicted in Figure 8. Gas capture starts at about 170 K and ends at approximately 210 K.

In addition to the processes of capture and release, we have studied the H—H orientation distribution inside the HQ clathrate channels. To do so, we perform a 200 ns NVT simulation at 250 K of an HQ box with occupation rate \(\theta = 1\). Then we used the MD trajectories to obtain the orientation histograms of the H—H bond with respect to the box coordinate axes \(X, Y,\) and \(Z\). \(X\) and \(Z\) axes are coincident with the crystal parameters \(a\) and \(c\), respectively, but \(Y\) is not coincident with \(b\). Nevertheless, we have preferred the box \(Y\) axis over \(b\) because of the symmetries of the system. \(a\) and \(b\) directions are equivalent, but \(Y\) is in the direction where the interchannel distance is minimum, whereas the distance available inside the channel is maximum (compare the \(b\) green arrow with a vertical imaginary \(Y\) axis in Figure 1). The results are illustrated in Figure 9 in three plots corresponding to each axis, where the orientation distributions were first normalized by the corresponding homogeneous distribution, and then to total probability that is equal to 1. The most prominent feature of this representation is the near equivalence of \(X\) and \(Y\) in spite of not being equivalent directions when considering the crystal symmetry. This implies that the orientations of the H₂ bonds are correlated mainly with the \(Z\) axis. In fact, the preferred orientation of the H₂ molecule is along the \(Z\) axis: we observe peaks at 90 in \(X\) and \(Y\) distributions corresponding to the peaks of 0 and 180 in the \(Z\) graph. Additionally, a region of diffuse peaks of around 30°–40° of tilt with respect to the main peaks is present in the three distributions. These secondary peaks are in good agreement with the calculated orientation using QM optimization as described previously, with the H₂ molecules pointing at the O atoms in the hydroxyl hexagons dividing the clathrate cages.

MD allows to study the diffusion of H₂ molecules inside the HQ clathrate through the determination of the mean square displacement (MSD). MSD is related with the diffusion coefficient \(D\) and can be obtained directly from the analysis of MD trajectories. Figure 10 shows the log—log plot of MSD with time at 300 K and at low occupancy rate \((\theta = 0.125)\), considering only one guest molecule per clathrate channel. The graph can be divided into three parts: the first one, below approximately 0.1 ns, corresponds to anomalous diffusion with almost zero slope, the second, in the central part of the graph, is a smooth transition between the two main regions, and the third, above 1 ns approximately, is a region of Fickian diffusion. This is the expected behavior of a system as the H₂@HQ clathrate, where the gas is free to move at small distances (inside each cage) but is confined at intermediate distances (the limits of the cage), and some friction appears at larger distances as a consequence of passing through the hexagonal faces. Therefore, at distances approaching the cage size, the behavior transits from an ideal gas regime to a Fickian regime. A very interesting and comprehensive study of this behavior in type II clathrate hydrate of H₂ has been presented by Cao et al. They use a two regime model and obtain \(D\) as one of the parameters of the fit. In our case, we selected the MSD values in the Fick regime to estimate the diffusion coefficient \(D\) directly from the slope of a linear fit. A dashed line in Figure 10 represents the curve predicted by the fit. The resulting diffusion coefficient is \(D = 8.49 \times 10^{-12} \text{ m}^2\text{s}^{-1}\). This value is of the order of magnitude of \(D\) values in the article of Cao et al.
and directly comparable with some of the particular cases they studied. At this point, this result came as no surprise, provided the notable similarities we observed between hydrate and HQ clathrates of H₂.

We have also noticed that the free evolution of the filled system at the occupation of θ = 1 led to an internal redistribution of the guests resulting spontaneously in cages with double occupancy. This was observed only occasionally, so we considered that the overall occupancy rate is not affected. Rozsa et al. have experimentally obtained double and triple occupation at pressures above 1.4 and 3 GPa, respectively. In the cited work, they also describe a nontrivial relation between the pressure of the cages and the number of occupation. These results are compatible with the observed behavior and suggest the convenience of future computational studies about the capacity of the HQ to enclathrate H₂ to assess the theoretical maximum and the dependence with pressure.

3. CONCLUSIONS

In this paper, we have studied the storage ability of H₂ by the HQ clathrate by means of molecular simulation. The particular objective is to assess the adequacy of the HQ clathrate as the H₂ storage medium, as a feasible alternative to other conventional methods. The results presented provide interesting hints, which need to be corroborated by further experimental studies, but undoubtedly evidence a promising alternative. Moreover, the results presented contribute to the understanding of the involved processes in H-bonded materials in general. As a previous step to perform MD simulations, the structure of the HQ clathrate containing H₂ was described within a quantum mechanical (QM) approach, including geometric parameters, effective point charges, and topological analysis of the electronic density. The HQ lattice is stable around the crystal voids and, therefore, around the channels resulting from aligned voids. The structure is flexible enough to allow the transport of molecules larger than H₂ along the channels, as it had been previously shown. Transition between different β-HQ structures is smooth, with the HQ lattice adapting to the guest shape. H₂ interacts with the lattice, having its equilibrium position center of mass displaced from the geometric center of the cage and being its axis oriented at about 47° from the channel axis, aligned with one of the O atoms defining the boundary between neighboring cages. We have also obtained a first estimation of the intercage transition barriers, about 0.1—0.34 eV depending on the rigidity of the channel, in good accordance with QM calculations for similar structures in vacuum and inside clathrate hydrates.

Using MD, we have observed the diffusion of H₂ inside the HQ lattice and also the occurrence of spontaneous double occupation per void during our simulations. The diffusion coefficient was estimated from MD through the guest determination of the MSD. This is a preliminary estimation, as this coefficient should be temperature- and occupancy-dependent, so its precise characterization needs further studies, applying the proposed methodology.

We have obtained the curves for capturing and releasing processes of H₂ by HQ, trying to reproduce the experimental conditions. These nonlinear curves resemble and are well fitted...
to logistic functions. The interval of temperatures, explored between the pressure ranges from vacuum to atmospheric pressure, is about 100 K for maximum release but only 40 K for capture, and there is a minimum occupancy value of about 0.1, in good agreement with experimental results in the literature. The processes of capturing and releasing the guest H₂ molecules are produced then within a narrow temperature interval, which is well below the temperature of dissociation of the clathrate structure in this pressure range. This fact underlines the ability of this material to be potentially used as the H₂ storage medium, with the possibility of operation in cycles.

The potential use of the HQ clathrate for the H₂ storage presents several advantages, as the high volumetric capacity, as well as the mild thermodynamic conditions involved in the processes of guest capture and release, with pressures near the atmosphere. Bearing these advantages in mind, our results support the feasibility of the HQ clathrate as a promising material for H₂ storage, representing an alternative to current strategies. Additionally, the presented results and conclusions emphasize the convenience of further advancing the search for optimal candidates among the family of H-bonded materials.

4. METHODS

4.1. QM Methods. For all QM calculations in this work, we have employed the Perdew, Burke and Ernzerhof (PBE) exchange–correlation DFT functional in combination with the 6-31g* Pople type basis set.

We have chosen PBE functional because of its good behavior in describing structures containing H bonds. It is a generalized gradient approximation type functional where the exchange and correlation contributions, in the original version, are directly included without any fitting parameter but derived from a Monte Carlo calculation. DFT is based on the theoretical work of Hohenberg and Kohn. Their theorems postulate that the electronic energy of the ground state can be fully described as a function of the electronic density (ρ(r)) alone. The types of calculations performed in this work make use of two recent approximations: independence of time and the Born–Oppenheimer approximation. The latter states that the movement of electrons can be considered independent of the nuclei, in virtue of the huge mass differences between them. The level of theory is limited to common hybrid DFT and a small Pople basis set because of the size of our systems. As we will see in more detail in Section 2.1, we considered two systems of 338 and 540 atoms, respectively. Yet nowadays, these numbers of atoms are huge to be properly treated with more accurate QM methods.

For the determination of the optimal transition paths and the study of the channel structures, the QTAIM framework has been used. QTAIM uses a topological analysis of the total electronic density to describe, for a given molecule, the particular role of its component atoms. In particular, the whole electronic density of the molecule can be obtained by the junction (not linear combination) of the corresponding atomic regions or basins. QTAIM rigorously describes characteristic points of the molecule, called NCP, BCP, RCP, and CCP, and also the paths connecting them, as, for instance, the bond lines, or as in our case, the transition paths between points of minimum energy. In QTAIM analysis, signature of the second derivatives (Hessian) of the electronic density is used to identify the type of CP. Electronic density, ρ, is a function of just the three space coordinates, ρ(x,y,z), and this fact permits to identify easily the CP types. Thus, if the point is a local maximum in all three (intrinsic) coordinates, it will be a NCP, if it is a maximum in two of them and a minimum in the other one, it will be a BCP, a minimum in two and a maximum in the other one, a RCP, and finally, a minimum in the three dimensions will correspond to a CCP.

QM calculations of the electronic structure were made using Gaussian 09 computational chemistry suite. QTAIM calculations were performed with Multiwfn tool, starting from wave functions previously calculated using Gaussian 09 at the level of theory described above. For the representation of molecules, we used VMD tool with the tachyon ray tracing system.

4.2. MD Methods. Release and capture of H₂ by HQ are dynamic processes where we can neglect overall effects of bond reordering or charge transfer, and therefore, they can be effectively modeled using MD. This technique is actually semiclassical, that is, it does not solve quantum equations but uses quantum foundations to set the effective interaction parameters. Cendagorta et al. reported that below 50 K, quantum effects are significant in H₂ hydrates, and at even lower temperatures, namely 25 K, quantum energy barriers for the diffusion of H₂ between adjacent cages overcome the classical ones. In our calculations, the range of temperatures for the release and capture starts at around 150 K, much higher than 50 K, and therefore, we consider that the classical treatment is appropriate here.

The force field used in this work for MD calculations is based in OPLS-AA force field, where the only difference is that geometric equilibrium parameters and partial charges were obtained for our particular structures using QM calculations. The partial charges of each atom were recalculated using charges from electrostatic potentials using a grid-based method scheme. The parameters for the HQ molecule have been described in detail in a previous work where the model was tested. The geometry and intramolecular force parameters were obtained automatically with the MKTOP utility and subsequently checked. Force field atom type, charges, and masses used are shown in Table 1. The H₂ model used here is rigid. It consists of two centers of mass located at the H nucleus positions and three centers of charge, calculated using the cited scheme, two of them of 0.4932e in the same positions.

Table 1. HQ Force Field Parameters

| atom (Figure 1) | element | OPLS atom type | recalculated charge | mass |
|-----------------|---------|----------------|---------------------|------|
| 1               | O       | opls_167       | −0.646863           | 15.9994 |
| 2               | C       | opls_166       | 0.385431            | 12.011 |
| 3               | C       | opls_145       | −0.149404           | 12.011 |
| 4               | C       | opls_145       | −0.29061            | 12.011 |
| 5               | C       | opls_166       | 0.385428            | 12.011 |
| 6               | O       | opls_167       | −0.646856           | 15.9994 |
| 7               | C       | opls_145       | −0.149377           | 12.011 |
| 8               | C       | opls_145       | −0.290596           | 12.011 |
| 9               | H       | opls_168       | 0.431862            | 1.008 |
| 10              | H       | opls_146       | 0.144041            | 1.008 |
| 11              | H       | opls_146       | 0.125532            | 1.008 |
| 12              | H       | opls_168       | 0.431853            | 1.008 |
| 13              | H       | opls_146       | 0.144037            | 1.008 |
| 14              | H       | opls_146       | 0.125522            | 1.008 |

OPLS-AA atom type, charge, and mass considered for each atom in the molecule topology are listed.
than the masses, and the third one of $-0.9864\epsilon$ in the center of the molecule at 74.14 pm of each nucleus. This way, the mass and total charge are the same as the neutral H₂ molecule and, at the same time, the quadrupole moment of the molecule is also described.

The standard values of charge in the original OPLS-AA force field are acceptable for macromolecules and, for these cases, the computational cost for recalculating them at the quantum level would be very high. The opposite is true for small molecules as H₂ or H₂O, the corresponding computational cost is very affordable, and the recalculated values improve the original molecular model significantly.

Simulations were performed either in the NVT (or canonical) ensemble, with fixed mole number, constant volume, and temperature, or in the NPT (or isothermal–isobaric) ensemble, with constant mole number, pressure, and temperature. Temperature was fixed with the thermostat introduced by Bussi et al. based in velocity rescaling. For the NPT simulations, pressure was kept constant by the Parrinello–Rahman barostat. The gas–clathrate interfaces in our simulation box are orthogonal to the $x$ axis, being the response to changes in pressure different in $x$ direction than in $y$ and $z$. To take this fact into account, we chose the semi-isotropic pressure coupling scheme, with double coupling constant in $x$ than in $y$, $z$ directions. The maximum time step in all calculations was 2 fs. As usual, the periodicity of the crystal bulk was modeled using PBCs and the minimum image convention. Cutoff values for Coulombic and Lennard-Jones intermolecular interactions were set to 1.1 nm, limited by the simulation box. Coulombic and Lennard-Jones interactions were evaluated using the four-order particle mesh Ewald method. To describe crossed interactions, we used the geometric mean of Good and Hope for equilibrium distances in the Lorentz–Berthelot scheme of combining rules.

All MD simulations have been carried out using GROMACS 5.1.4 software. Occupation rate values, shown in Figures 7 and 8, were obtained directly from the MD trajectory files. As there is no available standard tool in GROMACS for counting occupied sites, we coded an ad hoc tool in Python 3.6.4 using the module MDAnalysis.

### AUTHOR INFORMATION

**Corresponding Authors**

*E-mail: mmpineiro@uvigo.es* (M.P.-R.).

**Notes**

The authors declare no competing financial interest.

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