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Kinetics of Hydrogen uptake by scavenger molecules – insights from molecular modeling

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Abstract:

Mixed aromatic-alkyne molecules have been designed to scavenge and remove hydrogen in unwanted situations. Such materials in powdered solid form are mixed with catalytic metal particles that dissociate H_2 molecules into H radicals. However, many details of the H uptake mechanism remain poorly understood. Here we report molecular modeling studies, using both classical force fields and first-principles density functional theory, aimed at providing enhanced understanding of the uptake kinetics. Such insights are important in improving the H scavenging efficiency of the present and next-generation materials, as well as to provide molecular-scale interpretation of supporting experiments.

Keywords: Molecular modeling, hydrogen uptake, vapor pressure, binding energy

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Nearly spontaneous catalytic dissociation of H_2 molecules on transition metal surfaces has long been recognized as an important chemical reaction [1]. The resulting H radicals can then be used in subsequent reactions or stored either reversibly or irreversibly, depending upon the needs of a given application. Irreversible storage of H is usually aimed at preventing hydrogen accumulation in sealed containers, which may lead to hydrogen corrosion of nuclear materials, undesirable effects on electronic components, or an explosion hazard [2-4].

A common design of hydrogen scavengers (also known as *getters*) involve a middle part consisting of a highly unsaturated hydrocarbon, typically an alkyne, which is flanked on both sides by aromatic rings that have strong binding characteristics to transition metal surfaces. Two most known examples are 1,4-diphenyl-butadiyne (DPB) and a close variant, 1,4-bis(phenylethynyl) benzene (DEB) [5, 6]. For use as scavengers these compounds are combined with a hydrogenation catalyst such as a low weight percent of Pd on activated carbon (AC). The hydrogenation kinetics and thermodynamics of both DEB and DPB in such materials have been examined in the literature [7, 8], and the kinetic behavior has been found to be complex. This is particularly true for DPB, which displays intricate phase behavior during the course of hydrogenation [8]. Further, the ultimate uptake capacity of powdered samples of DPB mixed with a Pd-on-carbon catalyst appears sensitive to the average reaction rate [9], such that relatively high reaction rates lead to correspondingly lowered hydrogen capacities. Recent kinetic experiments [8] also reported a steady drop in the H uptake rate with increased consumption of the DPB getter pellets.

Although these experiments provide a first look into the details of the uptake kinetics, one intriguing fundamental issue has not been addressed: how can the reaction proceed to full or near completion at all, given the relative scarcity of available catalyst sites in 5 wt% Pd on carbon? Activated carbon (AC) substrates will have surface areas on the order of many hundreds of m^2/g. In combination with Pd particles that are typically 40Å in diameter, the resulting material has considerable intervening distance on average between catalyst sites at the usual 5 wt % Pd. When this material is then combined in a typical 1:3 weight ratio with DPB, the resulting instantaneous contact area between catalyst surface and getter compound is equivalently small. In order for the reaction to proceed to a significant extent, either DPB is continuously transported to the catalyst surface, or H atoms produced at the Pd surface spillover onto the carbon support for transport to fresh getter. Both of these cases raise further interesting questions. For instance, in the latter case, is there an extra driving force for getter molecules to diffuse to the metal surface as opposed to the AC support, and is the getter diffusion fast enough to explain experimentally observed hydrogenation rates? Insight into these questions is important not only in improving the scavenging efficiency of the current materials, but also crucial in designing the next generation of multifunctional materials with high scavenging capacity.

In this Letter, we address some of these questions through a combination of molecular modeling and plausibility arguments based on available experimental data. First, we show that

the observed vapor pressure of DPB and the associated heat of vaporization [8] can be rationalized through basic inter-molecular interactions in the known crystal phase. Next, based on computed activation barriers and reaction energetics we examine the possibility of spillover of H radicals onto the AC support and subsequent surface diffusion away from the metal catalyst. Finally, we compute the hydrogenated DPB binding energy to the predominantly exposed (111) surface of a Pd catalyst particle, and compare with that of a virgin (i.e. unsaturated) DPB in order to determine whether there is an extra driving force of the unsaturated species to diffuse to the metal surface and displace a saturated getter there.

Fig. 1 displays the structure of a DPB molecule and its packing in a known monoclinic crystalline phase with P21/c symmetry. One expects the sublimation (or cohesive) energy of a DPB crystal to be dominated by strong van der Waals interaction between the phenyl rings. Thus, standard Density Functional theory (DFT) (without a consistent inclusion of extra van der Waals contributions) severely underestimates the sublimation energy in such systems. This limitation of standard DFT led us to use classical force fields that are known to be accurate for organic molecules like DPB. For the present calculations, we used COMPASS [10], a state-of-the-art class II force field, which has specifically been parameterized for condensed systems, especially to yield accurate cohesive energies. The COMPASS force field employs a van der Waals interaction in the 6-9 Lennard-Jones form, and off-diagonal interactions are approximated by the sixth-power combination rule [11]. In our simulations, the long-range electrostatics was accurately computed using the Ewald summation technique.

The sublimation (or cohesive) energy of DPB was computed by taking the difference in lattice energy of the crystalline phase from the potential energy of isolated molecules, in which both were structurally relaxed by the COMPASS force field. The resulting computed energy was 28.2 kcal/mol, in good agreement with the experimentally measured heat of vaporization of 29.2 kcal/mol for the virgin DPB material [8]. To calculate the vapor pressure from this, we used the formalism of ref. [12], in which vibrational and rotational partition functions are computed and differences in the chemical potential between the vapor and the solid phases are expressed in terms of an effective frequency ν_{eff}. A similar approach was also used for the fully hydrogenated DPB. Fig. 2 plots the computed vapor pressure of both the virgin DPB (using $\nu_{eff} = 6.6\text{x}10^{12}$ sec^{-1} and a heat of vaporization ΔH_{vap} = 29.2 kcal/mol) and the hydrogenated DPB (using ν_{eff} = $6.1\text{x}10^{12}$ sec^{-1} and ΔH_{vap} = 27.0 kcal/mol) and compares with recent experimental results [8]. Effective frequencies such as these are somewhat smaller than that of a PETN molecule [12], which is consistent with DPB having roughly 2/3rd the mass of a PETN. The slightly smaller frequency of a hydrogenated DPB is in line with a slightly smaller ΔH_{vap} as compared to virgin DPB [8], which can primarily be attributed to: (i) a smaller non-bond interaction from saturated hydrocarbons [10]; and, (ii) the fact that hydrogenated DPB is in a disordered phase as opposed to a solid crystalline phase of the virgin DPB. We proceeded to determine how much of the 28.2 kcal/mol sublimation energy arises from the benzene rings of DPB and how much from the

alkyne (i.e. butadiyne) part. We found that roughly 28% of the cohesion results from the interaction of the butadiyne group with the rest of the crystal, while 36% is accounted for by each of the two phenyl groups. The computed cohesive energy contribution of each phenyl ring is consistent with the known heat of vaporization of benzene ~ 10.6 kcal/mol.

Next we attempted to address a crucial kinetic question, i.e., do the H radicals travel to the unsaturated bonds of the getter, or do the getter molecules diffuse to the H radicals on the metal surface? For H-radical diffusion as a plausible pathway one has to consider the possibility of either a direct desorption of H from the metal surface, or its spill-over onto the AC support followed by surface diffusion along the support material itself. The later mechanism is also relevant for hydrogen storage applications [13]. Since such processes involve the breaking of chemical bonds that cannot be addressed with (non-reactive) force fields like COMPASS, we performed first-principles calculations using Density Functional Theory (DFT) code DMol^3 [14, 15], which employs localized basis sets defined on a numerical grid. We modeled the Pd (111) surface with a periodic supercell in which a vacuum of 30 Å was placed above a three-atomic-layer slab parallel to the (111) plane. In order to accommodate a long molecule like DPB, we needed to create an extended 5x4 supercell from the smallest possible unit, thus requiring a total of 60 metal atoms (plus the DPB) in the computational cell. The electronic wave functions were expanded in a double-numeric polarized (DNP) basis set truncated at a real-space cutoff of 4.0 Å and represented on a "medium" numerical grid. The core electrons of the Pd atoms were represented by density-functional semi-core pseudopotentials (DSPP) [16], while all other electrons were represented explicitly. A nonlocal DFT Hamiltonian was used with gradient-corrected exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE) [17], while accurate Brillouin zone sampling was ensured by summing over a finite set of K points chosen according to the Monkhorst-Pack scheme [18] with a grid spacing of 0.05 Å^{-1}.

Table 1 summarizes the energetics for several important processes, and the main inferences can be drawn as follows. The process of H_2 dissociation on Pd(111) surface is exothermic by almost 10 kcal/mol (per H) as noted previously [19]. As more and more H is adsorbed into the metal, the energy gain drops gradually, saturating at 2.5 kcal/mol for Palladium Hydride (β phase of PdH) with a Pd:H molar ratio of 1:1. Direct desorption of a H radical into the gas phase is energetically costly (52.6 kcal/mol) and thus highly unlikely. Thus one of three possibilities can happen for the H radicals: (I) a pair can combine to form H_2 that escapes into the gas phase; (II) spill over onto the AC support; and (III) direct uptake by getter molecules that bind to the metal surface. Case (I) simply helps establish thermodynamic equilibrium between hydrogen in the gas phase and H dissolved in the metal. Below, we discuss cases (II) and (III) separately. For a model of the AC support we assume that it consists of finite fullerene fragments, as suggested by recent observations with transmission electron microscopy [20].

Case (II): In order for H to spill over onto the AC support two scenarios are possible: (a) in which the spilled H saturates a dangling edge state; and (b) the spilled H chemisorbs atop an sp^2

carbon away from the edge (thereby converting it to a sp^3 carbon). At graphene edges, the resulting H is energetically even more stable than when up taken by a getter (see Table 1). However, once all edge-states are saturated, chemisorption atop an sp^2 carbon could potentially lead to surface diffusion of H on the graphene (or graphene-like) surface provided a connected pathway is available. Even in this case two barriers need to be overcome: (i) a barrier to jump from the metal (or metal-hydride) to the support; and (ii) a surface diffusion barrier involving hops between atop-sp^2 sites on nearest-neighbor carbons. Just based on reaction energetics, the first barrier should be between 15 and 33 kcal/mol (see rows 3, 7 and 8 of Table 1). Such barriers can sometimes be lowered through the formation of "bridge" like structures between the catalyst and the support [21]. However, the second (i.e. diffusion) barrier of 26.2 kcal/mol indicates that even if initial spill-over occurs to support sites adjacent to the metal particle, long-range diffusion is unlikely. Thus, the surface diffusion constant D_{surf} is of the order of $a^2 \nu_{att}\, exp(-\Delta E/k_B T)$, where a is a C-C bond-length in graphene. Substituting $a \sim 1.4$ Å, $\nu_{att} \sim 10^{12}$ s^{-1}, and $\Delta E \sim 26.2$ kcal/mol, one obtains $D_{surf} \sim 10^{-19}$ cm^2/s even at an elevated T of 338 K, much too small for any real kinetic phenomena.

Case(III): From the above discussion it appears that the spilled-over H, if any, should remain on the AC support in the vicinity of the metal particles. Thus, uptake of H by the getter molecules should mostly occur when the latter bind to the metal surface. For this mechanism to be operative, several conditions need to be satisfied: (1) the DPB molecules should be more attracted to the metal surface than the surface of the AC support; (2) the diffusivity associated with getter transport to the metal centers should be fast enough to explain experimentally observed saturation rates; and (3) the residency time of the getter at the metal surface should be optimum (i.e. slow enough to permit enough time for the H radicals to saturate the unsaturated π bonds of the alkyne, but fast enough to detach and allow new unsaturated molecules to bind). We address these points below.

As for point (1) above, we computed the binding energy of both virgin and hydrogenated DPB to the Pd(111) surface using DMol[3], and found them to be similar, around ~ 40 kcal/mol [19]. This once again demonstrates that most of the binding occurs through the flanking phenyl rings of the DPB, and not the middle hydrocarbon part. On the other hand, COMPASS calculations indicate that unless the carbon support predominantly exposes flat extended graphene-like regions, the binding energy to the support is expected to be much smaller, around 10-15 kcal/mol, which is not enough to ensure stability on the support even at room temperatures. In fact, this binding is much smaller than getter binding within its own environment (see previous discussion on cohesive energy) as well as the binding energy to the metal surface. Thus, there should be a strong thermodynamic driving force of getter molecules to de-wet the support material and condense at the metal centers.

Arguments in favor of points (2) and (3) above greatly benefit from a single effect, i.e. significant amount of heat is generated from the hydrogenation of the getter at the metal surface.

Thus, a virgin DPB molecule incident on the Pd surface at room temperature should be highly stable, given a large (40 kcal/mol) binding. It was noted in [8] that at intermediate levels of hydrogenation DPB transforms into a liquid, presumably due to the formation of a distribution of alkene isomers with high conformational entropy. Through solvation modeling using COSMO [24] we verified that this binding is not affected by the presence of a liquid DPB environment above the Pd because of the non-polar nature of DPB, which leads to little screening. However, the hydrogenation of DPB is a highly exothermic process (see Table 1) that leads to significant amount of heating, which has in fact been observed in previous experiments. This should result in two effects: (i) quick release of the bound DPB; and (ii) heating up of the DPB liquid that creates a convection current, which in turn brings new non- or partially hydrogenated DPB to the metal surface. More detailed calculations of the self-diffusivity of DPB through explicit molecular dynamics calculations are currently underway.

In summary, from molecular mechanics calculations using both classical force fields and first-principles DFT and physically-based plausibility arguments we obtain the following picture of how hydrogen radicals are up taken by DPB getters: (i) H_2 spontaneously dissociates on the metal (Pd) catalyst surface -- the metal uptakes to a maximum 1:1 molar ratio of hydrogen until palladium hydride (PdH) forms; (ii) the resulting H radical has a significant barrier to diffuse on the support material, and thus essentially remains confined to the metal; (iii) the DPB getter molecules have a much weaker binding to the carbon support as compared to either binding to the catalyst surface or to its own condensed phase, which creates a thermodynamic driving force to accumulate over the catalyst centers; and (iv) significant heat generated during the strongly exothermic hydrogenation reaction leads to both the release of a hydrogenated getter from the catalyst surface and to a strong convection current that brings fresh non-reacted (or only partially reacted) getter molecules to the catalyst surface, which explains the relatively fast consumption of nearly all getter molecules in recent experiments.

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Table 1. DFT energies (per H atom) for hydrogen in various environments (states). The reference state is a free H_2 molecule in the ground state. Positive (negative) numbers imply lower (higher) energetic stability.

State of H	Energy per H atom (kcal/mol)
H_2 molecule	0
H_2 dissociated on Pd(111)	-9.7
H in PdH (β–phase)	-2.5*
Partial hydrogenation of DPB (alkyne → alkene)	-21.5
Full hydrogenation of DPB (alkyne → alkane)	-18.5
H (radical) desorbed from Pd surface	+52.6
H chemisorbed on sp^2 carbon in graphene (periodic)	+30.5**
H chemisorbed on sp^2 carbon in graphene fragment (see Fig. 3)	+12.6†
H chemisorbed at an edge of a graphene fragment (see Fig. 3)	-24.3†
Diffusion barrier to nearest neighbor site on graphene	+26.2‡

*Computed with respect to bulk Pd metal and H_2 molecules in gas phase

**This energy gets lower for subsequent H atoms chemisorbed at neighboring sites of an already chemisorbed H [22].

†This energy depends on the fragment size, the nature of the edge (e.g. armchair or zigzag) and on how many nearby edge sites are already H-terminated

‡Barrier is computed with respect to the chemisorbed minimum of H atop a sp^2 carbon in graphene. It increases when a second H is chemisorbed at a neighboring C-site [23].

Figure captions:

1. (left) A 1,4-diphenyl-butadiyne (DPB) molecule; (right) a unit cell of the DPB crystal with a monoclinic space group symmetry P21/c.

2. Equilibrium vapor pressure of virgin (triangle) and fully hydrogenated (square) DPB. Filled symbols are theoretical results (this work, see text), while open symbols are recent experimental measurements [8].

3. (a) A small curved-graphene-fragment representation of activated carbon (following ref. [20]); (b) H chemisorbed at en edge; (c) H chemisorbed atop a sp^2 carbon in the middle.

4. DFT-optimized structure of: (a) a virgin DPB molecule; and (b) a fully hydrogenated DPB molecule bound to the (111) surface of Pd. Fig. (a) is reproduced from ref. [19].

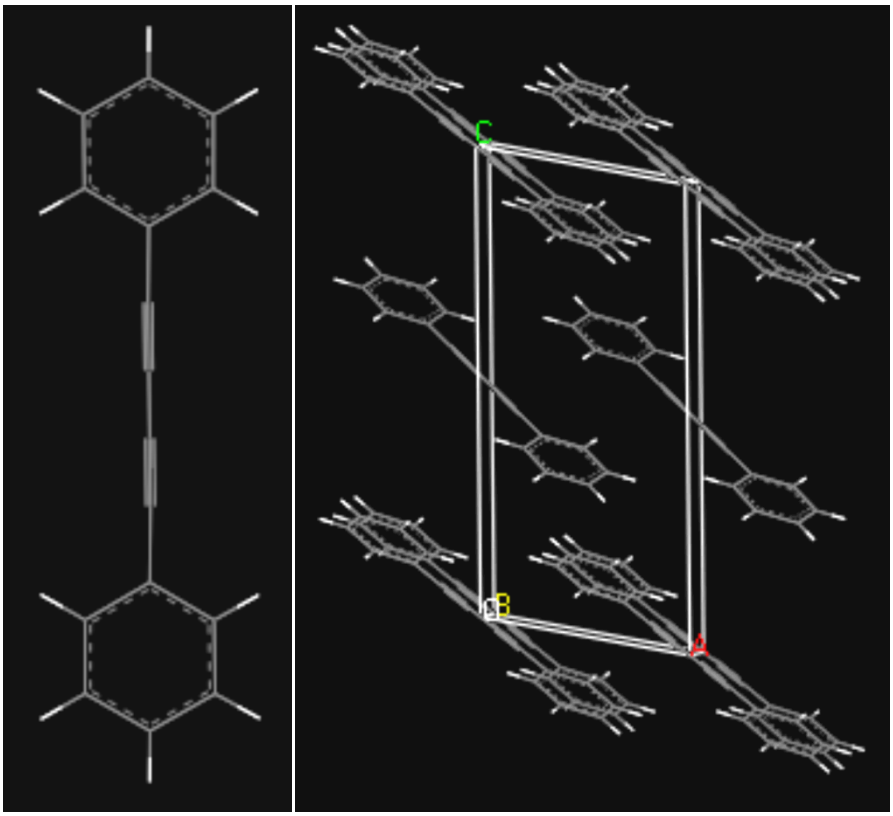


Figure 1

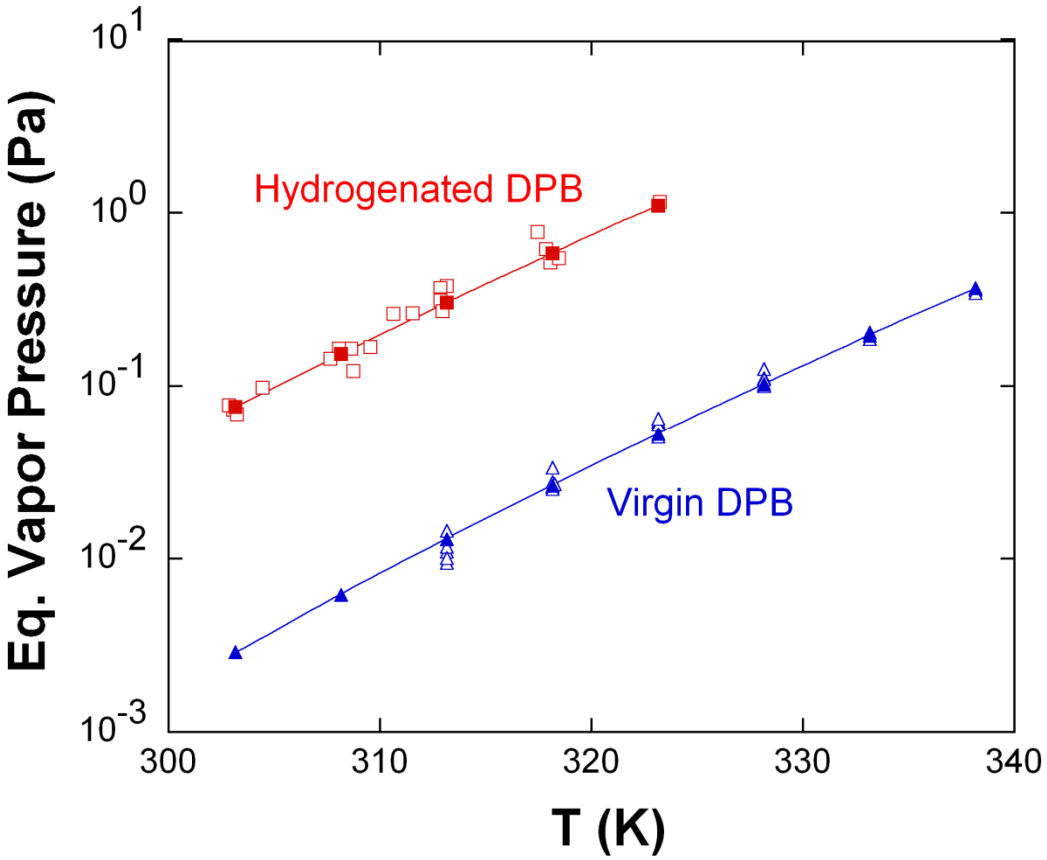
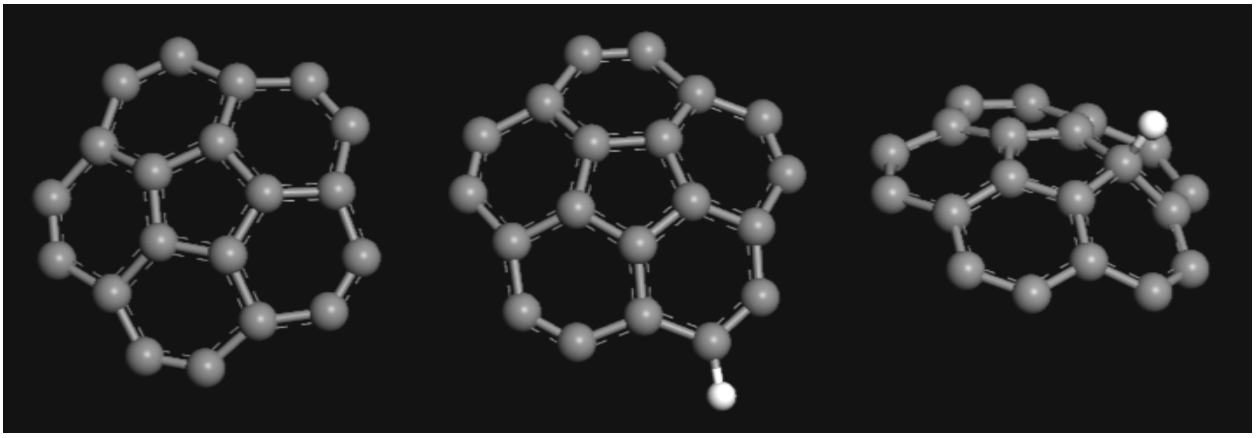
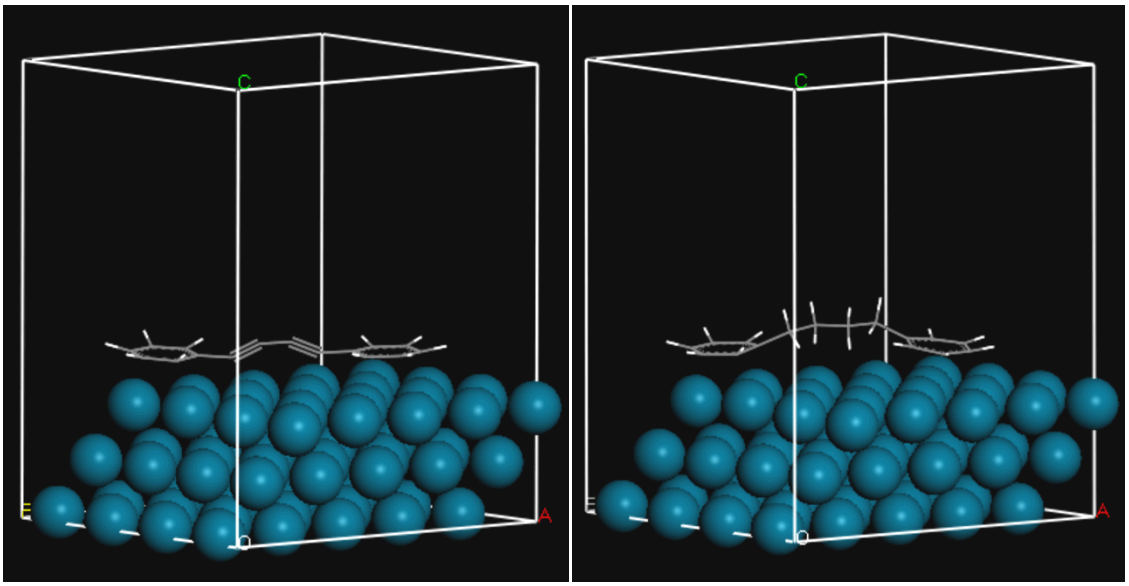

Eq. Vapor Pressure (Pa)
T (K)
Hydrogenated DPB
Virgin DPB
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
300
310
320
330
340

Figure 2



(a) (b) (c)

Figure 3



(a) (b)

Figure 4