

Mechanisms and Rates of Interstitial H₂ Diffusion in Crystalline C₆₀

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Parallel replica dynamics and minimum energy path calculations have been used to study the diffusion mechanisms of H₂ in fcc C₆₀. Isolated interstitial H₂ molecules bind preferentially in the lattice octahedral (O) sites and diffuse by hopping between O and tetrahedral sites. The simulations reveal an unexpected mechanism involving an H₂ molecule diffusing through an already occupied O site, creating an H₂ dimer, with a lower activation barrier than diffusion into an empty O site. Kinetic Monte Carlo simulations of a lattice model based on these mechanisms indicate that events involving dimers greatly enhance the self-diffusion rates of interstitial H₂ in fcc C₆₀.

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The interaction and transport of H₂ and other light gases in carbonaceous materials is of great interest because of the possible technological applications of these materials [1–5]. Solid C₆₀ (fullerite) is a useful material for understanding these interactions because of its highly ordered structure [6,7]. Above $T = 260$ K, C₆₀ forms an fcc lattice in which the C₆₀ molecules are rotationally disordered. At $T \sim 260$ K, fullerite undergoes a phase transition, in which the molecules form an orientationally ordered array while the centers of mass remain at their fcc positions [8,9]. A number of small atoms and molecules are known to intercalate into interstitial sites in solid C₆₀, including He [10], Ne [10,11], Ar [10], K [12], CO [13], and H₂ [6,7]. In this Letter, we present a study of the interstitial diffusion of H₂ in the room-temperature (orientationally disordered) fcc phase of fullerite. We use parallel-replica dynamics to directly simulate the classical diffusion dynamics for both low and high concentrations of H₂ at elevated temperatures. Rates determined for key mechanisms are provided as input for lattice-based kinetic Monte Carlo simulations, from which self-diffusion constants are determined for a wide range of loadings. A surprising result of this study is the importance of interstitial sites occupied by two (and sometimes even three) H₂ molecules, which increase the self-diffusion constant by 1 or 2 orders of magnitude over the prediction of a standard single-occupancy model.

Our calculations employed two-body interactions between C₆₀-C₆₀, C₆₀-H, and H-H pairs. We used the orientationally averaged C₆₀-C₆₀ potential of Pacheco *et al.* [14] to define interactions between C₆₀ molecules. At zero pressure, this potential yields a lattice constant of 14.13 Å. The interaction of H with C₆₀ was defined using the orientationally averaged potential of FitzGerald *et al.* [6]. This potential does not allow reactions to occur between H₂ and C₆₀, although these are known experimentally to occur at elevated temperatures and pressures [15]. We emphasize that our interest here is to describe the dynamics of H₂ at temperatures where reactions are not relevant.

For H-H interactions, we constructed a two-body version of the potential developed by Stuart *et al.* [16], defining the energy between any pair of H atoms to be $V_{\text{HH}}(r) = S(t)V_{\text{HH}}^{\text{bond}}(r) + [1 - S(t)]V_{\text{HH}}^{\text{LJ}}(r)$. Here, $V_{\text{HH}}^{\text{bond}}(r)$ is a bonded H-H potential [17], $V_{\text{HH}}^{\text{LJ}}(r)$ is a Lennard-Jones nonbonded potential [16], and $S(t) = \Theta(-t) + \Theta(t) \times \Theta(1-t)[1 - t^2(3-2t)]$ is a switching function [16], switching smoothly between $V_{\text{HH}}^{\text{bond}}(r)$ and $V_{\text{HH}}^{\text{LJ}}(r)$. Θ is the Heaviside function and $t = (r - r_{\text{min}})/(r_{\text{max}} - r_{\text{min}})$, with $r_{\text{min}}(r_{\text{max}}) = 1.2(1.6)$ Å. This potential gives an artificial barrier of ~ 5 eV for H₂ formation which, at the temperatures considered here, prevents any interchange of H bonding partners. For H₂-H₂ interactions, it yields binding energies in reasonable agreement with the very accurate H₂-H₂ potential of Diep *et al.* [18]. In a perpendicular configuration, we find a binding energy of 4.4 meV with an intermolecular distance of 3.25 Å; essentially identical to the *ab initio* result. The agreement is not as good in a parallel configuration, where our potential predicts a binding energy of 5.9 meV at a distance of 2.95 Å, compared to an *ab initio* binding energy of 1.7 meV at a distance of 3.4 Å. In both of these comparisons, we used the same H-H bond distance as Diep *et al.* [18].

All calculations employed an fcc lattice of 108 C₆₀ molecules, each treated as one particle, with periodic boundary conditions. The lattice constant was held at 14.13 Å, independent of H₂ loading, as is justified below. All other degrees of freedom were included in relaxations and dynamics, unless otherwise noted. Diffusion pathways and the corresponding energy barriers were calculated using the nudged elastic band (NEB) method [19].

We first examined the binding energy of a single H₂ in the C₆₀ lattice. We found a binding energy of 0.1135 eV for H₂ in the interstitial octahedral (O) site, relative to the gas phase. This value compares well with the experimental binding energy of 0.092 eV [7]. The energy of the tetrahedral (T) site is higher. Without allowing the C₆₀ positions to relax, the energy of H₂ in a T site is 0.1095 eV above the gas phase energy. This reduces slightly to

0.0982 eV when lattice relaxation is included. That the T site is not stable relative to the gas phase is consistent with experiments that found that the low temperature thermal population of H_2 in T sites is essentially zero [6].

To examine the variation in H_2 binding energy with H_2 loading, we calculated the energy of two H_2 molecules in adjacent O sites. The binding energy per H_2 in this configuration was essentially identical to that for a single H_2 . In addition, we optimized the lattice constant for a system in which every O site was occupied by H_2 . This lattice constant differed by less than 0.005 \AA (0.04%) from that of pure C_{60} , so, as mentioned above, we kept the lattice constant fixed at 14.13 \AA for all calculations. Our observations indicate that equilibrium adsorption of H_2 into O sites is accurately described as adsorption of independent particles into a set of uniform binding sites with a binding energy of $0.1135 \text{ eV/molecule}$. This description implies that the adsorption isotherm of H_2 in solid C_{60} should be a Langmuir isotherm, in excellent agreement with experimental observations [7].

We calculated the energy barrier for motion of an H_2 between an O and T site. Simulation data presented below confirms this is the correct pathway to consider. As might be expected, H_2 passes through the triangle formed by three C_{60} molecules separating O and T sites by aligning its molecular axis perpendicular to the triangle. Performing the NEB calculations while keeping the positions of the C_{60} fixed yields an energy barrier of 0.53 eV for the O to T transition. Relaxing these degrees of freedom reduces this barrier to 0.44 eV and gives a barrier for the reverse process of 0.23 eV . The potential energy surface (PES) for diffusion of isolated H_2 in C_{60} is shown schematically in Fig. 1. Analogous calculations examining the diffusion of H_2 from the (100) surface of fullerite into the bulk give very similar barriers.

To examine the overall diffusion behavior and discover important mechanisms under realistic conditions, we performed parallel-replica dynamics [20] (PRD) simulations at temperatures between 500 and 1000 K for two different H_2 loadings. The combined use of elevated temperatures and PRD, an accelerated dynamics method [21] that parallelizes time, allowed us to follow the

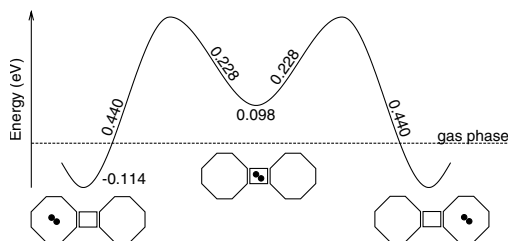


FIG. 1. Schematic PES for diffusion of an isolated H_2 molecule from one interstitial O site (octagons in insets) to an adjacent T site (square in insets) and on to a subsequent O site. The energy along each slope of the PES is the energy barrier for a transition between the two states. The dashed line indicates the energy of the H_2 molecule in the gas phase.

dynamics beyond the transient period dominated by the initial structure into a regime where unexpected processes might occur, where we believe we have seen all of the important types of events. It allowed us to observe a large number of events from which rate constants were determined. Below, we use these rate constants, combined with the activation barriers, to predict the H_2 diffusion behavior at lower temperatures. Detecting transitions is critical for PRD. We interrupted each trajectory every 10 fs, declaring a transition if the quenched position of any particle differed by more than 4.5 \AA from its original quenched position for the state. We used a dephasing time of 0.25 ps and a correlation time of 1 ps. Simulations were run on 20 processors, yielding a typical speedup of 15.

Extensive PRD simulations of systems containing one H_2 confirmed that H_2 diffusion occurs by alternating hops between adjacent O and T sites, as described above. Examination of PRD simulations with multiple H_2 present revealed many instances of an unexpected configuration: two H_2 molecules—an H_2 dimer—occupying a single O site. We minimized the energy of a number of these dimer configurations, confirming that they are indeed stable. We show below that these configurations play an important role in the net diffusion of H_2 in fullerite.

The barrier for H_2 to move from one O site into an already occupied O site and the resulting PES is shown in Fig. 2. It is clear that H_2 dimers are unfavorable relative to two H_2 in separate O sites, consistent with the experimental observation [6] that at low temperatures O sites are singly occupied by H_2 . Crucially, however, an H_2 dimer is energetically favored over occupying one O and one T site. Thus, under circumstances where transitions of H_2 are feasible, the formation of H_2 dimers is also feasible. The energy difference between dimers and isolated H_2 is large enough that no deviations from the experimentally observed Langmuir adsorption isotherm would be expected due to dimer formation in the pressure range for which experimental data is available [7].

The PES shown in Fig. 2 exhibits a diffusion pathway with a lower activation energy than that of a single H_2 . To examine the implications of this pathway in more detail, we performed PRD simulations at 700 K of a system with

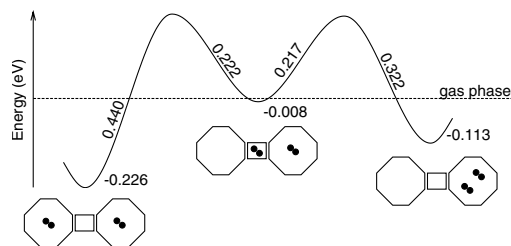


FIG. 2. The same as Fig. 1, but for two interacting H_2 molecules inside solid C_{60} . From left to right, the potential minima represent the two molecules in adjacent O sites, the two molecules in an adjacent T and O site, and the two molecules forming a dimer in a single O site.

TABLE I. Observed diffusion events from PRD simulation of H_2 diffusion at 700 K. The definitions of the average waiting time τ and the diffusion prefactor are given in the text. The “T to O” event type includes both transitions from T to an empty O site and transitions from T to an O site already occupied by one H_2 (leading to a dimer).

| Event type | No. observed | τ (ps) | ΔE (eV) | ν (1/s) |
|------------|--------------|-------------|-----------------|----------------------|
| O to T | 146 | 6629 | 0.440 | 2.2×10^{11} |
| T to O | 195 | 17.3 | 0.228 | 2.5×10^{12} |
| Dimer to T | 47 | 114 | 0.322 | 9.1×10^{11} |

27 H_2 molecules, corresponding to a loading of $\theta = 0.25$, starting from an initial condition in which the H_2 were placed in a regular array of O sites. The fractional loading, θ , is defined relative to the total number of O sites. During this simulation, we observed 388 diffusion events; the number and the associated average waiting time of each type of event are summarized in Table I. The average waiting time is defined as the average time required to observe a particular type of event in a system with only one molecule (or dimer) in the initial configuration for that event. For example, since our simulation initially has 27 H_2 molecules in independent O sites, one would expect $6629/27 = 246$ ps to elapse before one molecule hopped into an adjacent T site, on average, if many independent simulations were performed.

The prefactors, ν , in Table I were defined by assuming that the rates for each process are Arrhenius, $k = \nu \exp(-\Delta E/k_B T)$, an assumption we have not explicitly tested. The activation energy, ΔE , was determined from NEB calculations. For the dimer breakup event, ν is defined to give the rate for each molecule in the dimer. The energy barrier for H_2 to move from a T to an O site is essentially independent of the occupation of that O site, and we observed that the average waiting times for these two events are also quite similar. These two processes are thus grouped together in Table I. That the prefactor for hopping out of a singly occupied O site is substantially lower than for other types of events is consistent with the observation that the potential minimum of an O site is relatively wide and flat.

PRD simulations with $\theta = 0.25$ and $\theta = 1$ at 500 K and $\theta = 0.25$ at 1000 K confirm that the PES shown in Fig. 2 captures nearly all of the diffusion events in this system. The only additional events observed were in $\theta = 1$ simulations, where three H_2 molecules in one O site were observed. Calculations confirmed that these trimers are stable. The full PES for trimers is shown in Fig. 3. From the observed lifetimes of the trimers in our PRD simulations, we estimate the prefactor for trimer breakup to be $5.1 \times 10^{12} \text{ s}^{-1}$ per molecule (cf. Table I). Tetramers, however, are not stable.

To assess the impact of dimers and trimers on the net diffusion of H_2 in C_{60} , we performed kinetic Monte Carlo (KMC) simulations of a simple lattice gas (LG) model

that incorporates the main features of the PES shown in Figs. 1–3. In this model, particles representing H_2 molecules hop independently on a lattice with the topology of the fcc O and T sites. Hopping rates in our model were defined as listed in Table I and as described above for the breakup of trimers. At each step of our KMC simulation, a particle was chosen at random and a hop attempted into a nearest neighbor lattice site. The hop was successful if the neighboring O (T) site contained fewer than 3 (1) particles and a random number chosen uniformly between 0 and 1 was less than $k_{\text{attempt}}/k_{\text{max}}$, where k_{attempt} and k_{max} were the rate of the attempted hop and fastest possible event in the system, respectively.

H_2 self-diffusivities, D , were measured from our KMC simulations by computing the mean squared displacement of each particle and using the usual Einstein relation, $D = \lim_{t \rightarrow \infty} \langle r^2(t) \rangle / 6t$. Data was typically collected over time scales on which $\langle r^2(t) \rangle / 6t$ exceeded 10 times the fcc lattice spacing. The self-diffusivities at several temperatures are shown in Fig. 4 where D is normalized by the diffusion rate in the limit of zero occupancy. To highlight the effect of dimers on the overall diffusion rate, the self-diffusivities arising from a restricted LG model, where dimers and trimers are prohibited, are also shown (open symbols). For this model, D behaves as expected [22]; it decreases monotonically as the loading increases due to site blocking. D does not become zero at $\theta = 1$ in this restricted model because while, at this loading, all O sites are filled, H_2 can be promoted to empty T sites, allowing diffusion among O sites. The observed behavior of D is dramatically different when dimers and trimers are included. In this case, D increases monotonically with loading. The large increases in D at elevated loadings occur because H_2 can traverse clusters of partially occupied O sites much more quickly than they can move across regions of unoccupied O sites. The increased diffusion due to molecular clusters is essentially all due to dimers; calculations which exclude molecular trimers yield results that are almost indistinguishable from the full model shown in Fig. 4.

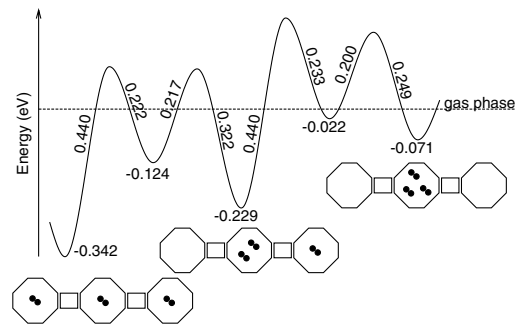


FIG. 3. The same as Fig. 1, but for three interacting H_2 molecules inside solid C_{60} . From left to right, the potential minima represent a series of states connecting a system with H_2 molecules in three adjacent O sites to a system with a molecular trimer in a single O site.

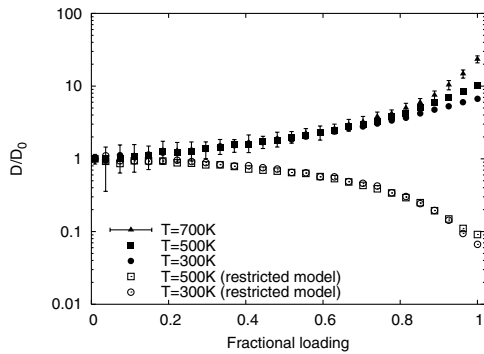


FIG. 4. Self-diffusivity of H_2 predicted by the LG model with and without the existence of interstitial dimers and trimers (filled and open symbols, respectively). At each temperature, the self-diffusivity is shown normalized by the self-diffusivity of an isolated interstitial H_2 , D_0 . Error bars, shown for the 700 K case with dimers, are similar for the other cases.

We have used results from our LG model with $300 \leq T \leq 700$ K to extract the net activation energy for H_2 self-diffusivity, ΔE_{net} , as a function of loading. For the restricted model at all loadings and for the full model when $\theta < 0.8$, this energy is essentially equal to the energy required for a single H_2 molecule to escape from an O site: $\Delta E_{\text{net}} \cong 0.44$ eV. When $\theta > 0.8$ for the full model, the net activation energy is reduced by the presence of dimers and trimers, but only to a small degree. For $\theta = 0.815, 0.889, \text{ and } 1.0$, our LG model yields $\Delta E_{\text{net}} = 0.42, 0.41, \text{ and } 0.37$ eV, respectively. Thus, although dimers greatly enhance the absolute diffusion rate, the rate determining step for diffusion at all loadings is the escape of a single molecule from an O site.

We note that it is the transport diffusivity, not the self-diffusivity, that describes the response of interstitial H_2 to concentration gradients inside solid C_{60} [22]. For models such as our restricted LG model, the transport diffusivity is known to be independent of concentration [23,24]. Comparing D for the restricted and unrestricted LG models strongly suggests that the transport diffusivity of interstitial H_2 in C_{60} will be a strongly increasing function of the interstitial concentration. It is possible to measure transport diffusivities using LG models [23,24], and we plan to do this in the future. Accounting for the details of this concentration dependence may be important in modeling experimental data that involves non-equilibrium conditions.

That two H_2 prefer to sit in one O site rather than an O and T site may be an artifact of our potential and one would like to test this with *ab initio* methods. Unfortunately, the high level of theory necessary to accurately describe the van der Waals interactions crucial to this system [18] make this goal inaccessible at present. We have examined the geometries of interstitial H_2 using the all-atom AIREBO potential, a detailed empirical potential that includes both bonded and van der Waals interactions [16]. These calculations indicate that a doubly

occupied O site is 0.18 eV lower in energy than O + T, supporting the main results of our study.

In conclusion, we have used parallel-replica dynamics simulations and molecular statics analysis to examine the adsorption and diffusion of H_2 in the interstitial sites of fullerite. We find that H_2 diffusion in this system can occur by a previously unreported mechanism involving the formation of metastable molecular clusters in the lattice octahedral sites. This mechanism appears to have significant consequences for the diffusion rate of H_2 in C_{60} , particularly at moderate and high concentrations of H_2 .

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