

Modeling Hydrogen Atom Sequestration in Siloxane Cages

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Abstract

Encapsulation of atoms or molecules in nanoscale cage or pore structures is a fundamental process in catalysis and is of recent interest in connection with storage of molecular hydrogen for use as a future energy source or for sequestration of atmospheric carbon dioxide. Here we extend the work described in [1] on modeling of the energetics of hydrogen atom isotopes encapsulated in three types of all-silicon zeolite cage structure.

Developing the Code

The results described in [1] are based on code written in the Wolfram Mathematica 2.0 language several years ago; a first goal was to update this code to run under the current 8.0 version of Mathematica, which required some modification to several of the algorithms. Development work on the code continues with the goal of incorporating new functions built into the programming language and to increase efficiency.

Parabolic Fit Computation Code

```
Needs["Combinatorica"];
$Path = Append[$Path, "C:\Users\jrvates\Desktop\School
Information\summer '11\data"];
indata = Transpose[ReadList["b3lypdata.out", Table[Number, {3}]]];
alist = indata[[1]];
elist = Table[435.97 *( indata[[2,i]] - Min[indata[[2]]]), {i,
1,Length[indata[[2]]}];
plist = indata[[3]];
tra1 = Table[{alist[[i]], elist[[i]], {i, 1, Length[elist]}};
tra2 = Table[{alist[[i]], plist[[i]], {i, 1, Length[elist]}};
HBar = 1.05459/10^14;
amu = 1.66056/10^27;
boltzmann = 1.380622/10^3;
amass=1.007825;
amass=amass*amu;
U[k_,Q_]:=1/2*k*Q^2;
Vpot[shift,k,Q]:=(shift+U[k,Q]);
fitpars={{shift,0.01},{k,1}};
outpars=FindFit[tra1,Vpot[shift,k,Q],fitpars,Q,MaxIterations@5000];
fitpars/=outpars;
Vfit[Q_]:=Vpot[shift,k,Q]/outpars;
Show[ListPlot[tra1,PlotStyle->PointSize[0.02],DisplayFunction-
>Identity],Plot[Evaluate[Vfit[Q]],{Q,-2,2},DisplayFunction-
>Identity],DisplayFunction->$DisplayFunction]
```

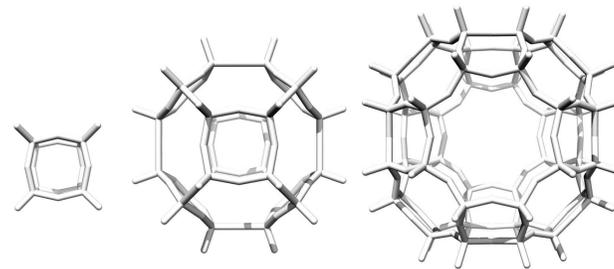
What the code does

The code above takes a set of points from the input data (of total energy vs displacement from the cage center) and fits a parabolic curve to these points. This represents the harmonic approximation, familiar from the classical physics of springs and pendulums, which is applied in many

chemical systems and which leads to a Schrödinger equation that is exactly solvable. The following graphs shows the degree to which a parabolic fit is appropriate for the data in several different cases.

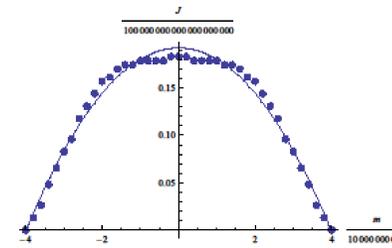
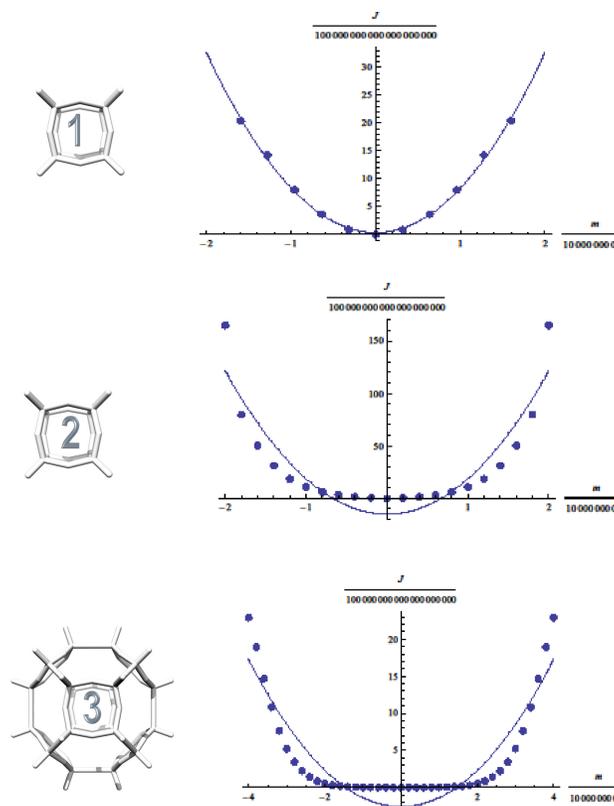
(See the accompanying *Demonstration* for an illustration of the features of the harmonic oscillator approximation.)

The Cages



The three cages studied, $\text{Si}_8\text{O}_{12}\text{H}_8$ (also studied in [1]), analog of the 4-ring channels linking sodalite cages, $\text{Si}_{24}\text{O}_{36}\text{H}_{24}$, analog of the sodalite cage itself, and $\text{Si}_{48}\text{O}_{72}\text{H}_{48}$, analog of the "supercage". In each case the cage symmetry is O_h , with the Si atom framework forming, respectively (and approximately) a cube, a truncated octahedron, and a truncated cuboctahedron. Principal directions in these cages are defined in terms of $\langle 100 \rangle$ directions passing through the centers of the Si 4-rings in the first two cages, and through the centers of the Si 8-rings in the supercage.

Fitting to Harmonic Potential Functions



Resulting Fit Equations with Harmonic k value

Figure 1: $8.09686 Q^2 + 0.303796$ with $k = 16.1937$

Figure 2 : $34.1513 Q^2 - 15.1936$ with $k = 68.3026$

Figure 3: $1.243 Q^2 - 2.59699$ with $k = 2.48599$

Figure 4: $0.19221 - 0.012107 Q^2$ with $k = -0.0242139$

Summary of Fit Results

The data sets used in these fits represent the results of density functional calculations (described in [2]) on H atom displacement in key directions within Si_8 , Si_{24} , and Si_{48} cages. Only in the first figure, representing the $\langle 100 \rangle$ directions (towards the face centers) in the Si_8 cage is the harmonic approximation a good fit. The remaining figures show, respectively, the $\langle 110 \rangle$ direction in the Si_8 cage (towards the bridging O atoms), the $\langle 111 \rangle$ direction in the Si_{24} cage (towards the center of the Si 6-ring), and the $\langle 100 \rangle$ direction (towards the Si 8-ring center) in the Si_{48} cage. Only in the first case is the harmonic approximation a good fit.

Remainder of Updated Code

```
k=k/.outpars;
shift=shift/.outpars;
omega = Sqrt[k/amass];
beta = Sqrt[HBar/(2*amass*omega)];
Eig[v_]:= (v+3/2)*HBar*omega;
hfi[Q_]:=Fit[tra2,{1,Q^2,Q^4,Q^6,Q^8},Q];
Plot[hfi[Q],{Q,-2,2},Epilog->({PointSize[0.01],Point[#1]}&)/@tra2];
qfitpars={{q0,1},{q2,0.001},{q4,0.001},{q6,0.001},{q8,0.001}};
QFn[q0_,q2_,q4_,q6_,q8_,Q_]:=q0+q2*Q^2+q4*Q^4+q6*Q^6+q8*Q^8;
qoutpars=FindFit[tra2,QFn[q0,q2,q4,q6,q8,Q],qfitpars,Q,MaxIterations-
>5000];
q0=q0/.qoutpars;
q2=q2/.qoutpars;
q4=q4/.qoutpars;
q6=q6/.qoutpars;
q8=q8/.qoutpars;
npars=5;
qq=Table[qoutpars[[kk,2]],{kk,1,npars}];
qq={q0,q2,q4,q6,q8};
Clear[i];
Krec[l_,j_,0]=KroneckerDelta[i,j];
Krec[l_,j_,l_]:=Sqrt[j+1]*Krec[i,j+1,l-1]+Sqrt[j]*Krec[i,j-1,l-1];
complist[jj_]:=Compositions[jj,3];
```

```
lenn[jj_]:=Length[complist[jj]];
mul[jj_,ll_]:=Multinomial[complist[jj][[ll,1]],complist[jj][[ll,2]],
complist[jj][[ll,3]]];
idim=10;
tot=Sum[lenn[lev],{lev,0,idim}];
Ahy=Table[0.,{tot}];
en=Table[0.,{tot}];
Clear[m];
For[m=1,m<=idim+1,m++,If[m==1,qm=0,qm=qm+lenn[m-2]];
For[mm=1,mm<=lenn[m-1],mm++,qqm=qm+mm;
Ahy[[qqm]]=qq[[1]]+Sum[qq[[kk+1]]*beta^(kk*2)*Sum[mul[kk,indx]*Pro
duct[Krec[complist[m-1][[mm,nn]],complist[m-
1][[mm,nn]],2*complist[kk][[indx,nn]],{nn,1,3}],{indx,1,lenn[kk]}],{kk,1,
npars-1}];
en[[qqm]]=Eig[m-1]];
Krec[i_,j_,0]=KroneckerDelta[i,j];
Krec[i_,j_,l_]:=Krec[i,j+1,l-1]+Krec[i,j-1,l-1];
tstep=1.;
tmin=100.;
tmax=350.;
nstep=(tmax+1-tmin)/tstep;
AofT=Table[0.,{nstep}];
temp=Table[0.,{nstep}];
T=tmin-tstep;
For[i=1,i<=nstep,i++,T=T+tstep,temp[[i]]=T,Atemp=0,Ptemp=0,bT=boltzmann*T,For[j=1,j<=tot,j++,{expenrg=E^(-
en[[j]]/bT),Atemp=Atemp+Ahy[[j]]*expenrg,Ptemp=Ptemp+expenrg}],A
onP=Atemp/Ptemp,AofT[[i]]=AonP];
Clear[i];
tdep=Table[{temp[[i]],AofT[[i]]},{i,1,nstep}];
Show[ListPlot[tdep,PlotStyle->PointSize[0.02],DisplayFunction-
>$DisplayFunction]
```

What the code does (II)

The remaining part of the code uses the isotropic harmonic oscillator approximation in three dimensions to calculate energy eigenvalues for different H isotopes (μ , H, and D) and compute the temperature-dependent isotropic hyperfine coupling constant, which can be compared with experiment.

Future Research

The next step in this project is to develop algorithms utilizing quantum-mechanical models beyond the harmonic approximation. Even in one dimension, this must be done using approximate methods. We propose to solve the quantum-mechanical problem in the basis of the harmonic oscillator eigenfunctions. Subsequently, we plan to develop a fully anisotropic three-dimensional anharmonic model, involving discretization of the potential energy functions over the surface of the sphere.

References

- [1] M. Päch, R. M. Macrae, I. Carmichael, J. Amer. Chem. Soc. 128, (2006), 6111.
- [2] R. M. Macrae, "Hydrogen atom isotope dynamics and hyperfine interactions in analogues of all-silicon zeolite cages: Density functional theory studies", poster presented at CERMACS 2011, Indianapolis, IN, June 8-10, 2011.