MIGRATION OF HYDROGEN GUEST MOLECULES THROUGH CLATHRATE CAGES

Saman Alavi[*]
Department of Chemistry, University of Ottawa, Ottawa, ON, K1N 6N5, CANADA

John Ripmeester
The Steacie Institute for Molecular Sciences, National Research Council of Canada
100 Sussex Drive, Rm 111, Ottawa, Ontario, K1A OR6, CANADA

ABSTRACT

Electronic structure calculations are performed to determine the barriers to migration of molecular hydrogen in clathrate cages. The barriers are used in a chemical reaction rate expression to determine the rate of H_2 migration and the diffusion coefficient for the hydrogen guest molecules. Calculations are performed for migration of hydrogen guests through pentagonal and hexagonal clathrate cage faces. Cage faces where the water molecules obey the water rules and cage faces with Bjerrum L and D defects are considered. The migration barriers were calculated to be $\approx$25 kcal/mol from the pentagonal faces and between 5 to 6 kcal/mol for the hexagonal faces, depending on the orientation of the hydrogen molecule.

Keywords: gas hydrates, hydrogen storage, hydrogen migration kinetics

NOMENCLATURE

$A(T)$ Arrhenius pre-exponential factor [s^{-1}]
E_0 activation barrier to guest migration [kcal mol^{-1}]
D_{self} diffusion coefficient of guest molecule [m s^{-2}]
k_{tot} total migration rate constant [s^{-1}]
k_{class} classical transition state theory migration rate constant [s^{-1}]
ℓ tunneling length
$V(x)$ potential energy profile for guests inside clathrate cages [kcal mol^{-1}]
κ tunneling correction to migration rate constant
λ hop distance for diffusion [m]
v_s imaginary frequency corresponding to the tunneling barrier [s^{-1}]
τ hopping time [s]

INTRODUCTION

Pure hydrogen and deuterium structure II (sII) clathrates and mixed hydrogen / tetrahydrofuran (THF) sII clathrates have been suggested as materials for hydrogen storage. In addition to the capacity of these materials for hydrogen gas storage under different temperature and pressure conditions, the stability of the guest H_2 molecules in the clathrate structure must be established. Experimentally, it is possible to determine the stability of the hydrogen clathrate by following the guest Raman and/or NMR peak intensities over long periods of time. Theoretically, the stability of H_2 guests in the clathrate cages can be determined by a study of the migration rates of the guests between the clathrate cages. In this work, we use electronic structure calculations to estimate the energy barriers to the diffusion of hydrogen guest molecules through pentagonal and hexagonal clathrate cage faces. Specifically, we study the diffusion of the H_2 through a pentagonal face of a dodecahedral 5^{12} clathrate cage and a hexagonal face of a hexakaidecahedral $5^{12}6^4$ clathrate cage. The barrier to diffusion through the faces will be determined for H_2 guest orientations perpendicular and parallel to each face. The calculations are performed at the B3LYP levels with the large 6-311++G(d,p) basis set. The energy barriers and profiles are used to estimate escape rates from the cages using a simple Arrhenius expression. Quantum mechanical tunneling contributions to the escape rate are also considered. These studies indicate that hydrogen migration through clathrates can occur and kinetic considerations can be very important in determining the structure and hydrogen storage capacity of clathrates.

[*] Corresponding author: Phone: +1 613 265 5335 Fax +1 613 998 7833 E-mail: saman.alavi@nrc-cnrc.gc.ca

The pure sII hydrogen clathrate can be synthesized at pressures between 180 to 600 MPa for temperatures near room temperature.[1,2] The hydrogen clathrate is kinetically stable at 1 bar for temperatures lower than 140 K.[3] The cubic sII *Fd3m* space group has a unit cell with 136 water molecules composed of a framework with sixteen dodecahedral cages with pentagonal faces (5^{12}) and a cavity radius of 3.91 Å. The unit cell has eight hexakaidecahedral cages, with twelve pentagonal and four hexagonal faces ($5^{12}6^4$) arranged in tetrahedral geometry about the cage centre.[4] The cavity radius of the large cages is 4.73 Å.[5]

The experimental stoichiometric ratio of H_2 to H_2O in the clathrate is determined to be 0.35-0.48 which indicates multiple hydrogen guest occupancies of the cages. The occupancy of the large cages in the hydrogen and deuterium clathrates are considered to be four.[1],[6] Direct microscopic volumetric measurements and Raman vibron intensities indicate[1] the double occupancy of the small cages, however, separate models derived from neutron diffraction studies of the D_2 sII clathrate[6] suggest that the small cages are only singly occupied. The occupancies of the cages are observed to decrease as the temperature of the clathrate is raised.

The binary sII H_2+THF clathrate can be synthesized at lower pressures (15 MPa) with the THF molecules occupying the large cages and the H_2 molecules occupy the small sII clathrate cages.[7] The small cages in the binary clathrate have been assigned single occupancy (or lower) to hydrogen in the small cages,[7-9] but studies with non-stoichiometric THF sII clathrates shown evidence of double occupancy[10] of the small cages by H_2.

Experimental and computational[11,12] work performed to-date implicitly assume that the occupancies of the cages in H_2 or H_2+THF clathrates remain constant over time. There is experimental and computational[13] evidence that the occupancies of the small cages in sII H_2+THF clathrates change over a time scale of hours to days, even at low temperatures. We calculate the barrier and rate of escape of hydrogen molecules from faces of the small and large clathrate cages. High migration and quantum mechanical tunnelling rates of the hydrogen guests would show the need to revisit the interpretations of previous experiments.

In our calculations, experimental X-ray crystallography of the sII clathrate unit cell[4] is used to determine the positions of the water oxygen atoms. The disordered hydrogen atoms of the water molecules are attached to the oxygen atoms in a manner consistent with the ice rules. An isolated small and large cage were selected from this unit cell. The hydrogen guest molecules are placed at the center of small and large sII clathrate cages and moved towards the center of chosen pentagonal or hexagonal faces. Parallel and perpendicular orientations of the H_2 guest axis are maintained as it is moved towards the face. The initial and final placements of the hydrogen molecule in the small and large cages are shown in Figure 1. The cages and hydrogen guest molecule were considered rigid in determining the energy of the configurations and ten placements between the center of the cage and the center of the face were considered to obtain a smooth energy profile for the guest in the cage.
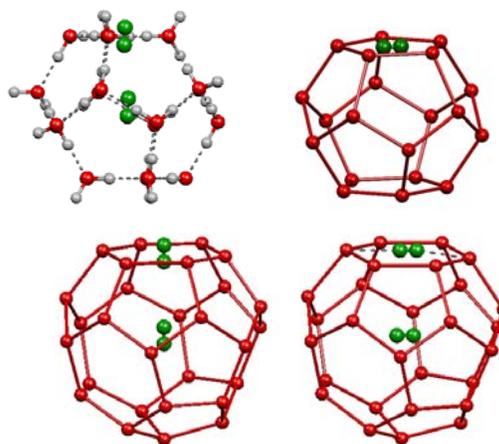

Figure 1. The sII small and large cages with the H_2 guest molecule in the center of the cage and in the center of a pentagonal or hexagonal faces. The energy of the hydrogen in the small cage was calculated for ten points between these two limits. The cage atoms and bond length of the H_2 guest were considered fixed.

The energy as a function of the distance of the hydrogen guest centre of mass from the centre of the large sII clathrate cage is shown in Figure 2. The energy was determined from electronic structure calculations with Gaussian 98[14] at the B3LYP level with the 6-311++G(*d,p*) basis set. The energy profile for guest migration was determined after introducing L- and D-type Bjerrum defects in the faces. These profiles are

also shown in Figure 2. A similar profile for the H_2 migration through a pentagonal face of a small sII cages is shown in Figure 3.
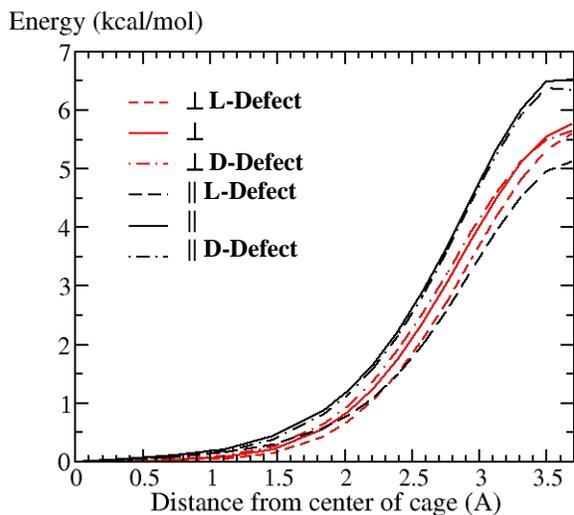
Energy (kcal/mol)

Figure 2. The energy profile for hydrogen guest migration through a pentagonal face of a small cage for orientations shown in Fig. 1.
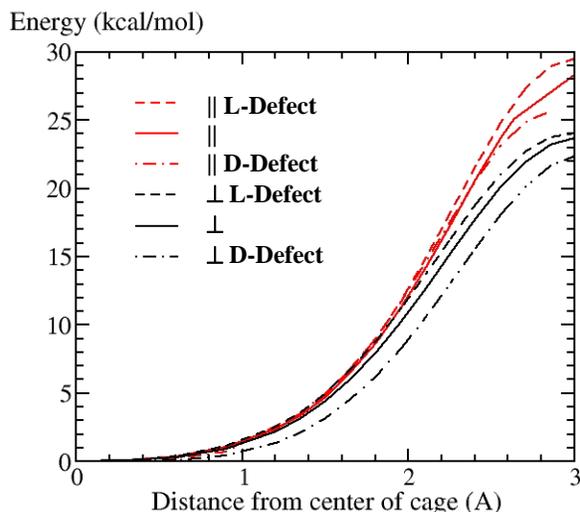
Energy (kcal/mol)

Figure 3. The energy profile for hydrogen guest migration through a hexagonal face of a large cage for orientations shown in Fig. 1.

The energy required for the H_2 guest to migrate through a hexagonal face of a large cage is between 5 to 6.5 kcal/mol. The energies of the perpendicular configuration (left panel of Fig.1) are smaller than the parallel configuration (right panel of Fig.1). The L-type Bjerrum defects in a face decrease the barrier heights considerably. The barrier to migration through the smaller pentagonal faces of the small cages are much larger and between 23 and 29 kcal/mol, depending on the orientation of the hydrogen molecule and the presence of defects. In reality, due to molecular rotation, the hydrogen guests are effectively spherical and the barriers to migration through the cages will lie in between values determined for the two limiting orientations.

The total rate constant for the migration of hydrogen through these barriers, $k_{tot}(T)$, can be estimated by a classical transition state theory (TST) expression, $k_{class}(T)$, and the quantum mechanical tunnelling correction, $\kappa(T)$,[15]

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

The shape of the tunneling barrier is determined by the energy profile shown in Fig. 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 Fig. 2 are fit to the one-dimensional Eckart sech² model,[16]

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

where E_0 is the migration barrier and ℓ is a characteristic length related to the magnitude of the imaginary frequency corresponding to the tunneling barrier, $|v_s|$. Using the guest reduced mass, μ it can be shown that,

$$|v_s|^2 = \frac{E_0}{2\ell^2 \mu}. \tag{3}$$

The calculated energy profile shows a good fit to the functional form of Eq. (2) and the corresponding Eckart potential parameters for the cases studied in this work are given in Table 1.

Cage (orientation)	E_0 / kcalmol⁻¹	ℓ / Å	v_s / 10^{12} s⁻¹
Small cage, $\perp$	24.1	3.26	15.330
(S) L-defect, $\perp$	22.4	2.99	16.118
(S) D-defect, $\perp$	24.7	3.38	14.972
Small cage, $\parallel$	29.1	3.09	17.774
(S) L-defect, $\parallel$	26.6	2.68	19.621
(S) D-defect, $\parallel$	30.1	3.12	17.923
Large cage, $\perp$	5.8	3.35	7.339
(L) L-defect, $\perp$	5.7	3.20	7.573
(L) D-defect, $\perp$	5.6	3.50	6.981
Large cage, $\parallel$	7.1	3.92	6.926
(L) L-defect, $\parallel$	6.6	3.49	6.984
(L) D-defect, $\parallel$	5.1	3.30	7.486

Table 1. The Eckart potential parameters for the tunneling barrier to hydrogen migration. The S or L signifies the small or large cage.

The tunneling correction at each temperature is determined from,

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

The Eckart model parameters are used to calculate the tunneling corrections at different temperatures by using Eq. (4).

The classical rate constant of hydrogen migration, k_{class}, is calculated with a simple transition state theory expression,

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

where $A(T)$ is the Arrhenius pre-exponential factor (s^{-1}) which is related to the rattling frequency of the hydrogen guests in the small and large cages, and E_0 is the activation barrier to migration. The frequency of rattling motion of hydrogen in the small and large cages was determined by molecular dynamics calculations. The Fourier transforms of the normalized velocity autocorrelation function, $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle/\langle\mathbf{v}(0)\cdot\mathbf{v}(0)\rangle$, for the center of mass of the hydrogen molecules in the large and small cages were used to calculate the vibrational frequencies and periods. As expected, the hydrogen guests in the small cages have a higher rattling frequency (~3 THz) than those in the large cages (~1.5 THz). These frequencies are used as estimates for the pre-exponential factor, A, in the TST expression for the classical rate constant given in Eq. (5).

The total rate constants for migration of H_2 guests through in the hexagonal and pentagonal faces are shown in Figs. 4 and 5, respectively.
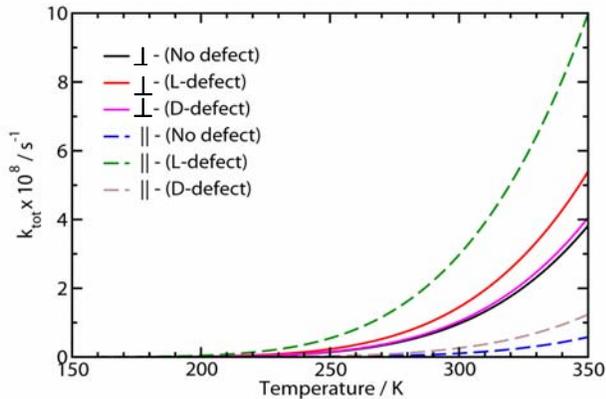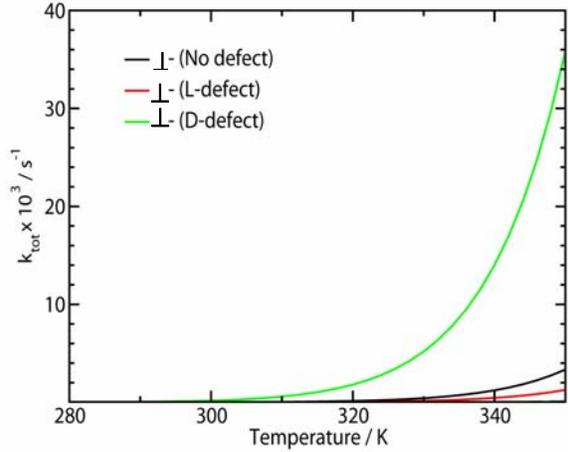

Figure 4. The total rate constant for migration of molecular hydrogen through the hexagonal faces of sII large cages.

The rate constant for the migration of hydrogen from the large cages is roughly four orders of magnitude larger than the rate constants for migration from the small cages.

the large cages in this model are comparable smaller $O(10^{-10}$ m^2/s) than diffusion coefficients measured for H_2 in zeolites which are $O(10^{-8}$ m^2/s).[17]

The migration rates and diffusion coefficients calculated in this work are lower limits to the experimental migration rates. The cages and H_2 molecules are considered to be rigid. Recent computational studies of the diffusion of H_2 in the silica zeolite sodalite[18] show that cage flexibility allows the opening of the polyhedral faces through which the hydrogen guests diffuse and this leads to a substantial decrease in the energy barrier to migration. Presumably, allowing flexibility in the clathrate cages would also decrease the energy barrier to hydrogen migration, thus increasing the rate of migration and the diffusion coefficient of the hydrogen guests. To our knowledge experimental measurements of the migration of H_2 in the sII clathrates have not been published.

A direct molecular dynamics calculation of the migration rate would account for the flexibility of the cages, the effects of multiple occupancies of the cages on the rattling frequencies and barrier heights of the guests, the external pressure, and the possibility of Bjerrum defects modifying the tunnelling barriers. In ice lattices and clathrates, Bjerrum defects are formed in the same temperature region as guest migration and have an activation barrier of 6-15 kcal/mol.[18] In the clathrate hydrates, barriers to the formation of Bjerrum defects, as judged from the reorientational dynamics of water molecules are guest-dependent. As seen in Figures 4 and 5, these defects decrease the energy barrier to migration through the faces of the polyhedra.

The quantum mechanical translation / rotation eigenvalues and eigenstates of H_2 in the small sII clathrate cage show that at temperatures above 150 K, the translational motion of hydrogen inside the cage is predominantly classical.[19] The zero-point energies of each hydrogen molecule in the small cages are ≈2 kcal/mol. 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 in this work.

Our calculations show that the rate of hydrogen migration, especially through large cages at temperatures above 150 K can be considerable. In the small cages, the rates of migration are much smaller.

Hydrogen migration is also expected to occur from the large cages of sH and sI clathrates since the size of the hexagonal faces in these clathrates are comparable with the hexagonal faces of the sII large cages. The large cages of 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 hydrogen migration through the small cages.

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