Dynamical cage behaviour and hydrogen migration in hydrogen and hydrogen-tetrahydrofuran clathrate hydrates

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Keywords: Molecular Dynamics, Hydrogen Hydrate, THF Hydrate, Breathing Modes, Migration

Classical equilibrium molecular dynamics (MD) simulations have been performed to investigate dynamical properties of cage radial breathing modes and intra- and inter-cage hydrogen migration in both pure hydrogen and mixed hydrogen-tetrahydrofuran sII hydrates at 0.05 kbar and up to 250K. For the mixed H₂-THF system in which there is single H₂ occupation of the small cage (labelled ‘1SC 1LC’), we find that no H₂ migration occurs, and this is also the case for pure H₂ hydrate with single small-cavity occupation and quadruple occupancy for large cages (dubbed ‘1SC 4LC’). However, for the more densely-filled H₂-THF and pure- H₂ systems, in which there is double H₂ occupation in the small cage (dubbed ‘2SC 1LC’ and ‘2SC 4LC’, respectively), there is an onset of inter-cage H₂ migration events from the small cages to neighbouring cavities at around 200 K, with an approximate Arrhenius temperature-dependence for the migration rate from 200 to 250 K. It was found that these ‘cage hopping’ events are facilitated by temporary openings of pentagonal small-cage faces with the relaxation and reformation of key stabilising hydrogen bonds during and following passage. The cages remain essentially intact up to 250 K, save for transient hydrogen bond weakening and reformation during and after inter-cage hydrogen diffusion events in the 200 to 250 K range. The ‘breathing modes’, or underlying frequencies governing the variation in the cavities’ radii, exhibit a certain overlap with THF rattling motion in the case of large cavities, while a there is some overlap of small cages’ radial breathing modes with lattice acoustic modes.

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To view the final edited and published work see http://www.dx.doi/10.1063/1.3677188
INTRODUCTION

Gas hydrates are crystalline inclusion compounds with a water lattice forming a periodic array of cages, with each cage large enough to contain one, or possibly more, gas molecules\(^{[1,2]}\). Given our interest in hydrogen and tetrahydrofuran sII hydrates in this study, a unit cell in sII\(^{[3]}\) hydrate consists of 136 water molecules forming sixteen small cages and eight large cages. The small cages are pentagonal dodecahedrons \((5^{12})\) and the large cages are hexaicosahedrons \((5^{12}6^4)\). Each \(5^{12}\) cage may contain one, or possibly two, \(\text{H}_2\) molecules, while each \(5^{12}6^4\) cage may contain a single THF molecule or up to four \(\text{H}_2\) molecules\(^{[4]}\).

Possible exploitation of sII hydrates for hydrogen storage has been studied extensively \(^{[5-7]}\). The extreme pressure needed for formation of pure hydrogen hydrate has been a limiting factor and has led to the study of mixed stabiliser-\(\text{H}_2\) hydrates\(^{[8,9,10]}\), in the hope that a stabilising compound will allow hydrate formation at lower pressures. Hydrates stabilised by THF have attracted interest in this respect as they have been reported to be stable at close to room temperature, and at much lower pressures than pure hydrogen-hydrate.\(^{[4,5,8,11]}\) Although the concept of large-scale seasonal storage is not new\(^{[12]}\), the proposal of using mixed THF-\(\text{H}_2\) hydrate for such efforts\(^{[13]}\) is attractive, as it is a completely reversible physical hydrogen storage material. However, the exact weight percentage of hydrogen in such a system is still disputed, with estimates ranging from 1-4 wt% \(\text{H}_2\)\(^{[8,13]}\) affecting its viability as a storage medium substantially. It is understood that hydrate structures which enable multiple occupancy of hydrogen will likely be required for clathrate hydrate to be a practical hydrogen storage medium. Ref. 14 presents part of a Tokyo-based feasibility study of large-scale \textit{in situ} storage of hydrogen in the form of clathrate hydrates, in which it is concluded that a large portion of the energy which could be extracted from hydrogen hydrate would be needed to power the necessary refrigeration. However, their industrial design does not address the possibility of the seasonal, geologic storage of hydrates, \textit{i.e.}, possible storage in large-scale underground caverns where lower temperatures may be achieved at a lower energy cost, for seasonal physical storage and reversible release.\(^{[14]}\)
The achievement of higher hydrogen concentrations for storage in clathrate hydrates is of interest to this study. In particular, the realisation and stabilisation of possible triply-occupied small cavities is a matter of direct relevance to the underlying goals of this work, given that very transient triple occupations were observed herein (*vide infra*), during ‘cage-hopping’ inter-cage diffusion events involving small cavities. The imposition of larger pressures would be required to achieve triple-occupancy in practice, given that single-occupation in small cavities is that which is observed most typically in the moderate, desired pressure range considered (up to ~50-70 bar);\(^{[13]}\) double occupation in small cavities at such pressures is now judged much less likely than single-occupancy;\(^{[13]}\) despite more initial suggestions that double-occupancy was likely.\(^{[5]}\) Naturally, the impositions of larger pressures, especially for large-scale, geologic-based, seasonal storage approaches, would not be considered economically feasible.

As a first step towards the goal of predictive, simulation-based design of mixed-H\(_2\) hydrates with desirable properties for possible industrial or geologic-scale storage properties, we have performed equilibrium molecular dynamics (MD) simulations to probe hydrogen migration between cavities of pure- and mixed-hydrogen clathrates. The transport of guest molecules within clathrates has been investigated for methane hydrates by Peters *et al.*\(^{[15]}\) via path-sampling simulation methods due to the large energy barriers for larger methane molecules’ inter-cage diffusivity making direct MD observation for such rare events unfeasible. Demurov *et al.*\(^{[16]}\) have also used similar simulation methods to probe guest-migration in CO\(_2\) hydrates. Saha and Deng\(^{[17]}\) have estimated from experiment that hydrogen diffusivities in H\(_2\)-THF hydrates are of the order of 10\(^{-18}\) to 10\(^{-19}\) m\(^2\)/s at 270 K and 65 bar. However, Okuchi *et al.*\(^{[18]}\) have used high-pressure diamond anvil cell NMR to probe surprisingly more rapid hydrogen transport in hydrates at 3.6 GPa, almost liquid-like in its characteristics and temperature dependence, with molecular rotation and diffusion contributing thereto. Senadheera and Conradi\(^{[19]}\) commented that their NMR line-shape results for enclathrated H\(_2\) motion appeared to suggest larger energy barriers towards inter-cage hydrogen diffusion vis-à-vis experimental observations of faster H\(_2\) diffusion in TDF/H\(_2\) D\(_2\)O clathrates of Okuchi *et al.*\(^{[20]}\)
and more in line with experimental data of hydrogen diffusion of Mulder et al.\cite{21} Bearing in mind these direct experimental observations of H$_2$ diffusion in clathrates,\cite{17,18,20,21} together with observations by Alavi and Ripmeester via electronic structure calculations to characterise energy barriers and diffusion pathways,\cite{22,23} and direct observation of inter-cage H$_2$ diffusion in classical MD simulations of Frankcombe and Kroes,\cite{24} there is an open question as to the extent of H$_2$ inter-cage migration and its dependence on temperature and cage occupation. Although the investigation of quasi-liquid-like hydrogen transport at high-pressure is of interest for molecular simulation,\cite{18,20} the goal of this study was to carry out direct, equilibrium MD calculations of pure- and THF-hydrogen hydrates in the general pressure range of practical interest for storage (~50 bar) and up to the temperature range of maximum stability (circa 250-270 K) for our systems to elucidate the fundamental mechanisms of inter-cage hydrogen transport, particularly with a view to assessing the effects of temperature and small-cavity occupancy thereon. The smaller size of hydrogen molecules vis-à-vis CO$_2$ and methane, coupled with the possibility of double-occupation in small cages (although, admittedly less likely than single occupation\cite{13}) leading to greater de facto local internal pressures (or chemical potential driving forces) therein, renders the possibility of direct MD sampling of inter-cage migration events, together with probing the frequency modes contributing to dynamical fluctuations in cage radii.

**METHODOLOGY**

A sII hydrate 1088-H$_2$0 molecule supercell, consisting of 2x2x2 unit cells, with the fundamental unit cell length ~17Å\cite{3} was constructed. The Bernal-Fowler rules\cite{25} were used in selecting the initial orientation of the water molecules so that the total dipole moment would be vanishingly small, and the Rahman-Stillinger procedure was used to achieve a small total dipole moment\cite{26}. Four systems were constructed, two of pure hydrogen hydrate (with quadruple occupation in the large cavities and single- and double-occupation in the small cages) and two of mixed THF/H$_2$
hydrate (again, with single- and double-occupation in the small cages by \( \text{H}_2 \)). These systems are described further in Table I, along with the naming convention. The guests’ initial positions in the system were generated by mass-centring, \textit{i.e.,} by placing the THF centre-of-mass (COM) at the geometric large-cage centres, and mass-centring the single \( \text{H}_2 \) molecules in the small cages (cf. Table I). For the cages containing multiple \( \text{H}_2 \) molecules, the molecules were arranged around the cage centre at energetically reasonable distances from each other and the cage.

[ insert Table I about here ]

The water model used was TIP4P-2005\textsuperscript{[27]}. For THF and \( \text{H}_2 \), the Alavi \textit{et al.} parameterisation\textsuperscript{[28]} was used for the charges and Lennard-Jones (LJ) interactions, along with geometric combining rules \( \varepsilon_{ij}^0 = (\varepsilon_{ii}^0 \varepsilon_{jj}^0)^{1/2}, \quad \sigma_{ij}^0 = (\sigma_{ii}^0 \sigma_{jj}^0)^{1/2} \),\textsuperscript{[29]} for water-guest and guest-guest LJ interactions, for consistency with Alavi \textit{et al.} Equilibrium MD simulations were performed using DL-POLY 2. Long-range interactions were calculated via the Smoothed Particle Mesh Ewald method\textsuperscript{[30]}, and a van der Waals cutoff distance of 10 Å. Rigid constraints for the \( \text{H}_2\text{O} \), THF and \( \text{H}_2 \) were employed which implement the NOSQUISH algorithm of Miller \textit{et al.}\textsuperscript{[31]}, using velocity-Verlet\textsuperscript{[32]} integration. 100 ps of Nosé-Hoover\textsuperscript{[33]} NVT simulations were run at 150, 200, 215, 230 and 250 K for each system with a 1 fs time-step, and a rather mild 0.5 ps thermostat relaxation time. These were followed by 100-400 ps NPT\textsuperscript{[34,35]} runs at 0.05 kbar, with thermostat and barostat periods of 0.5 and 2 ps respectively, to allow each system volume to settle. NPT production runs, with the same thermostat and barostat, were performed on the relaxed systems for a further 100 ps with a 2 fs time-step. These systems were then used to study hydrogen migration and the dynamical behaviour of cage radii.

In order to assess approximately the melting points of the four systems, a roughly equal number of liquid-state water molecules were also placed in contact with the 2x2x2 unit cells in a manner described in previous work for two-phase methane hydrate interfacial systems,\textsuperscript{[36]} and NPT
simulations used to relax the system pressure to 0.05 kbar for 500 ps at an initial temperature of 240 K. Following this, various NVT runs were performed at 5 K intervals up to 290 K for up to 1.5 ns to assess if the hydrate system remained intact, as gauged by use of the geometric Báez-Clancy criteria.[37] Briefly, these distinguish between the hydrate, ice lattices, and liquid-phase, and involve the calculation of an angular order parameter to quantify the tetrahedral nature of bonding for nearest-neighbour water molecules, followed by the recognition of five-membered rings of water molecules present in hydrate structures but absent in liquid water and ice. This allows a preliminary classification of hydrate-, ice- and liquid-like molecules, which is refined further by grouping hydrate-like molecules into clusters and taking into account the identities of neighbouring water molecules. It was found from this approximate approach that the melting points of 1SC4LC, 2SC4LC, 1SC1LC and 2SC1LC systems were 257±5, 252±5, 287±5, 282±5 K. This compares to a melting point for ice Ih of around 250 K using TIP4P-2005.[27] The presence of THF appears to lead to substantially greater stability, which was also observed by Frankcombe and Kroes;[24] the 1SC4LC result of 257±5 K is also consistent with the TIP4P-2005 result of Ref. 24. The double occupation of the small cavity also leads to a lower melting point, due to thermally activated vibrations of both hydrogen molecules in the smaller cages leading to greater collisions with the surrounding water molecules. In any event, all of the systems are stable up to 250 K.

It should be pointed out that the use of classical MD to treat hydrogen molecules’ motion, in particular, below around 150 K is approximate in nature, and the lack of provision of quantum effects like zero-point H$_2$ cage-rattling motions and quantisation of H$_2$ rotational motion becomes less satisfactory at lower temperature. Bačić et al have studied these effects in much detail for hydrogen-containing clathrates,[38-44] including explicit path-integral MD simulation.[42] Based on these studies, it should be stressed that the classical MD results below 150 K need to be interpreted with some caution due to the limitations of classical MD to describe accurately H$_2$ motion at low temperatures. Therefore, the present work does not report any observations below 150 K. Indeed, although the current study attempts to gain a qualitative understanding to radial breathing modes
and hydrogen diffusion and the dependence on temperature, it would be inappropriate to conclude that the results are quantitatively accurate even at 150 K. Although this is less than ideal, it is not as much of a drawback given that the current study aspires towards a qualitative understanding of the mechanisms of dynamical cage behaviour.

To investigate dynamical behaviour of the cage radii, normalised auto-correlation functions of the variation in each radius \( r_i(t) \) for cage \( i \) vis-à-vis that particular cavity’s underlying simulation time-averaged radius \( \bar{r}_i \) (i.e., \( \Delta r_i(t) = r_i(t) - \bar{r}_i \)), were computed and averaged, and termed RACFs; they were subsequently averaged across each cage type (small and large), i.e.,

\[
RACF_T(t) = \frac{\langle \Delta r_i(t) \Delta r_i(0) \rangle}{\langle \Delta r_i(t) \Delta r_i(0) \rangle_T}
\]  

where the type ‘T’ is either large or small. The instantaneous radius \( r_i(t) \) for cage \( i \) was defined as the averaged distance of each constituent water molecules’ centre-of-mass from the hypothetical ‘centre-point’ of each cage, with the central point \( r_C(t) \) computed from the sum of the constituent water molecules’ centres of mass, i.e.,

\[
r_{C,i}(t) = \sum_{j=1}^{N_{T,i}} r_{j,i}(t)
\]  

where \( N_{T,i} \) denotes the number of constituent water molecules in the cage \( i \) of type T (i.e., 20 for the small cavity and 28 for large cages). The cages were found to be stable in structure throughout and the identity of the constituent water molecules remained constant. The frequency modes of the RACFs contributing to motion are revealed via their power spectra (Fourier transforms).

**RESULTS AND DISCUSSION**

The average cage radii are reported in Table II for each system, along with standard errors. As expected, the radii increase with increasing temperature, as do the corresponding standard errors. As mentioned previously, the cage structures were found to remain intact throughout the simulation, with the same identity of constituent water molecules in each case. The radii of the doubly-occupied small cages is around 1.5 - 4.5 % larger than their singly-occupied counterparts,
with the disparity increasing at higher temperatures; the corresponding result is about 1 - 2 % for large cavities. The general lattice expansion at higher temperatures (as characterised by decreasing overall system densities\[^{45}\]) leads to a marginally greater local expansion in doubly-occupied small cavities, albeit limited by the lattice and cage structures remaining intact. The cage radii are in good agreement with respective experimental data for small and large sII cage radii of 3.90 and 4.68 Å\[^{46}\] and 3.91 and 4.73 Å.\[^{47}\] However, this experimental data is close to the 250 K temperature range, and is not specifically for pure- or THF-mixed hydrogen hydrates; therefore, quantitative comparison with the cage radii in Table II is necessarily limited.

[ insert Table II about here ]

The power spectra of the RACF are depicted in Fig. 1, to examine the underlying frequency modes of variation in cage radii at 200 K; there was not found to be a particularly strong temperature dependence in the spectra in the 200-250 K range. In some cases, the various peaks are not so distinct, so some of the arguments and conclusions are necessarily tentative. Nonetheless, we believe that it is worthwhile attempting to characterise them. The principal modes at \textit{circa} 38 and 68 cm\(^{-1}\) for the small cavities in the doubly-occupied mixed H\(_2\)-THF system (2SC 1LC), with a shoulder at 100-115 cm\(^{-1}\), are shifted downwards in frequency by around 30 % vis-à-vis the corresponding modes in the singly-occupied THF-H\(_2\) hydrate (1SC 1LC) (cf. Fig. 1a); the double occupation of the small cage in this case serves to lead to closer hydrogen-lattice contact and reduces the frequency of cage ‘breathing’. The shoulder in the 100-115 and 115-150 cm\(^{-1}\) range manifests, to some extent, interaction of the small cages’ radial modes with acoustic modes of the lattice translational density of states (\textit{i.e.}, of water oxygen atoms from power spectra derived from their velocity ACFs\[^{45}\]). However, these would also be expected to reflect overlap with rattling and O-O modes (which may be gleaned from the power spectra of velocity ACFs\[^{45}\]) – it is difficult to isolate conclusively which type of overlap of the small cages’ radial modes dominates. For the
pure-hydrogen hydrates, the small cages’ radial mode is present at around 170 cm$^{-1}$ in the singly-occupied case (1SC 4LC), but effectively absent, conspicuously, for the double-occupation case (2SC 4LC); this arises due to H$_2$-H$_2$ and closer hydrogen-lattice interactions leading to an increase in frequency above this of small-cage hydrogen rattling modes (as determined from respective VACF spectra$^{[45]}$). Selected simulations were also carried out with empty small cages, and similar results were obtained for the small singly-occupied cages’ radial mode at around 170 cm$^{-1}$ (vide supra); this is due to the more limited interaction of a single hydrogen molecule with the cage (unlike for double occupancy). Similar shoulders in the in the 100-115 and 115-150 cm$^{-1}$ range were also observed for empty small cavities.

[ insert Figure 1 about here ]

In the case of the large cages, there is more evidence of coupling of radial breathing modes to THF rattling modes in the case of mixed THF-H$_2$ hydrates at 90-110 cm$^{-1}$ (cf. Fig. 1b); the primary peaks at around 35 and 46 cm$^{-1}$ for double- and single-occupation of the small cages (2SC 1LC and 1SC 1LC, respectively) arise due to a similar downward shift in radial frequency for more intimate hydrogen-lattice contact (and the concomitant effect, or coupling, of radial modes with respect to large cavities). In the radial modes of the pure-hydrogen system’s large cavities, there is no evidence of any such frequency modes due to the absence of THF molecules.

Hydrogen migration events were monitored by consideration of the evolution of the distance of each hydrogen molecule from the instantaneous centre of each cage of which it was part at the beginning of the simulation. Once this distance exceeded the cage radius, this was classified as a ‘migration event’. However, the term ‘migration’ in this context may be somewhat misleading, as much of these events were intra-cage: the hydrogen molecule was often observed to move to, say, the pentagonal face of the small cages and stay in that region for a short time (a few picoseconds or less), and subsequently move back towards the centre of the cavity. Occasionally, however, inter-
cage migration events take place, where a hydrogen molecule will move to the face of small cavity, and after some period of up to several picoseconds, one of the stabilising hydrogen bonds of the water molecules in the face will weaken to allow a temporary opening of the face to allow passage of the hydrogen molecule to a neighbouring cage. Such ‘cage-hopping’ events were observed in this study only from and to doubly-occupied small cavities, leaving some small cavities temporarily singly or triply occupied. Naturally, this is very system and temperature-dependent. One example of such a relatively rare event in the mixed THF-H$_2$ hydrate at 200 K is depicted visually in three snapshots in Fig. 2. In Fig. 2a, the pentagonal face has opened, with weakening and temporary breakage of a stabilising hydrogen bond, while this face has been restored in Fig. 2c following passage of the hydrogen molecule to another small cavity. In 2SC 1LC mixed systems (and for the pure-hydrogen 2SC 4LC system), it was found that inter-cage diffusion just took place from and to small cavities.

[ insert Figure 2 about here ]

No diffusion events into large cavities, whether occupied by hydrogen molecules only in pure hydrogen hydrates or by THF molecules in mixed hydrates, were observed. Given the observed hydrogen diffusion at and above 200 K in doubly-occupied small-cavity systems, we carried out a simulation at 250 K with double occupation of the small cage and half of the large cavities containing THF, with the other half containing four hydrogen atoms, labelled as 2SC $\frac{1}{2}$(1LC) $\frac{1}{2}$(4LC). No hydrogen diffusion into cavities containing THF was observed.

To quantify the lifetimes of intra- and inter-cage migration, normalised probability distributions of these lifetimes are provided in Fig. 3 for the systems with doubly-occupied small cages at 200 and 250 K, measured to the time to the end of the 100 ps production run in terms of the distance from the centre of the cage of origin having been exceeded per event (given that the particular hydrogen molecule may return to the centre of the cage prior to perhaps returning the small cavity’s face and
either returning again to the cage centre or migrating to a neighbouring cage); the lifetime is in some sense artificial in that the guests may not return to their cage of origin post inter-cage migration and may migrate subsequently to other cavities. As mentioned previously, the shorter lifetime events (up to a few picoseconds) reflect hydrogen molecules at the very edge of the cavity, i.e., giving rise to partial distortion of the faces with the faces' hydrogen bonding structure remaining intact, while longer-time events are inter-cage migration events, which tended to be irreversible in this study. The preponderance of short-time intra-cage events is observed to lessen somewhat at higher temperatures, as there is a growing probability of ‘cage-hopping’ propagating through small cavities in the lattice (cf. Fig. 3). If one counts the number of such inter-cage events over longer 500 ps simulations, they were observed to exhibit an approximate Arrhenius-type of temperature dependence (i.e., $\exp \left( -E_a/RT \right)$) with activation energies of circa 21.2 and 25.6 kJmol$^{-1}$ for doubly-occupied mixed THF- and pure-H$_2$ hydrates (2SC 1LC and 2S 4LC), respectively, with respective 95 % confidence intervals of ± 6.2 and 7.6 kJmol$^{-1}$ from four-point regression fits (200 to 250 K); these are shown in Fig. 4. It can be seen that the number of inter-cage diffusion events is larger in the pure-hydrogen hydrate than the mixed hydrate. Reference to Fig. 1b shows a greater ‘shoulder’ of large-cage breathing modes in the 160-200 cm$^{-1}$ range for the 2SC 4LC pure-hydrogen system vis-à-vis the 2SC 1LC mixed system. It would appear that the greater extent of these more rapid cage-breathing modes in the large cages occupied by hydrogen molecules may lead to a greater propensity for weakening of hydrogen bonds in the adjoining doubly-occupied small cavities, facilitating a larger extent of inter-cage migration events.

[ insert Figures 3 and 4 here ]

It has been found by Alavi and Ripmeester$^{[22,23]}$ from electronic structure calculations that activation energies for hydrogen diffusion were 23.7 – 28.4 kJmol$^{-1}$ for small-cavity transfer in singly-occupied small-cage systems. Frankcobe and Kroes$^{[24]}$ also observed an activation energy of
32 ± 12 kJmol⁻¹ from MD for the temperature dependence of hydrogen diffusion in singly-occupied small-cage hydrogen hydrates. Both of these results are consistent with a temperature-dependent activation energy of 25.6 ± 7.6 kJmol⁻¹ observed here for 2S4LC systems.

**CONCLUSIONS**

In this study, equilibrium MD simulations were carried out to investigate cage radial breathing modes and (inter-cage) hydrogen migration in both mixed- and pure-hydrogen hydrates at 50 bar and up to 250K. For double occupation in the small cage, there is an onset of inter-cage H₂ ‘hopping’ events from and to small cages at around 200 K, with an approximate Arrhenius temperature-dependence for the migration rate from 200 to 250 K. It was found that these ‘cage hopping’ events are facilitated by temporary openings of pentagonal small-cage faces with the relaxation and reformation of key stabilising hydrogen bonds following passage. Up to 250 K, the cages remain essentially intact, however, save for transient passages in the 200 to 250 K range, and the ‘breathing modes’ of underlying frequencies governing the variation in the cavities’ radii show overlap with THF rattling motion for large cavities, and a certain overlap with lattice acoustic modes for small cavities.

**ACKNOWLEDGEMENTS**

This material is based upon works supported by the Science Foundation Ireland (SFI) under Grant No. [07/SRC/B1160].
REFERENCES


46 E.D. Sloan, Jr., Clathrate Hydrates of Natural Gases (Marcel Dekker, New York, 1990).
Table I. The four systems used: 1SC 1LC – singly occupied small and large cages; 2SC 1LC – doubly occupied small cage and singly occupied large cage; 1SC 4LC – singly occupied small cage and quadruple occupation in the large cage; 2SC 4LC – doubly occupied small cage, quadruple occupation in the large cage.

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<th>T (K)</th>
<th>Small 1SC1LC</th>
<th>Small 1SC4LC</th>
<th>Small 2SC1LC</th>
<th>Small 2SC4LC</th>
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Table II. Large and small cage radii (Å).
FIGURE CAPTIONS

Figure 1. Power spectra of the normalised radial variation ACF at 200 K for (a) small, and (b) large cavities.

Figure 2. Depiction of the cage-hopping of a (blue-coloured) hydrogen molecule after (a) 76, (b) 77.6, and (c) 84.8 ps, from a doubly-occupied small cavity in the 2SC1LC system at 200 K, showing only the cavity’s set of constituent water molecules and the two guests. The temporary opening of the pentagonal face on the right is seen to facilitate migration to a neighbouring cavity – it has opened somewhat in step (a) and has closed again in step (c). This particular cage-hopping event is irreversible, giving a ‘lifetime’ to the end of the 100 ps production run of around 23 ps, the signature of which may be seen in Fig. 3. Hydrogen bonds are depicted by dotted lines.

Figure 3. Normalised probability distributions of the intra- and inter-cage migration events’ lifetimes (measured to the end of a 100 ps production run in terms of the distance from the centre of the cage of origin having been exceeded). The shorter lifetime events (up to a few picoseconds) reflect hydrogen molecules at the very edge of the cavity, i.e., giving rise to partial distortion of the faces with the faces’ hydrogen bonding structure remaining intact (labelled as intra-cage migration) which may act as a pre-cursor to eventual face-distortion and subsequent migration therefrom, whilst the longer-time events tend to be irreversible inter-cage migration events: here, the guests have not returned to their cage of origin and the lifetime is in some sense artificial, in that they may migrate subsequently to other cavities.

Figure 4. Arrhenius plots of the number of inter-cage diffusion events over 500 ps simulations between 200 and 250 K for the systems with doubly-occupied small cavities.
**Fig. 1a** Small, 200 K

**Fig. 1b** Large, 200 K
Fig. 2a  76 ps

Fig. 2b  77.6 ps

Fig. 2c  84.8 ps
Fig. 3
Fig. 4