On the Mechanism of Carborane Diffusion on a Hydrated Silica Surface

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Studies of motion of carborane wheel-like molecules on glassy surfaces provide an important contribution to the practical goal of designing molecular nanoscale transporters called nanocars. In these vehicles, carborane wheels are chemically coupled to chassis allowing these devices to participate in translations over the surface. As a preliminary step toward modeling dynamics of these species, we have investigated interactions of the p-carborane molecule with the hydrated (1010) surface of α-quartz. Quantum calculations with the CP2K package (cp2k.berlioz.de) have been performed for a series of model systems in order to explicitly estimate interaction energies between the carborane wheel and the surface. It was found that 8 kJ/mol for absorption of carborane on the surface provides a reasonable estimate for this interaction. Correspondingly, the four-wheeled vehicle would require at least 32 kJ/mol to activate its diffusion on the glassy surface. The latter value is consistent with experimental estimates of 42 kJ/mol for the activation energy as follows from single-molecule measurements of temperature dependence of the diffusion coefficient. It is argued that the translation of the four-wheeled carborane nanocars might be consistent with both rolling and hopping mechanisms of motion.

Introduction

Development of nanoscale vehicles intended to perform diverse operations at the molecular level including the transport of molecules and cargoes presents a significant technological challenge. To accomplish directional motion and molecular transport, several single-molecule devices that resemble the coupled chassis and wheels of a car, called nanocars, have been synthesized and characterized experimentally and computationally.[1−5]

The first generation of nanocars was based on the C_{60} fullerene wheels. Their translational motion along the gold crystal surface has been visualized by means of scanning tunneling microscopy.[3,4] Surface transport of these nanocars due to a wheel-like rolling mechanism has been proposed based on the fact that at the same conditions no translational movement for a three-wheeled nanocar analogue of similar size and molecular weight has been observed.[4] However, due to the substantial interaction energy between C_{60} and an Au surface, the four-wheeled nanocars move relatively slowly and only at fairly high temperatures of up to 500 K. To overcome this obstacle, a new class of faster single-molecule transporters, namely, the carborane-wheeled nanocars, designed to move along different surfaces has been proposed.[1,5]

Single-molecule fluorescence imaging of dye-labeled carborane-wheeled nanocars on a glass surface showed an intensive (4.1 nm/s) coupled translational and rotational motion at room temperature with the estimated thermal activation energy of 42 ± 5 kJ/mol.[1] The rolling mechanism was assumed as in the case of fullerene wheeled species by comparing with the

stationary behavior of a three-wheeled nanocar with the unbound dye molecules. When considering molecular mechanism of the interaction of a carborane-wheeled nanocar with a glassy surface, it was suggested that upon attachment to the surface each wheel formed three hydrogen bonds between the surface oxygen atoms and the carborane hydrogen atoms.[1] Correspondingly, the rolling-type motion would require cleavage of only one of three hydrogen bonds per wheel per one moving step, and energetically, it would be easier to roll than to hop with full detachment of the wheels from the surface. In spite of qualitative correlation with the observed activation energy, such an assumption was not confirmed by further experimental or theoretical evidence.

In this work, we study interactions of the carborane wheel-like molecule with a model glassy surface at the atomic level by using quantum chemistry methods. This is a necessary first stage preceding molecular dynamics (MD) simulations of the carborane-wheeled nanocars on glass similarly to the theoretical approach applied before for modeling the fullerene-wheeled nanocars on metal surfaces.[2,6] In those works, the rigid body MD trajectories were analyzed for the models in which the fullerene wheels and the chassis of the nanocars were represented by rigid fragments coupled with each other through the carbon−carbon bonds. This method allowed one to keep the basic features of the real systems and to reduce the cost of simulations significantly.

Compared to the fullerene-wheeled vehicles on metal surfaces, here we encounter additional difficulties. First, the structure of glassy surfaces at the atomic resolution should be much more disordered compared to the crystal-like surfaces. Amorphous silica is characterized by a complex aperiodic structure. It cannot be perfectly cleaved; hence, its surface has lots of defects like geminal silanols and lattice defects. Thus, modeling dynamics of carborane wheel nanocars on glass surfaces seems to be considerably more

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difficult compared to that on metal crystals. Since the previous MD simulations[2] revealed that surface structure and the interaction potentials are critically important for understanding dynamics of nanocars, the model of the proper surface presents a difficult task. In this respect, the use of the quartz-like surfaces imposing the periodical boundary conditions seems to be a reasonable compromise, at least at the first steps of computer simulations. Second, there are no reliable empirical force field parameters to model adsorption and motion of the carborane molecule on glassy surfaces. Therefore, we need to create such set of parameters for MD applications in future work relying mostly on explicit quantum chemistry calculations, which are described in this paper.

In this work, we performed a series of calculations to evaluate the adsorption energy of a carborane molecule adhered to various sites of (1010) quartz surface. We choose the p-$C_2B_{10}H_{12}$ species, since this molecule was used as a wheel in the nanocars.[1,5] A model system of the finite size mimicking the α-quartz surface was constructed. We varied the width and the depth of the quartz slab in order to estimate possible errors induced by periodic boundary conditions or an insufficient slab size.

Limited experimental data on carborane adsorption and formation of hydrogen bonds involving B—H groups can be found in the literature. Several studies involving scanning tunneling microscopy, photoemission, and electron spectroscopy showed that $C_2B_{10}H_{12}$ chemisorbs on Pt(111), Cu(100), Ag, Co, and Au surfaces.[7−11] The X-ray crystallography studies showed that o-, m-, and p-$C_2B_{10}H_{12}$ carboranes tend to form hydrogen bonds C—H⋯(OMe)$_2$ and C—H⋯F—C and to be involved in C—H⋯π interactions similar to the dihydrogen bonds between negatively charged hydrogen atoms bound to boron and positively charged hydrogen atoms of several aminoacids.[12,13] To the best of our knowledge, there are no reports on the carborane adsorption on silica or related surfaces.

Models and Methods

We have chosen a model surface to be represented by a fully hydrated (1010) α-quartz surface. The quartz surface exhibits quite a rich diversity of chemical groups. Terminal silanols are bound to a Si atom involved in three Si—O—Si siloxane groups, whereas geminal silanols complete the coordination sphere of a Si atom involved in two siloxane groups. The recent X-ray studies confirmed the predominance of terminal silanol groups over the amorphous silica surface.[14] Therefore, in our model we used the fully hydrated ideally cleaved SiO$_2$ surface with only terminal silanol groups.

Calculations of equilibrium geometry configurations and interaction energies were performed using the CP2K code.[15] The technique based on the Quickstep[16] implementation of the density functional theory (DFT) method has been utilized for electronic structure calculations. It utilizes the pseudopotential and plane wave methodology in addition to the conventional Gaussian basis set approximations (the Gaussian and Plane Wave method, GPW)[17] to make practical modeling of extended systems. We used the generalized gradient functional PBE[18] and the Goedecker-Teter-Hutter pseudopotentials[19] in conjunction with triple-ζ basis sets with polarization functions (TZVP). The plane wave basis was extended to the density cutoff of 500 Ry. Such a computational scheme was successfully applied before in studies of point defects in silica and organosilanes adsorption on silica surfaces.[20] For all model systems, the periodic boundary conditions with the wavelet-based Poisson equation solver have been applied along the *XY* plane to allow for slab-boundary conditions. The adsorption energies were estimated as the difference between the lowest energy of the composite model
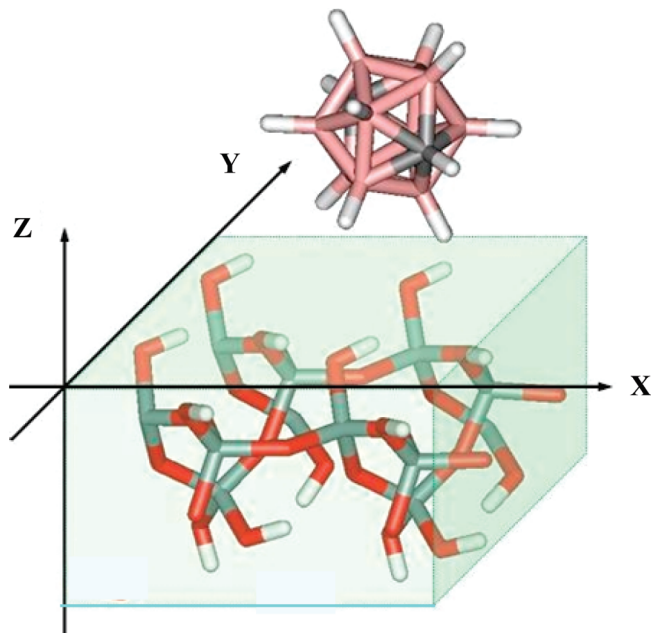

Figure 1. An example of the simulation cell used in calculations showing the carborane molecule over a slab of the smallest size. Periodic boundary conditions are supposed along the *X* and *Y* directions. In this and other figures, carbon atoms are shown in gray, oxygen in red, boron in pink, and hydrogen in white.

system and the lowest energies of its constituents. The basis set superposition error should not present a serious concern in these calculations because of the use of pseudopotentials as well as the use of the plane wave basis, and all model systems are computed in an identical size box.

Figure 1 illustrates the simulation cell used in calculations showing the carborane molecule over a slab of the smallest size considered in this work. The periodic boundary conditions were imposed along the *X* and *Y* directions.

Results and Discussion

We started the procedure by creating a single, fully hydrated α-quartz (1010) surface cell. Quartz is characterized by a hexagonal structure belonging to the space group $P3_121$. We considered a unit cell with the parameters $a = b = 4.914$ Å, $c = 5.405$ Å; α = β = 90°, γ = 120°.[21] The initial structure of the SiO$_2$ surface was built using the *VESTA* visualization program that is a part of the *VENUS* package.[22] We used an α-quartz 4 × 4 × 4 supercell which was rotated in such a way that the required surface remained perpendicular to the *b* axis of the simulation cell. It was also truncated to form a small surface cell ($a = 4.9$ Å, $b = 8.5$ Å, $c = 5.4$ Å, α = β = γ = 90°). Dangling oxygen atoms were then saturated by hydrogen atoms, which yielded the fully hydroxylated surface. Two upper layers of the SiO$_4$ tetrahedrons were allowed to relax in the course of geometry optimization. The lower layer represented the rest of the crystal and was kept fixed at its bulk equilibrium positions. After geometry optimization, neighboring SiOH groups formed the zigzag hydrogen-bond chains of the vicinal hydroxyls (Figure 1). Due to the high OH surface density, the shortest H⋯O distance is 1.72 Å, which shows a strong hydrogen bond interaction with the neighboring silanol groups. The optimized geometry parameters, the Si—O bond lengths, the Si—O—Si and O—Si—O angles, are in good agreement with the experimentally observed values.[20] As a result of the geometry parameter relaxation, the Si—O—Si angles are slightly smaller,
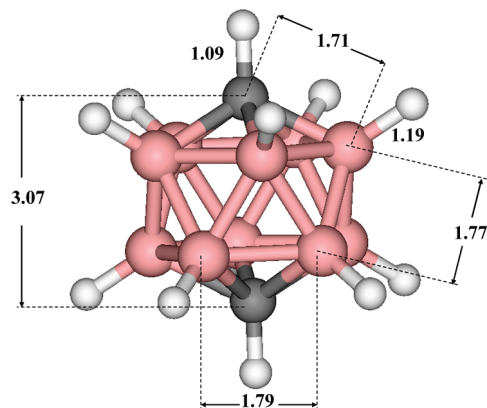
Figure 2. Equilibrium geometry configuration of the carborane (p-$C_2B_{10}H_{12}$) molecule showing distances in angstroms.

Figure 3. Extended (left) and deep (right) model slabs.

and the Si—O bonds are slightly longer than the values known for bulk silica.

As a validation of the calculation methods used in this work for analyzing the carborane—quartz interaction, we have also modeled the adsorption energy of a single water molecule on the quartz surface. It is known that water can be adsorbed to the surface silanols forming hydrogen bonds, and the corresponding adsorption energy is estimated between 44 and 51 kJ/mol.[23–25] Therefore, at the preliminary stages of this work we computed the equilibrium geometry configuration and interaction energy of a water molecule on the same model quartz surface as used in simulations of the carborane species. When water is added, the weak surface hydrogen-bond chains are broken and the corresponding hydroxyl groups reform hydrogen bonds with H_2O molecules. We studied the configuration of a single isolated water molecule hydrogen-bonded to the terminal silanol and to the bridging oxygen atom. As a result of geometry relaxation, the zigzag hydrogen-bond chains are distorted and new hydrogen bonds between the surface and the water molecule are formed. The computed binding energy of the water molecule on the slab is 47 kJ/mol, which is close to the adsorption energy obtained in other experimental[24] and theoretical works[23,25] for water on vicinal silanols. This provides an additional support to our theoretical method.

Computed equilibrium geometry parameters of the carborane molecule, p-$C_2B_{10}H_{12}$, shown in Figure 2 correlate well with the experimental values obtained by the gas-phase electronic diffraction.[26]

When modeling interaction of the carborane molecule with the small silica slab (Figure 1), we found three sites which represented different local minima on the potential energy surface of the system. Complete optimization of coordinates was performed in each case. The corresponding binding energies were as follows: 7.8, 6.1, and 8.1 kJ/mol. We verified that these energies are sensitive to the calculation details, and we recomputed equilibrium geometry parameters and the energies near the first site with the initial energy 7.8 kJ/mol. First of all, we removed the periodic boundary conditions and enlarged the cell parameters to $a = 20$ Å, $b = 25$ Å, and $c = 20$ Å. The newly computed binding energy was 8.8 kJ/mol. Then, we applied another basis set TZV2P that resulted in the binding energy estimate of 6.4 kJ/mol.

Also, two larger slab models illustrated in Figure 3 have been considered. To construct the extended quartz slab (left panel in Figure 3), we replicated the initial fully hydrated surface cell along a and c directions in order to obtain an $8 \times 1 \times 8$ supercell with the parameters $a = 19.7$ Å, $b = 25.0$ Å, and $c = 20.2$ Å. The deep model slab (right panel in Figure 3), $Si_{32}O_{72}H_{16}$, is
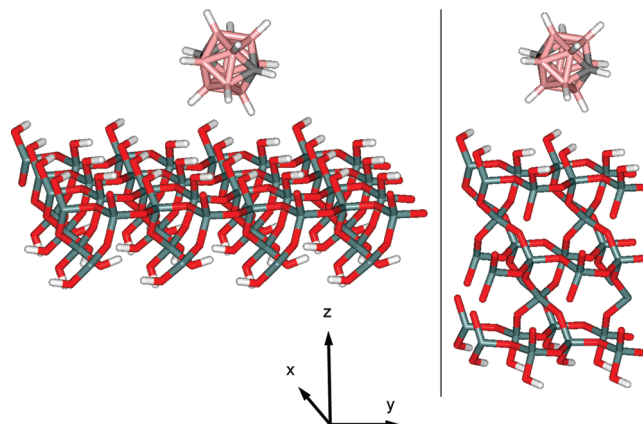
characterized by the parameters of the cell $a = 9.8$ Å, $b = 30.0$ Å, $c = 10.1$ Å; $\alpha = \beta = \gamma = 90°$. It was formed from the small $4 \times 1 \times 4$ supercell by adding extra layers of underlying SiO_4 tetrahedrons. The computed binding energies of the carborane molecule with those model slabs were 8.1 and 8.7 kJ/mol, correspondingly. Comparing results of these calculations for different modes, we can conclude that a reasonable estimate of the binding energy for a single p-carborane molecule on the hydrated (1010) surface of α-quartz is close to (8 ± 1) kJ/mol.

Finally, we note that a careful search has been accomplished for various local minima on the potential energy surfaces, and only those reported in this work have been found for these model systems. We do not exclude that using other models and other methodologies would result in a larger number of competitive local minima as, for instance, in the Car—Parrinello molecular dynamics simulations.[27]

Discussion

A carborane-wheeled nanocar may be constructed by coupling three or four p-carborane molecules along the corresponding carbon—carbon axes to a chassis. The observed movement of the four-wheeled nanocar on the glassy surface at room temperature[1] is due to the shifts of the carborane wheels from the binding sites on the surface. According to our calculation results, the energy of at least 32 kJ/mol (4×8 kJ/mol) is required to activate movement a machine with four carborane wheels along the hydrated silica surface. The experimentally estimated thermal activation energy of the dye-labeled carborane-wheeled nanocar on the glass surface was 42 ± 5 kJ/mol.[1] One could argue that the difference between these values is due to the fact that other parts of the nanocars might also interact with surface increasing the activation barrier. In addition, we also did not take into account that the device considered experimentally also included the fairly large dye label, which must contribute to the interaction of the nanocar with the surface. Furthermore, possible lattice defects might considerably slow down these nanocars, also effectively increasing the corresponding thermal activation barriers. The calculated energy 32 kJ/mol should be corrected toward a somewhat larger value approaching closer to experimental observations. Therefore, our theoretical results obtained by the brute-force quantum-based calculations agree reasonably well with the experimental results.

To understand the dynamics of carborane-wheeled nanocars, it is important to estimate the role of rolling motion in the overall surface transport. When interpreting the motion of the carborane-wheeled nanocar on a glass surface, arguments have been put forward favoring the rolling mechanism of the device. It was
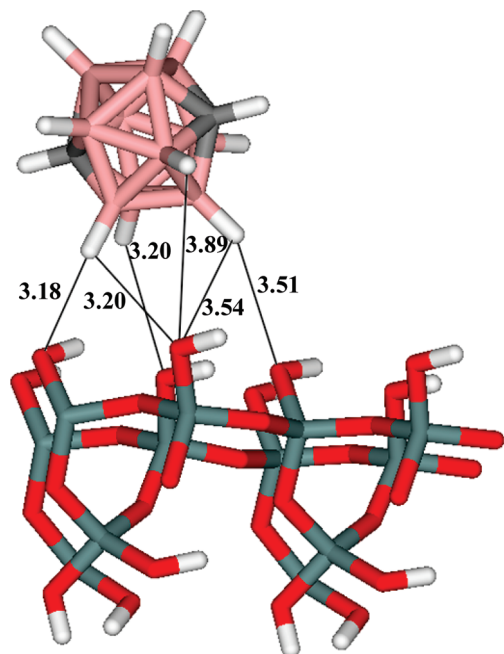
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Figure 4. Selected distances between the carborane hydrogen atoms and silanol oxygen atoms of less than 4 Å at one of the binding sites.

suggested that upon attachment to the surface each wheel formed three hydrogen bonds between the surface oxygen atoms and the carborane hydrogen atoms.[1] Correspondingly, the rolling-type motion would require cleavage of only one of three hydrogen bonds per wheel per one moving step, and energetically, it would be easier to roll than to hop with the full detachment of the wheels from the surface. In light of the obtained theoretical results, we believe that such a model[1] presents an oversimplified picture of actual dynamics. Our theoretical calculations do not support the existence of localized hydrogen bonds. In contrast, the interaction with the surface seems to be fully delocalized.

Figure 4 illustrates the equilibrium geometry configuration of the carborane molecule on the slab for one of the binding sites. We draw attention to the distances between carborane hydrogen atoms and silanol oxygen atoms—those shown are the distances less than 4 Å. For all other model systems, the picture is essentially similar. A roughly average B−H···O distance 3.3 Å which corresponds to the reported B−H···N distances in the reported structure of the complex of carborane with the nickel(II) macrocycle is observed.[12] There are no apparent strong, localized interactions between hydrogens of the carborane and oxygens of the silanols, and the surface hydrogen bond network is not distorted or broken when carborane adsorbs, unlike the case of water adsorption. It is not possible to distinguish "three hydrogen bonds between the surface oxygen atoms and the carborane hydrogen atoms" as was assumed in ref 1. Therefore, according to presented calculation results we cannot discriminate the hopping mechanism or rolling mechanism of the diffusion of carborane-based vehicles on the glass.

Conclusions

By analyzing the results of quantum-based simulations, we found that the binding energy of the carborane wheel with the model glassy surface is about 8 kJ/mol. Correspondingly, the four-wheeled vehicle would require of at least 32 kJ/mol to activate its diffusion on the glassy surface. The latter value is consistent with the experimental estimate of 42 kJ/mol for the activation energy as follows from measurements of temperature dependence of the diffusion coefficient.[1] Our results suggest that translation of the four-wheeled carborane nanocars may be consistent with both rolling and hopping mechanisms of motion. More detailed theoretical calculations and single-molecule experimental studies are needed in order to fully understand mechanisms of the motion of carborane-wheeled nanocars on glass surfaces.

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