Trapping of Hydrogen Atoms in All-Silicon Zeolite Cages: Density Functional Theory Studies

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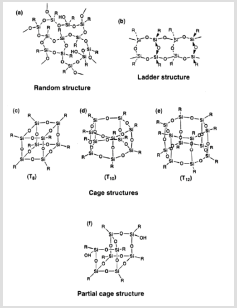
Introduction

Interest in caged, microporous materials, such as zeolites and silsesquioxanes, has increased in recent years. Zeolites, a hydrated aluminosilicate, are of particular interest for their uses in catalysis, small molecule adsorption, and ion exchange. The capacity of zeolites to adsorb hydrogen makes them of some interest as prototype hydrogen storage materials.

Silsesquioxanes are molecular analogues of zeolites with the empirical formula $RSiO_{1.5}$ where R is a hydrogen atom or any alkyl, alkylene, aryl, arylene, aryl, or organo-functional derivatives of these groups. Silsesquioxanes can exhibit a variety of different structural motifs including ladders, cages, or partial cages, but can also exhibit random structures [1].



Whereas abundant data exist on the properties and behaviors of zeolites and there has been much research into silsesquioxane chemistry, little is known about the fundamental characteristics of silsesquioxane cages and their interactions with guest atoms or molecules. In particular, computational studies that model the cages and their inner surface properties are somewhat lacking. For example, a good description of the dependence of the internal energy surface on cage size and symmetry is not yet available.

Hyperfine Interaction

In the present work, the properties of silsesquioxane cavities are studied through the interactions between the cage and a trapped hydrogen atom. Some calculations have already been published on the model system HT_8 [2]. The properties studied are the overall energy and the hyperfine splitting, in particular the isotropic Fermi contact component. The hyperfine splitting is a small splitting in the hydrogen atom spectrum originating from the interaction between the electron and nuclear spins. The hyperfine splitting is of the free hydrogen atom occurs at a frequency of 1420MHz, and is the origin of the 21cm line (a forbidden transition) much used in radio astronomy [3].

The hyperfine interaction is comprised of an isotropic and an anisotropic term. The isotropic contribution is known as the Fermi contact term and is proportional to the unpaired spin density at the nucleus.

$$A_{iso} = \frac{8\pi}{3} g_{el}\beta_{el} g_N \beta_N \langle \Psi | \hat{\rho}_N(\mathbf{r}) | \Psi \rangle$$

where g_{el} is the electronic g factor, g_N is the nuclear g factor, β_{el} is the electronic Bohr magneton, β_N is the nuclear Bohr magneton, and $\rho(\mathbf{r})$ is the spin density at the nucleus.

The anisotropic term is known as the dipolar term. In the free H atom, only the Fermi contact term needs to be considered because of the atom's spherical symmetry. However, in systems of lower symmetry the anisotropic term must also be taken into consideration. In this study, for example, the anisotropic term is zero only when the hydrogen atom is located at the cage center.

(Only the Fermi contact term is discussed in this poster.)

TeraGrid

The TeraGrid is a national distributed high performance computational infrastructure, consisting of numerous supercomputers located around the United States. Some of these supercomputers are located at Indiana University (IU), National Center for Supercomputing Applications (NCSA), Pittsburg Supercomputing Center (PSC), Texas Advanced Computing Center (TACC), San Diego Supercomputer Center (SDSC), Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL).

The calculations featured here were carried out using the *Cobalt* cluster, located at NCSA, which is a conglomeration of 1100 Itanium 2 processors, and has roughly 3 Terabytes of memory.

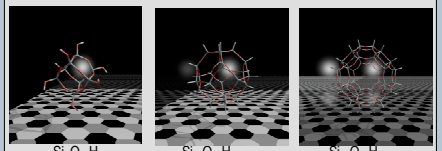
Materials/Methods

Geometry optimizations and frequency calculations on the empty cages, together with caged hydrogen calculations were all carried out using several methods and basis sets. Here, two hybrid density functional theory methods (MPw1Pw91 and B3LYP) are compared with Hartree-Fock theory. The basis sets used were aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z. In order to model the behavior of the electrons near the nucleus, the basis sets were decontracted and additional rapidly decaying functions with geometrically related exponents were incorporated into the basis set. The software packages Gaussian 03 [4] and Gaussian 09 [5] were used to carry out the calculations.

Results

Optimized geometries of three prototypical silsesquioxane cages (analogues to LTA zeolite structures).

Channel Sodalite Cage Supercage



$Si_8O_{18}H_8$ $Si_{24}O_{36}H_{24}$ $Si_{48}O_{72}H_{48}$

The channel and supercage exhibit O_h symmetry, while the sodalite cage is D_{3d}.

Computed values:

B3LYP		Hartree-Fock		MPW1PW91	
Basis Set	Fermi Contact Term (MHz)	Basis Set	Fermi Contact Term (MHz)	Basis Set	Fermi Contact Term (MHz)
aug-cc-pVTZ_1t	1350.264	aug-cc-pVTZ_1t	1303.356	aug-cc-pVTZ_1t	1337.302
aug-cc-pVTZ_2t	1407.917	aug-cc-pVTZ_2t	1357.166	aug-cc-pVTZ_2t	1393.653
aug-cc-pVTZ_3t	1416.408	aug-cc-pVTZ_3t	1365.169	aug-cc-pVTZ_3t	1401.869
aug-cc-pVQZ_1t	1396.421	aug-cc-pVQZ_1t	1346.449	aug-cc-pVQZ_1t	1382.492
aug-cc-pVQZ_2t	1433.366	aug-cc-pVQZ_2t	1381.086	aug-cc-pVQZ_2t	1418.285
aug-cc-pVQZ_3t	1438.748	aug-cc-pVQZ_3t	1386.053	aug-cc-pVQZ_3t	1423.729
aug-cc-pV5Z_1t	1441.058	aug-cc-pV5Z_1t	1388.257	aug-cc-pV5Z_1t	1425.959
aug-cc-pV5Z_2t	1457.823	aug-cc-pV5Z_2t	1403.969	aug-cc-pV5Z_2t	1442.209
aug-cc-pV5Z_3t	1460.265	aug-cc-pV5Z_3t	1406.229	aug-cc-pV5Z_3t	1444.675

For the free H atom, the Hartree-Fock method is exact in the infinite basis set limit; for smaller basis sets, the Fermi contact coupling is consistently underestimated. This also holds true for the caged H atoms studied here. The best results are obtained using the largest basis set, here the 5ζ correlation-consistent basis with three additional functions to describe the behavior near the nucleus.

For molecular and supramolecular systems open-shell Hartree-Fock methods are susceptible to problems such as spin contamination, leading to the necessity of choosing an optimum density functional approach. From the present study it appears that B3LYP using a 3ζ basis and 3 tight functions may be the best approach for extended studies.

Future Work

Ongoing work focuses on probing the potential energy and hyperfine coupling surfaces along significant directions in the cage.

All-Si zeolites have recently been synthesized by self-assembly from functionalized silsesquioxane subunits [6]. Electron spin resonance studies of H diffusion and detrapping behavior in these materials will form a useful test of the present calculations.

Literature Cited

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[3] S.G. Karshenboim, Simple atoms, quantum electrodynamics, and fundamental constants. *Precision of Simple Atomic Systems*; Lecture Notes in Physics, Vol. 627; Karshenboim, S.G., V.B., Eds; Springer: Berlin, 2003; pp141-162.

[4] Gaussian 03 website, http://www.gaussian.com/

[5] Gaussian 09 website, http://www.gaussian.com/g_prod/g09.htm

[6] A. Corma et al, *Nature*, 431, (2004), 287

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