Electronic-Structure Calculations

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Hydrogen-Gas Migration through Clathrate Hydrate Cages**

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Over the past few years, there has been considerable interest in using clathrate hydrates for H_2 storage. Pure H_2, pure D_2, and mixed H_2/THF structure-II (sII) clathrate hydrates have been synthesized. Open questions in these studies are whether the H_2 guest molecules can migrate between the clathrate cages in these materials and whether H_2 is released from the clathrate once it is formed. In this work, we use electronic-structure calculations to estimate the energy barriers to the escape of H_2 guest molecules from the pentagonal and hexagonal faces of the cages of the sII clathrate hydrate. The energy barriers are used to estimate the escape rates from the cages with a simple Arrhenius expression. Tunneling contributions to the escape rate are also considered. These studies indicate that H_2 migration through clathrate hydrates can occur and that kinetic considerations can be very important in determining the structure and H_2-storage capacity of clathrate hydrates.

The H_2 sII clathrate hydrate can be synthesized by pressurizing H_2 gas and water at 180–600 MPa at temperatures approaching room temperature.[1,2] The clathrate is stable, at least kinetically, at 1 bar at temperatures lower than 140 K.[3] The sII clathrate hydrate has a cubic unit cell (space group $Fd3m$) containing 136 water molecules, which form a framework with 16 dodecahedral and 8 hexakaidecahedral cages. The small dodecahedral (5^{12}) cages have 12 pentagonal faces, and the large hexakaidecahedral ($5^{12}6^4$) cages have 12 pentagonal and 4 hexagonal faces arranged in a tetrahedral geometry about the cage centre.[4] The cavity radii of the small and large cages are 3.91 and 4.73 Å, respectively.[5]

The experimentally determined H_2/H_2O mole ratios in the sII clathrate range from 0.35 to 0.47 which indicates that the cages are occupied by multiple H_2 molecules, although the occupancy numbers have been the subject of some debate. The occupancy of the large cages in the H_2 and D_2 clathrate hydrates is taken to be four.[1,6] Initial experiments using direct microscopic volumetric measurements and Raman vibron intensities indicated the double occupancy of the small cages;[1] however, separate models derived from neutron diffraction studies of the D_2 sII clathrate hydrate suggested that the small cages are only singly occupied.[6] Upon heating the clathrate hydrates above 140 K, changes are detected in the relative intensities of the Raman peaks for H_2 guests in the small and large cages and in the occupancies determined from neutron diffraction for D_2 guests in the large cages.[6]

In the binary H_2/THF sII clathrate hydrate, the THF molecules occupy the large cages, and the H_2 molecules occupy the small cages.[7] Integration of the H_2 signal in the ^{1}H NMR spectrum and volumetric analysis of the hydrate dissociation products have been used to assign single occupancy (or lower) to H_2 in the small cages.[7] An adsorption study of the THF sII clathrate hydrate[8] and a neutron diffraction study of the binary D_2/[D_8]THF sII clathrate hydrate[9] also indicated a singly occupied small cavity. Studies of H_2/THF sII clathrate hydrates with THF contents insufficient for full occupancy of the large cages have shown evidence of both double occupancy[10] and single occupancy[8] of the small cages by H_2.

Statistical-mechanical models with ab initio quantum-chemical cluster calculations,[11] ab initio calculations with periodic plane-wave basis sets,[12] lattice dynamics,[13] and classical molecular dynamics[14] have been used to study H_2 sII clathrate hydrates. Molecular-dynamics modeling of the binary H_2/THF clathrate hydrate has also been performed.[15] Varying conclusions have been drawn from these studies regarding the H_2 occupancy of the cages.

Most experimental and theoretical work performed to date has implicitly assumed that the occupancy numbers of the cages in the H_2 and H_2/THF clathrate hydrates remain constant over time. However, there is experimental evidence that the occupancies of the small cages in H_2/THF sII clathrate hydrates change over a time scale of hours to days, even at low temperatures.[16] Herein, we calculate the energy barrier to the escape of H_2 molecules and the rate of escape from the small and large cages of the sII clathrate hydrate, as well as the contribution of tunneling of the light H_2 guest molecules to the migration rate. High migration and quantum-mechanical tunneling rates of the H_2 guests would show the need to revisit the interpretations of previous experiments.

The initial positions of the oxygen atoms of the water molecules of the large and small cages of the sII clathrate hydrate used in the calculations were determined by X-ray crystallography.[4] The disordered hydrogen atoms of the water molecules were placed among the oxygen sites in a manner consistent with hydrogen bonding. The H_2 guest molecule was placed at the center of the small or large cage and was moved towards the center of a chosen face, a pentagonal face in the case of the small 5^{12} cages or a hexagonal face in the case of the large $5^{12}6^4$ cages. The orientation of the H_2 guest was kept either parallel or perpendicular as the molecule was moved. The initial and final placements of the H_2 molecules in the small and large cages are shown in Figure 1. The cages and the H_2 guest

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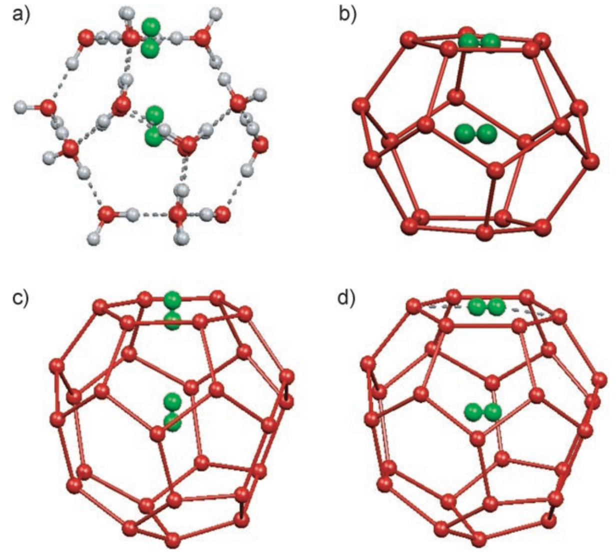

Figure 1. The initial (in the cage center) and final (in the face center) positions of the H_2 guest molecule (green) in the cages of the sII clathrate hydrate. The positions of an H_2 molecule oriented a) perpendicular or b) parallel to a pentagonal face of the small cage. The positions of an H_2 molecule oriented c) perpendicular or d) parallel to a hexagonal face of the large cage. In (a), the water molecules (O red, H gray) of the cage and the hydrogen bonds (gray dashed lines) between them are shown; in (b–d), only the oxygen atoms of the cages are shown. In (d), the H_2 molecule lies along a face diagonal, which is indicated by a dashed gray line. The energy of the H_2 molecule in the cages was calculated for 10 points between the two limits. The cages and the H_2 molecule were considered to be rigid.

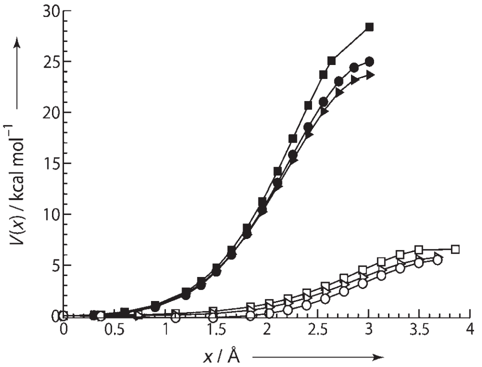

Figure 2. The energy ($V(x)$) of an H_2 molecule in the cages of the sII clathrate hydrate as a function of the distance (x) from the cage centers: for a molecule oriented perpendicular (●: MP2, ▶: B3LYP) or parallel (■: B3LYP) to a pentagonal face of the small cage; for a molecule oriented perpendicular (○: MP2, ▷: B3LYP) or parallel (□: B3LYP) to a hexagonal face of the large cage (see Figure 1). The calculations were performed with the 6-311++G(d,p) basis set.

molecule were considered to be rigid in the determination of the energy of the configurations.

The energy ($V(x)$) as a function of the distance of the center of mass of the H_2 guest from the center of the clathrate cage (x) was determined from electronic-structure calculations with Gaussian 98[17] at the B3LYP and MP2 levels of theory with the 6-311++G(d,p) basis set (Figure 2; see the Supporting Information for details).

The energy required for the H_2 guest to migrate through a hexagonal face of the large cage is 5–6 kcal mol^{-1} for both the perpendicular and parallel configurations (Figure 1 c,d). The energy barrier to migration through the smaller pentagonal faces of the small cages is much larger, ranging from 25–29 kcal mol^{-1}, depending on the orientation of the H_2 molecule (Figure 1 a,b). The energy barriers calculated at the B3LYP and MP2 levels are consistent to within 1 kcal mol^{-1}, which is within the error margin of these calculations. In reality, rotation makes the H_2 guests effectively spherical, and the energy barriers to migration through the cages will lie between the values determined for the two limiting orientations.

The total rate constant ($k_{\mathrm{tot}}(T)$) for the migration of H_2 through these energy barriers can be estimated from the classical rate constant ($k_{\mathrm{class}}(T)$) determined by transition-state theory (TST) and the quantum-mechanical tunneling correction [$\kappa(T)$; Eq. (1)].[18] The shape of the tunneling barrier is determined by the energy profile shown in Figure 2. Since migration takes the H_2 guest to a similar cage, the barrier is symmetric about the highest point, and the energy profiles of Figure 2 are fit to the one-dimensional Eckart model [Eq. (2)].[19] In this expression, E_0 is the tunneling barrier, and l is a characteristic length that is related to the magnitude of the imaginary frequency corresponding to the tunneling barrier ($|\nu_s|$) according to Equation (3), where μ is the guest reduced mass. The fit of the calculated barrier energies to Equation (2) is good, and the corresponding Eckart-potential parameters are given in Table 1.

$$k_{\mathrm{tot}}(T) = \kappa(T)\, k_{\mathrm{class}}(T). \tag{1}$$

$$V(x) = \frac{4\,E_0 \exp(2\pi x/l)}{[1+\exp(2\pi x/l)]^2} \tag{2}$$

$$|\nu_s|^2 = \frac{E_0}{2\,l^2 \mu} \tag{3}$$

The tunneling correction at each temperature is determined from Equation (4), where k is the Boltzmann constant,

$$\kappa(T) = 1 + \frac{1}{24}\left|\frac{h\nu_s}{k\,T}\right|^2 \left(1 + \frac{k\,T}{E_0}\right) \tag{4}$$

using the Eckart-model parameters. This correction can increase the rate by a factor of three at temperatures below 100 K (see the Supporting Information).

The classical rate constant of H_2 migration is calculated with a simple TST expression [Eq. (5)], where $A(T)$ is the

$$k_{\mathrm{class}}(T) = A(T) \exp(-E_0/R\,T), \tag{5}$$

Arrhenius pre-exponential factor, which is related to the rattling frequency of the H_2 guests in the small and large cages (E_0 same as above).

Table 1: The parameters of the Eckart potential for the tunneling barrier to H_2 migration.

Cage, orientation[a]	E_0 [kJ mol^{-1}]	l [Å]	ν_s [10^{12} s^{-1}]
H_2 in small cage, $\perp$	23.687	3.30	7.345
H_2 in small cage, $\parallel$	28.414	3.14	8.431
H_2 in large cage, $\perp$	5.758	3.35	3.564
H_2 in large cage, $\parallel$	6.533	4.17	3.055

[a] See Figure 1.

The frequency of the rattling motion of the H_2 molecules in the small and large cages was determined by molecular-dynamics calculations. The Fourier transforms of the normalized velocity autocorrelation functions ($\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$) for the center of mass of the H_2 molecules in the large and small cages were used to calculate the vibrational frequencies and periods (see the Supporting Information). As expected, the H_2 guests in the small cages have a higher rattling frequency (ca. 3 THz) than those in the large cages (ca. 1.5 THz). These frequencies were used as estimates for the pre-exponential factor in the TST expression for the classical rate constant [Eq. (5)].

The flux ($\boldsymbol{J}$) of the H_2 guest molecules through the clathrate is determined by Fick's first law, $\boldsymbol{J} = -D_{\mathrm{self}} \nabla c$, where c is the concentration and D_{self} is the self-diffusion coefficient. In the jump–diffusion model for zeolites,[20,21] the self-diffusion coefficient is determined from the shortest hop distance (λ) and the time interval (τ) between two hops [Eq. (6)]. The hop distance in the clathrates is the distance

$$D_{\mathrm{self}} = \lambda^2 / 6\tau \qquad (6)$$

between the centers of neighboring cages, and the hopping time is the inverse of the total rate constant for H_2 migration (that is, $\tau = 1/k_{\mathrm{tot}}(T)$).

The tunneling corrections, along with the classical rate constants, were used to calculate the total rate constants and self-diffusion coefficients (Figure 3). The total rate constants for the migration of H_2 from the large cages are roughly two orders of magnitude larger than those for migration from the small cages. The diffusion coefficients of the H_2 guests in the large cages are comparable with those measured for H_2 molecules in zeolites (ca. 10^{-8} m^{2}s^{-1}).[22] The Arrhenius plots for the total rate constants are shown in the Supporting Information.

The calculated migration rates and diffusion coefficients are lower limits to the true values. The cages and H_2 molecules in our calculations were considered to be rigid. Recent computational studies of the diffusion of H_2 in sodalite, a silica zeolite, showed that cage flexibility allows the opening of the polyhedral faces through which the H_2 guests diffuse, leading to a substantial decrease in the energy barrier to migration.[23] Presumably, allowing flexibility in the clathrate cages would also decrease the energy barrier to H_2 migration, thus, increasing the rate of migration and the diffusion coefficient of the H_2 guests. To our knowledge, experimental measurements of the migration of H_2 in the sII clathrate hydrates have not been published.

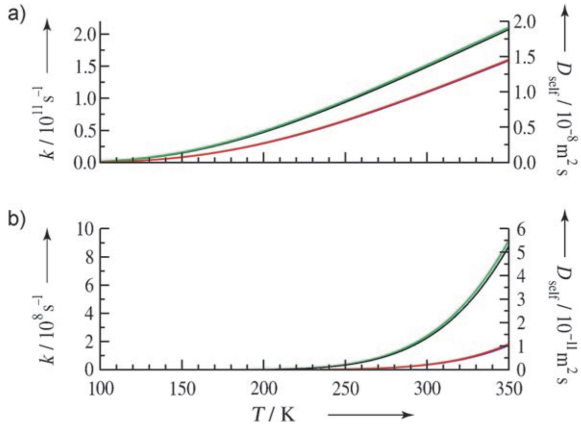

Figure 3. The rate of H_2 migration (k; left axis) and the self-diffusion coefficient (D_{self}; right axis) through the cages of the sII clathrate hydrate as a function of temperature: a) for an H_2 molecule oriented perpendicular (red: with tunneling, blue: without tunneling) or parallel (green: with tunneling, black: without tunneling) to a hexagonal face of the large cage; b) for an H_2 molecule oriented perpendicular (red: with tunneling, blue: without tunneling) or parallel (green: with tunneling, black: without tunneling) to a pentagonal face of the small cage (see Figure 1).

A direct molecular-dynamics calculation of the migration rate would take into account the flexibility of the cages, the effects of multiple occupancies of the cages on the rattling frequencies and the barrier heights of the guests, the external pressure, and the possibility of Bjerrum defects modifying the tunneling barriers. In ice lattices and clathrate hydrates, Bjerrum defects, where two hydrogen atoms lie between neighboring water oxygen atoms in the lattice (positive Bjerrum defects) or no hydrogen atoms lie between neighboring water oxygen atoms (negative Bjerrum defects) are formed in the same temperature region as that in which guest migration takes place and have an activation-energy barrier of 6–15 kcal mol^{-1}.[24] In the clathrate hydrates, barriers to the formation of Bjerrum defects, as judged from the reorientational dynamics of water molecules, are guest-dependent and are expected to decrease the energy barrier to migration through certain faces of the polyhedra. If coupled to guest motion, these defects may lead to an increase in the diffusion rate. Such a molecular-dynamics calculation is in progress.

The quantum-mechanical translation eigenvalues and eigenstates of H_2 in the small sII-clathrate cage[25] shows that, at temperatures above 250 K, the motion of the molecule is predominantly classical. The zero-point energy of each H_2 molecule in the small cages is approximately 2 kcal mol^{-1}. This zero-point energy decreases the effective energy required to pass over the diffusion barrier and will increase the rate of migration compared to the values calculated herein.

Our calculations show that the rate of H_2 migration, especially through the large cages at temperatures above 100 K, can be considerable. In the small cages, the rates of migration are smaller; nonetheless, at temperatures near 250 K, the migration rate from the small cages increases. The migration of the H_2 guests between the different cages or between the cages and the fluid phase provides an explanation for the variations with temperature seen in the relative intensity of the Raman peaks due to the H_2 guests[1] and in the occupancy of the large cage cavity determined from neutron scattering data.[6]

The temperature dependence of the tunneling correction is shown in the Supporting Information. The tunneling correction for diffusion is largest at temperatures below 100 K. For both types of faces, H_2 migration rates are only appreciable at temperatures above this value; therefore, tunneling is not expected to have a large effect on rate of diffusion.

H_2 migration is also expected to occur from the large cages of structure-H (sH) and structure-I (sI) clathrate hydrates, since the size of the hexagonal faces in these clathrates is comparable with that of the hexagonal faces in the sII structure. The large cages of the sI, sII, and sH clathrates are also coupled to the small cages through pentagonal faces. The diffusion through these faces should be comparable to that of H_2 migration through the small cages.

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