Confined Quantum Molecule Degrees of Freedom

Symmetry-breaking in $H_2@C_{60}$ Endofullerene

Jianying Sheng
University of Waterloo
April 21, 2017

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OUTLINE

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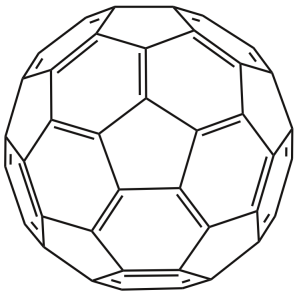
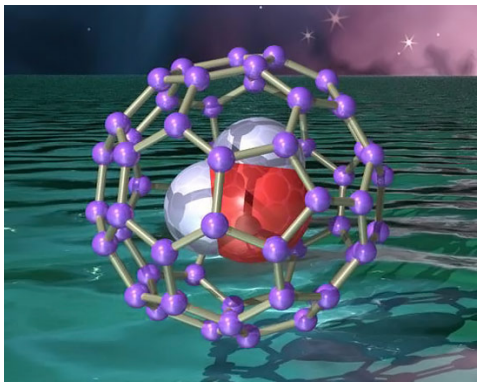
MOLECULES: H2@C60,H2O@C60,HF@C60



C60,gas:Ih, solid:C_{3i}

(a) $H_2@C_{60}$



(b) $H_2O@C_{60}$

(c) $HF@C_{60}$

- $H_2@C_{60}$:Koichi Komatsu,Michihisa Murata, Yasujiro Murata,VOL 307, SCIENCE,2005
- $H_2O@C_{60}$:Kei Kurotobi and Yasujiro Murata, VOL 333 SCIENCE, 2011
- $HF@C_{60}$:Andrea Krachmalnicoff,Richard J.Whitby,NATURE CHEMISTRY VOL 8 , 2016

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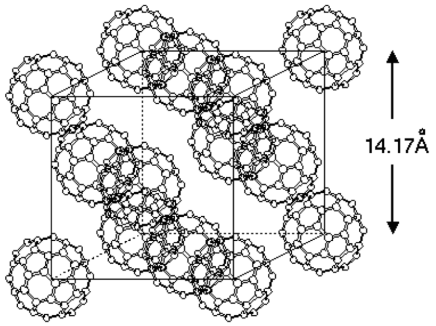
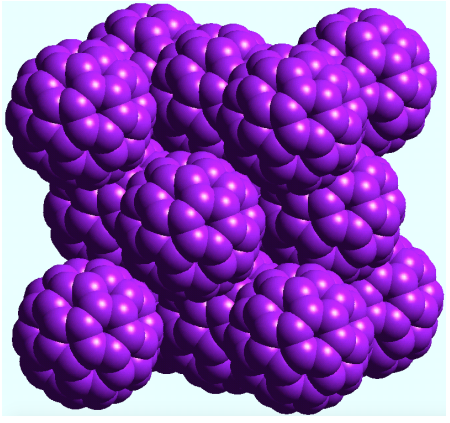
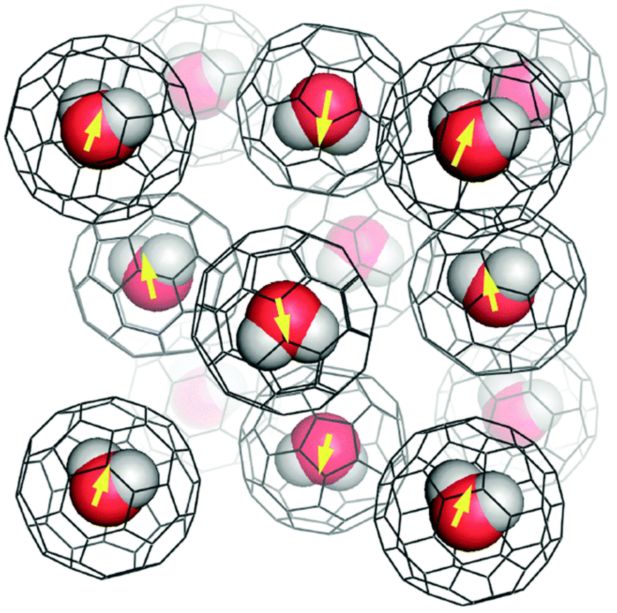
C_{60} LATTICE VS H2O@C60 LATTICE





molecular surgery



Shinobu Aoyagi,Yasujiro Murata,Chem. Commun 2014, 50,524

- Same lattice structure(FCC)
- Same group symmetry($Pa\bar{3}$)
- Same structure phase transition

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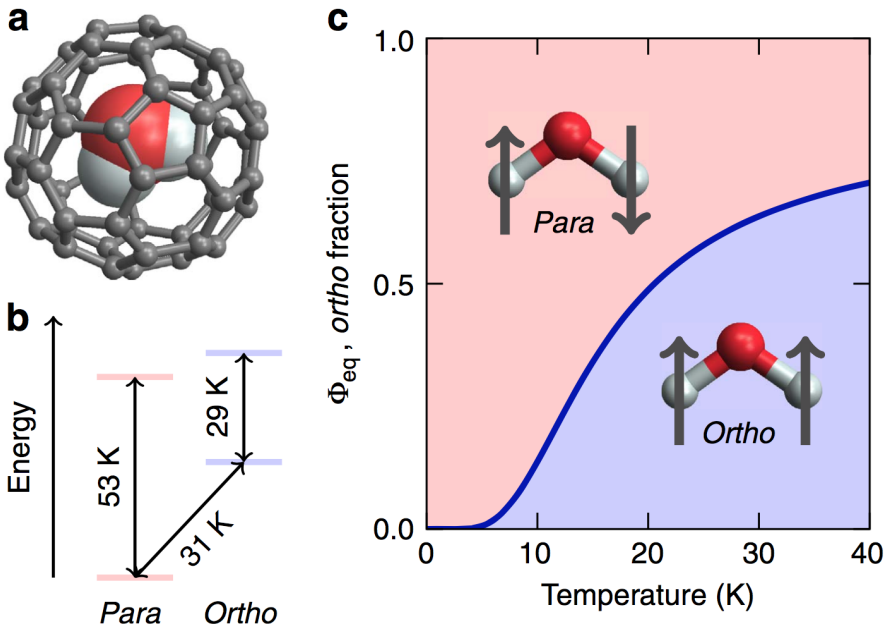
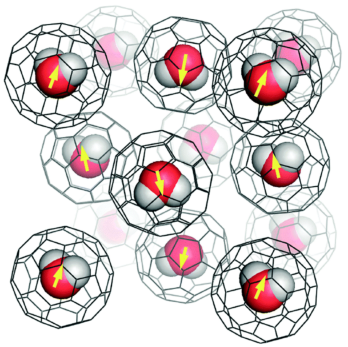
THE ORTHO PARA CONVERSION OF $H_2O@C_{60}$

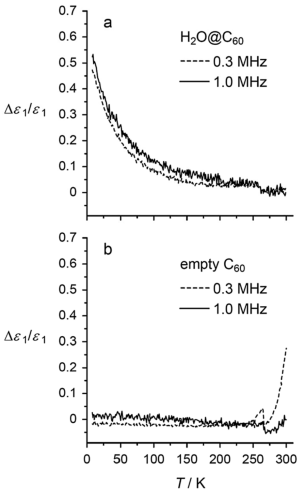


- the observation of two spin isomers is not possible due to the fact that molecular rotation is restricted from hydrogen bonding
- stable substance to see spin isomer conversion through dielectric measurements

Meier, B. et al. Electrical detection of ortho para conversion in fullerene-encapsulated water. Nature. Commun(2015)

ELECTRIC DIPOLAR LATTICES:H2O@C60,HF@C60





- By trapping water in C_{60} cage, the resultant lattice could result in a net polarization

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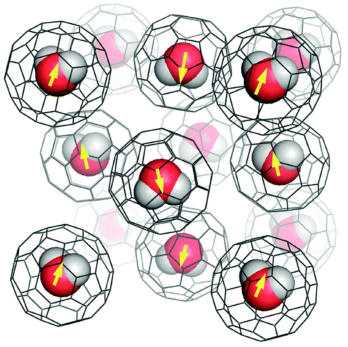

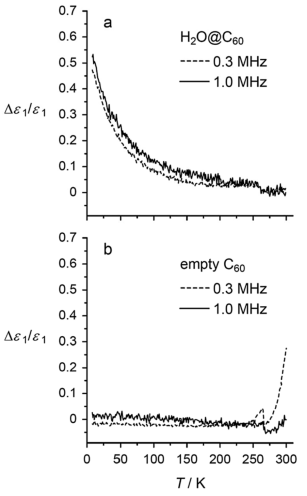

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- The $H_2O@C_{60}$ can theoretically, exhibit ferroelectric phase transition as predicted by Cioslowski and Nanayakkara in 1992.

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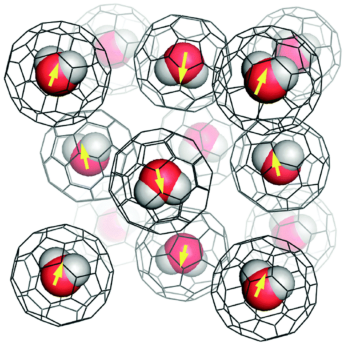

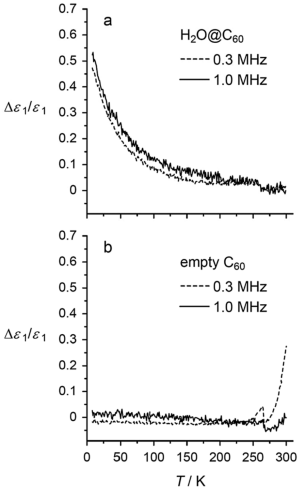

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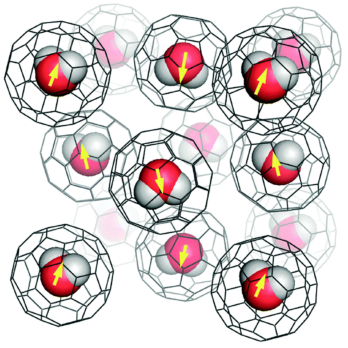

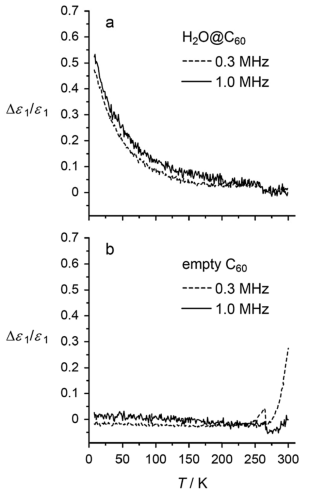

- By trapping water in C_{60} cage, the resultant lattice could result in a net polarization
- The $H_2O@C_{60}$ can theoretically, exhibit ferroelectric phase transition as predicted by Cioslowski and Nanayakkara in 1992.
- Experiment shows there is no ferroelectric phase transition down to 8K
- Theoretical efforts are needed in order to predict the collective orientation of dipolar water and phase transition diagrams

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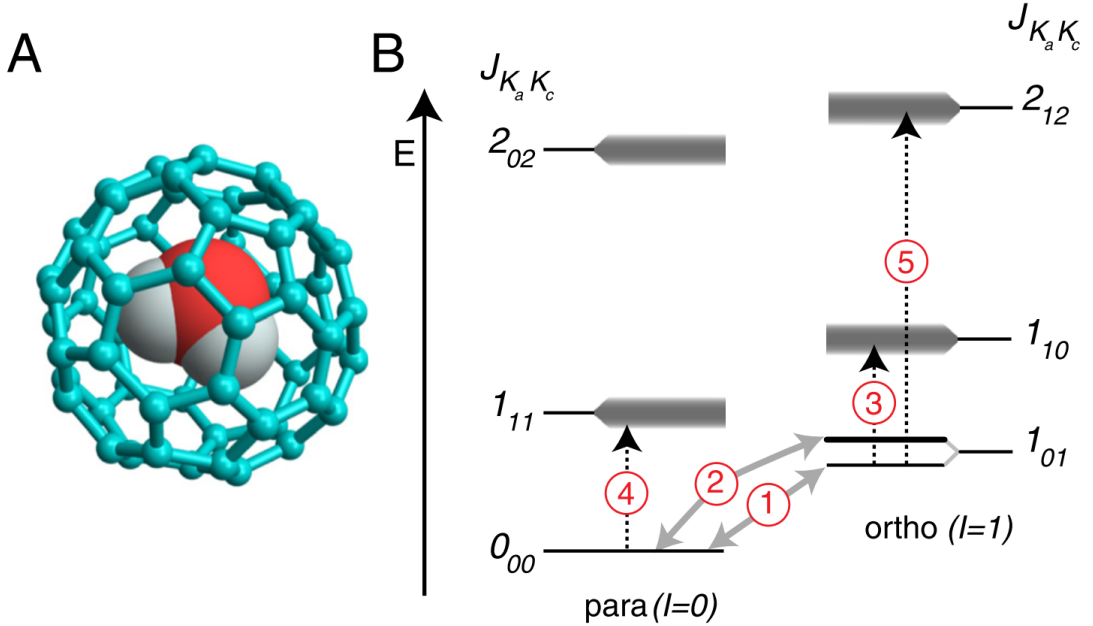
Shinobu Aoyagi,Yasujiro Murata,Chem. Commun 2014, 50,524

SYMMETRY-BREAKING IN THE ENDOFULLERENE H2O@C60



- Three-fold rotational ground state lifting to doubly degenerate upper level and non-degenerate lower level.

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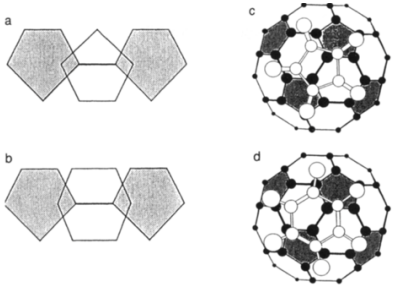
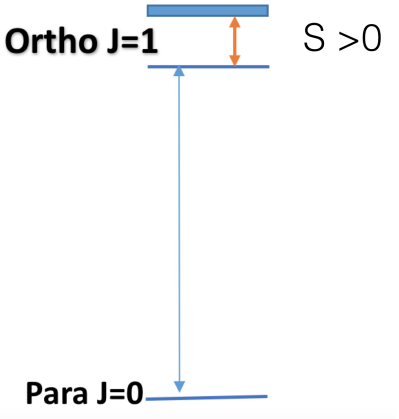
C. Beduz, et al Proceedings of the National Academy of Sciences of the United States ofAmerica109, 12894 (2012).

SYMMETRY-BREAKING IN THE ENDOFULLERENE H2@C60





P-phase: double bonds face the pentagons of neighbouring cage
H-phase: double bonds face the hexagons of neighbouring cage

P phase S= 1.0889cm^{-1}
H phase S = 1.3711cm^{-1}

- Three ortho levels split into a low energy non-degenerate level and a high energy doubly degenerate level
- The splitting are different for P-phase and H-phase neighbouring orientation

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S.Mamone et al, DOI: 10.1039/c5cp07146a

SYMMETRY-BREAKING FOR SMALL MOLECULE TRAPPED INTO ENDOFULLERENE:QUESTION

- What is the nature of the symmetry breaking interaction that gives rise to the splittings?

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- What is splitting sensitive to?
  - ”distortion” or ”neighbouring orientation”

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EXACT DIAGONALIZATION OF $H_2@C_{60}$: THEORY

- Assumption:
  - C_{60} is rigid and non-rotating
  - H2 bond length is fixed
  - No ortho-H2,para-H2 conversion

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- Hamiltonian

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + B_\nu \mathbf{j}^2 + V(x, y, z, \theta, \phi) \tag{1}$$

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- Lennard-Jones potential

$$V = \sum_{j=1}^{2}\sum_{i=1}^{60} 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \omega\sum_{i=1}^{60} 4\epsilon\left[\left(\frac{\sigma}{r_{i,m}}\right)^{12} - \left(\frac{\sigma}{r_{i,m}}\right)^{6}\right] \tag{2}$$

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- Basis Wavefunction

$$\Psi(x, y, z, \theta, \phi) = \langle x, y, z, \theta, \phi| \left(\left|n_x, n_y, n_z\right\rangle \otimes |l, m\rangle\right) \tag{3}$$

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EXACT DIAGONALIZATION OF $H_2@C_{60}$: PARAMETER

- L-J potential

$$V = \sum_{j=1}^{2}\sum_{i=1}^{60} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \omega \sum_{i=1}^{60} 4\epsilon \left[\left(\frac{\sigma}{r_{i,m}}\right)^{12} - \left(\frac{\sigma}{r_{i,m}}\right)^{6}\right] \tag{4}$$

$\epsilon(\mathrm{cm}^{-1})$	σ(Å)	ω
2.99	2.95	7.5

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EXACT DIAGONALIZATION OF $H_2@C_{60}$: PARAMETER

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$\epsilon(\mathrm{cm}^{-1})$	$\sigma(\text{Å})$	ω
2.99	2.95	7.5

- Rotational constant,H_2 bond length:

$$B_\nu = B_{eq} - \alpha(\nu + \frac{1}{2}), \quad r_\nu = \frac{\hbar}{(2\mu B_\nu)^{1/2}}$$

$B_{eq}(\mathrm{cm}^{-1})$	$\alpha(\mathrm{cm}^{-1})$
59.3	2.98

$\nu = 0$ or $\nu = 1$

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JCP130, 224306 (2009)

DIAGRAMMATIC REPRESENTATION

-  H_2 inside one C_{60} molecule with Ih symmetry

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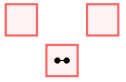
-  H_2 in central distorted C_{60} with 12 distorted P-phase neighbouring C_{60} ($Pa\bar{3}$)

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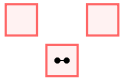
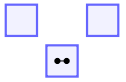
-  H_2 in central distorted C_{60} with 12 distorted P-phase neighbouring C_{60} ($Pa\bar{3}$)
-  H_2 in central distorted C_{60} with 12 distorted H-phase neigbouring C_{60} ($Pa\bar{3}$)

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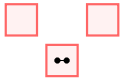
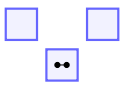
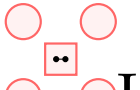
-  H_2 in central distorted C_{60} with 12 distorted P-phase neighbouring C_{60} ($Pa\bar{3}$)
-  H_2 in central distorted C_{60} with 12 distorted H-phase neigbouring C_{60} ($Pa\bar{3}$)
-  H_2 in central one distorted C_{60} with 12 Ih P-phase neigbouring C_{60}

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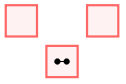
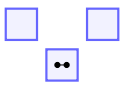
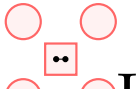
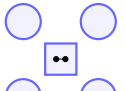
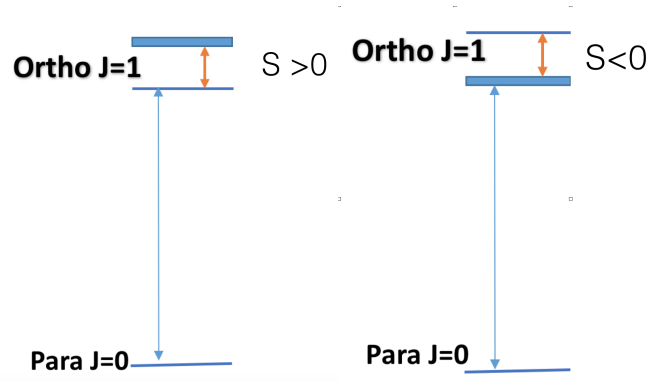
-  H_2 in central distorted C_{60} with 12 distorted P-phase neighbouring C_{60} ($Pa\bar{3}$)
-  H_2 in central distorted C_{60} with 12 distorted H-phase neigbouring C_{60} ($Pa\bar{3}$)
-  H_2 in central one distorted C_{60} with 12 Ih P-phase neigbouring C_{60}
-  H_2 in one central distorted C_{60} with 12 Ih H-phase neigbouring C_{60}

COMPARISON OF 1 CAGE VS 13 CAGES



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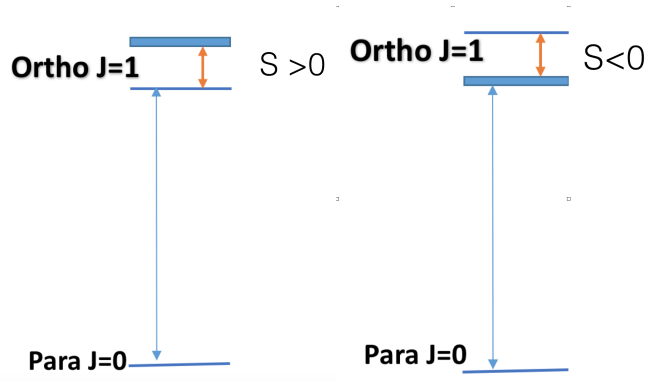
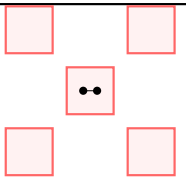


Experimental measurement:

- P phase S= 1.0889cm^{-1}

Representation	S(cm^{-1})
	-0.0160
	-0.0175

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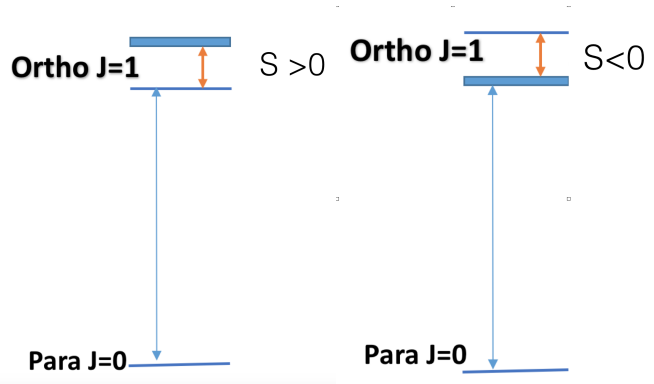

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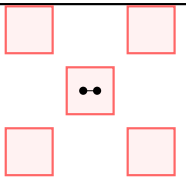	-0.0175

- Splitting mainly comes from the symmetry breaking of central C_{60}: more than 90% percent splitting in fact

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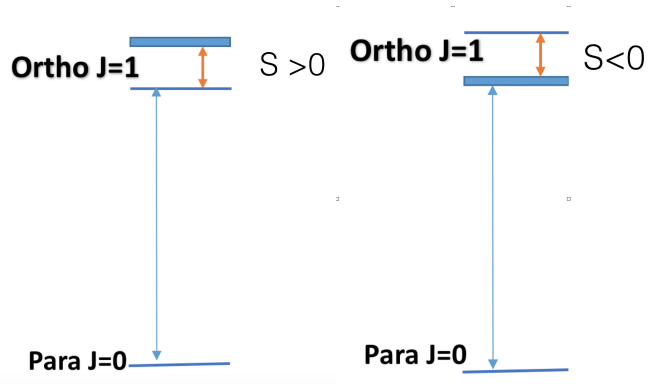

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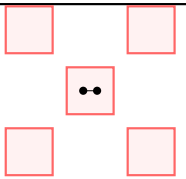
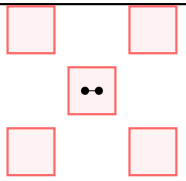
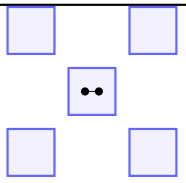
	-0.0175

- Splitting mainly comes from the symmetry breaking of central C_{60}: more than 90% percent splitting in fact
- The calculated splitting is much smaller than experimental measurements

COMPARISON OF ALL P-PHASE WITH ALL H-PHASE

Representation	S(cm^{-1})
	-0.0175
	-0.0141

Experimental measurement:

- P phase S= 1.0889cm^{-1}
- H phase S = 1.3711cm^{-1}

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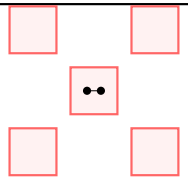
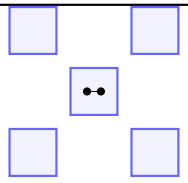
COMPARISON OF ALL P-PHASE WITH ALL H-PHASE

Representation	S(cm^{-1})
	-0.0175
	-0.0141

Experimental measurement:

- P phase S= 1.0889cm^{-1}
- H phase S = 1.3711cm^{-1}

- The calculated splitting of all H-phase is slight different with P-phase
- The calculated splitting is much smaller than experimental measurements

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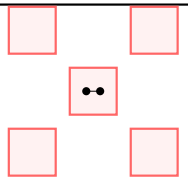
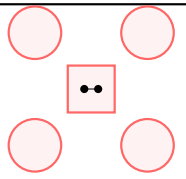
COMPARISON OF DISTORTED NEIGHBOURING CAGES WITH IH NEIGHBOURING CAGES

Representation	S(cm^{-1})
	-0.0175
	-0.0181

- The splitting is not sensitive to the geometry of neighbouring cages
- The splitting mainly comes from the symmetry breaking of the central cage

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QUESTION

- Why is the splitting much smaller than experimental measurements?
- What is the splitting sensitive to?

SENSITIVITY ANALYSIS OF SPLITTING ON CAGE GEOMETRY

10 independent coordinates $\vec{R}_i^{exp}$ (i from 1 to 10) measured by experiment

$$R_{ix} = R_{ix}^{\exp} + dx_i$$
$$R_{iy} = R_{iy}^{\exp} + dy_i$$
$$R_{iz} = R_{iz}^{\exp} + dz_i$$

C_{3i}

A random distorted cage

distorted slightly different from the experimental cage but with same symmetry

dx_i, dy_i, dz_i are randomly taken from normal distributions with $N(\mu = 0, \sigma = 0.001\text{Å})$

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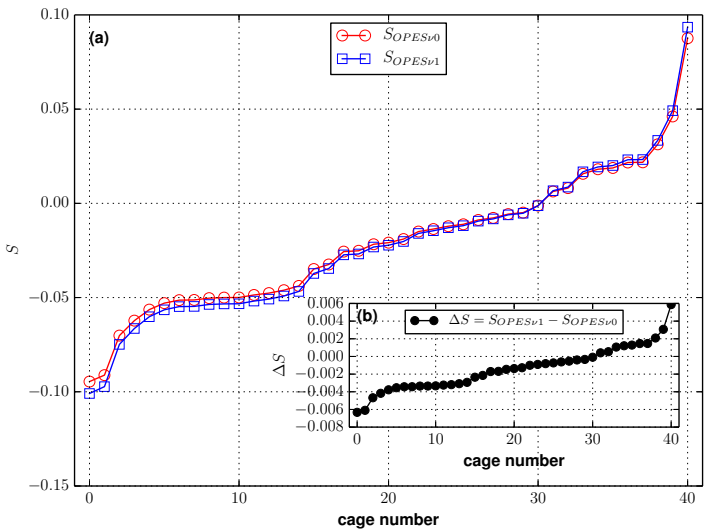
THE RESULTS OF SENSITIVITY ANALYSIS ON CAGE GEOMETRY

- Experimental measurements:
  - P phase S=1.0889cm^{-1}
- Calculated splitting with the original cage:
  - S=-0.0160cm^{-1}



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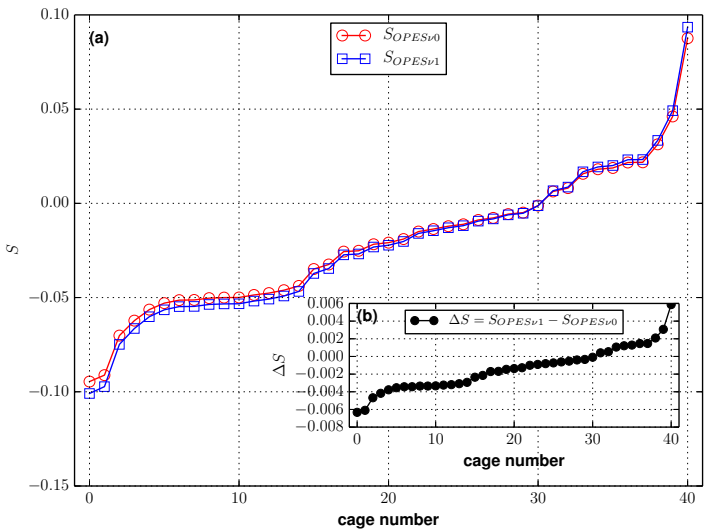

- Some geometries give positive splitting and some give negative splitting

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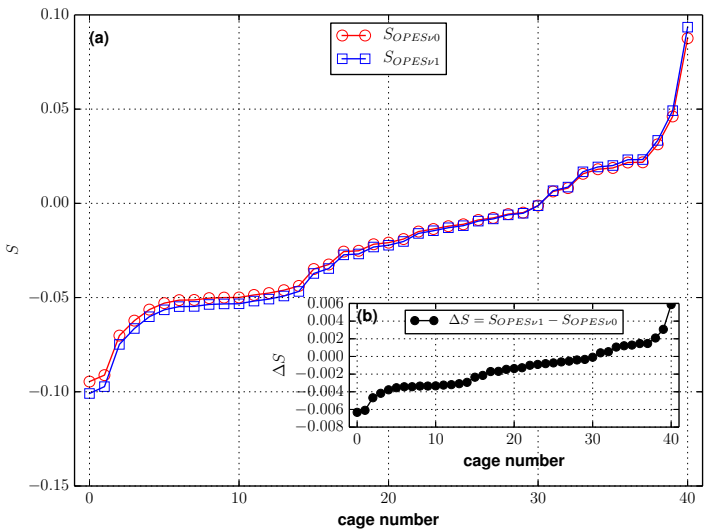

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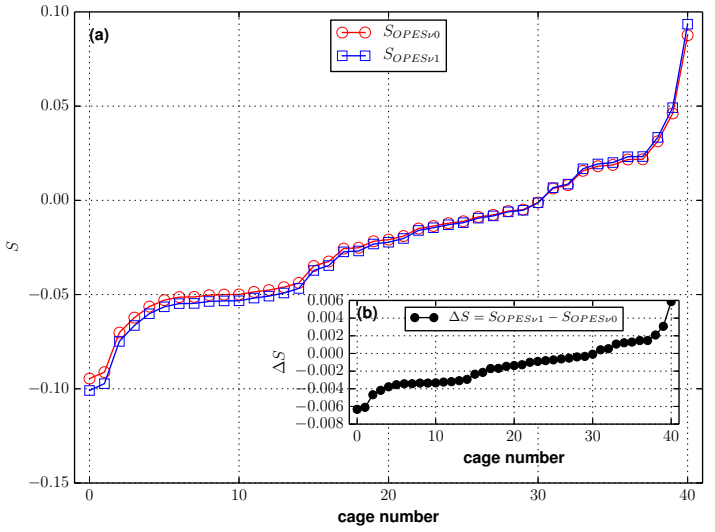

- Some geometries give positive splitting and some give negative splitting
- The splitting is extremely sensitive to the cage geometry
- Larger d_{H_2},larger splitting, but very little difference for H_2 at vibrational $\nu = 0$ or $\nu = 1$ state

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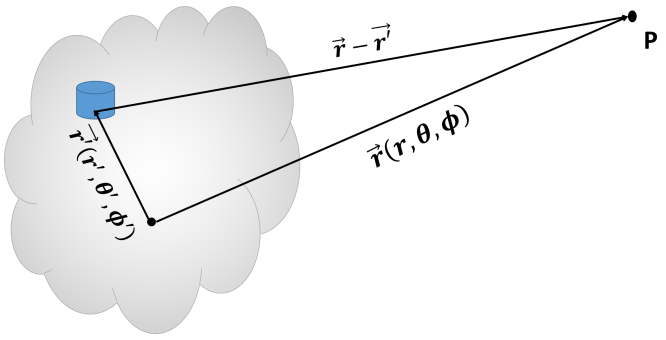
QUESTION

- Can we trust these results?
- Can we analytically solve this problem?

COULOMB POTENTIAL MULTIPOLE EXPANSION



$$V_{\text{Coulomb}} = \frac{1}{4\pi\epsilon_0}\frac{Q}{|\vec{r}-\vec{r'}|}$$

$$\frac{1}{|\vec{r}-\vec{r'}|} = \frac{1}{r}\sum_{l=0}^{\infty}\sum_{l=-m}^{l=m}\frac{4\pi}{2l+1}\left(\frac{r'}{r}\right)^{l}(-1)^{m}Y_{lm}^{*}(\theta',\phi')Y_{lm}(\theta,\phi)$$

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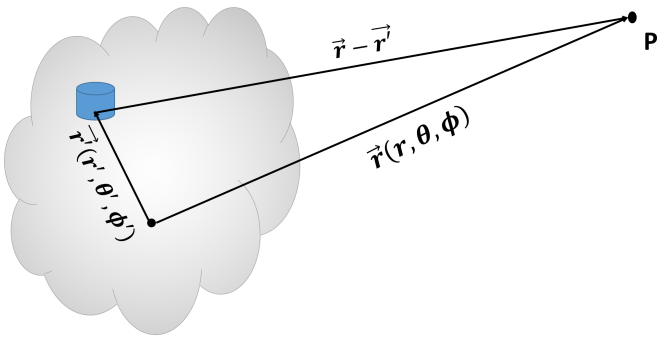

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$$\begin{aligned} V(\vec{r}) &= \frac{1}{4\pi\epsilon_0}\int\frac{\rho(\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r'} \\ &= \frac{1}{\epsilon_0}\sum_{l,m}\frac{1}{2l+1}\int Y^*_{lm}(\theta',\phi')(r')^l\rho(\vec{r'})d\vec{r'}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}} \\ &= \frac{1}{4\pi\epsilon_0}\sum_{l=0}^{\infty}\sum_{m=-l}^{m+l}\frac{4\pi}{2l+1}q_{lm}\frac{Y_{lm}(\theta,\phi)}{r^{l+1}} \end{aligned}$$

q_{lm} are called multipole moments: $q_{1,0}, q_{1,-1}, q_{1,1}$ are dipole moments

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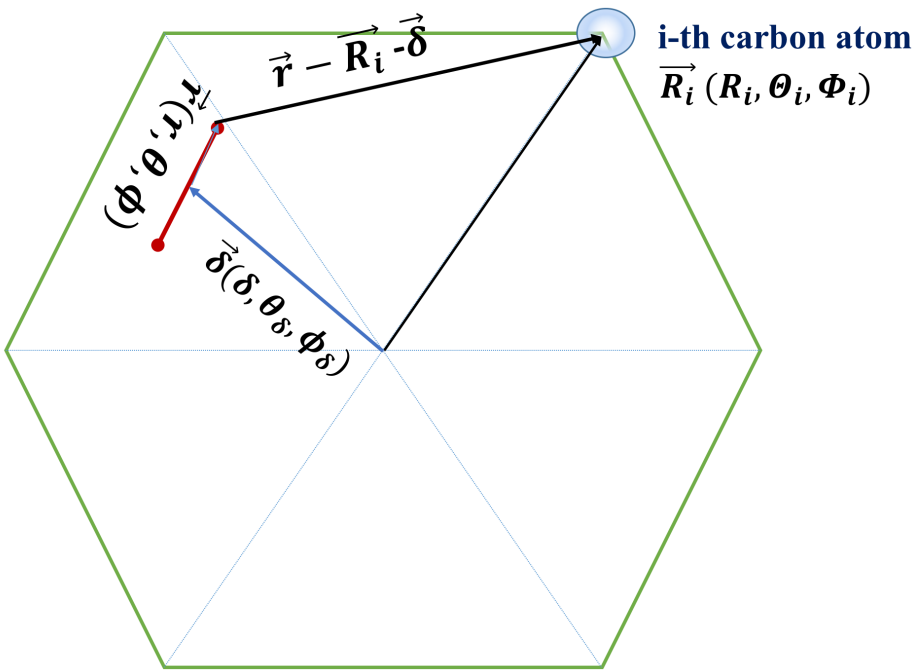
MULTIPOLE EXPANSION SETUP

- $\vec{r}(r, \theta, \phi)$ the orientation of H_2 respect to center of mass.
- i-th carbon atom at $\vec{R_i}(R_i, \Theta_i, \Phi_i)$
- center of mass of H_2 at $\vec{\delta}(\delta, \theta_\delta, \phi_\delta)$



MULTIPOLE EXPANSION RESULT

Assuming H_2 is in translational ground state

$$\langle 000|\,\hat{V}\,|000\rangle = \int_0^{\infty}\int_{-1}^{1}\int_0^{2\pi} |R_{00}(\delta)|^2\,\delta^2|Y_{00}(\theta_\delta,\phi_\delta)|^2 V(|\vec{R_i}-\vec{r}-\vec{\delta}|)d\delta d\cos\theta_\delta d\phi_\delta$$

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$$\langle 000|\,\hat{V}\,|000\rangle = \sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'} A_{l'\,m'}\,Y_{l'\,m'}(\theta,\phi)$$

$$A_{l'\,m'} = \sum_{k'=0}^{\infty}\sum_{k=0}^{\infty}\sum_{i=1}^{60}\int_0^{\infty} |R_{00}(\delta)|^2\,\delta^{2+2k}d\delta\,\frac{4\pi}{2l'+1}$$
$$\left(4\epsilon\sigma^{12}B^{6}_{2k,k}B^{k+6}_{l'+2k',k'}\frac{|\vec{r}|^{l'+2k'}}{|\vec{R_i}|^{l'+2k'+2k+12}} - 4\epsilon\sigma^{6}B^{3}_{2k,k}B^{k+3}_{l'+2k',k'}\frac{|\vec{r}|^{l'+2k'}}{|\vec{R_i}|^{l'+2k'+2k+6}}\right)Y^{*}_{l'\,m'}(\Theta_i,\Phi_i)$$

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$$\left\langle 1M'\right|\langle 000|\,V\,|000\rangle\,|1M\rangle = \sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}\int Y^*_{1M'}(\theta,\phi)\,A_{l'm'}\,Y_{l'm'}(\theta,\phi)\,Y_{1,M}(\theta,\phi)\sin(\theta)d\theta d\phi$$

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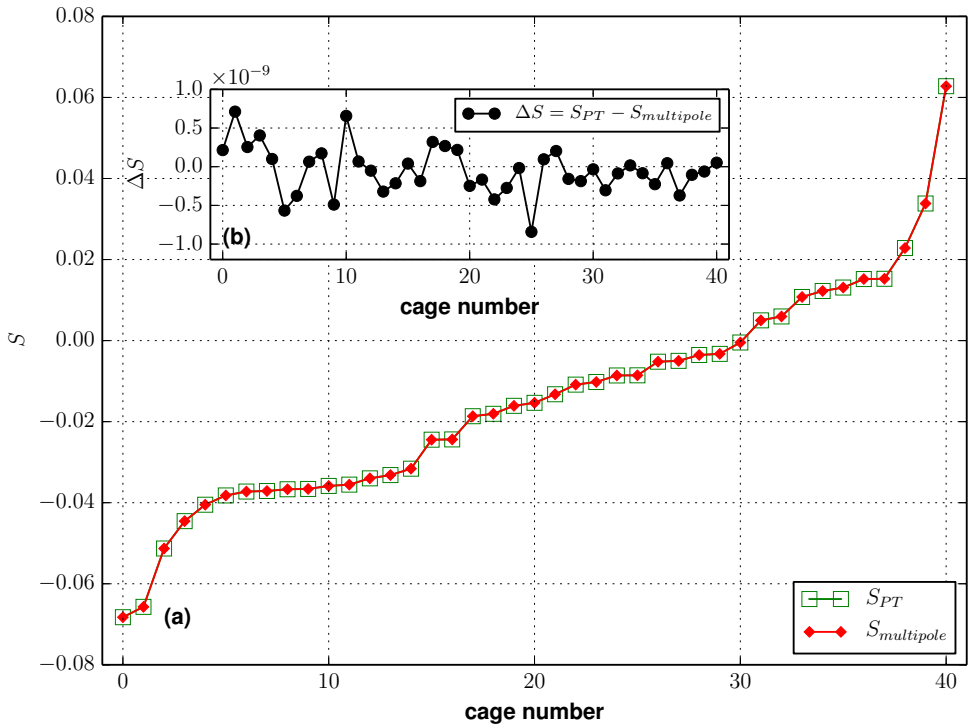
FIRST ORDER DEGENERACY PT: NUMERICAL VS MULTIPOLE EXPANSION

- $S_{\text{multipole}}$ is splitting analytically calculated through multipole expansion
- S_{PT} is the splitting calculated by numerical block diagonalization



- Multipole expansion agrees with numerical block diagonalization

ADVANTAGE OF DOING MULTIPOLE EXPANSION

- An analytical check of our numerical calculations

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- A physical perspective understanding of the degeneracy lifting in ortho ground state(perturbation theory).

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- A good explanation of positive splitting and negative splitting: The sign of splitting depends on the sign of A_{lm} which is given by C_{60} geometry
- A physical perspective understanding of the degeneracy lifting in ortho ground state(perturbation theory).
- Much lower computational cost (time and storage) compared with exact diagonal

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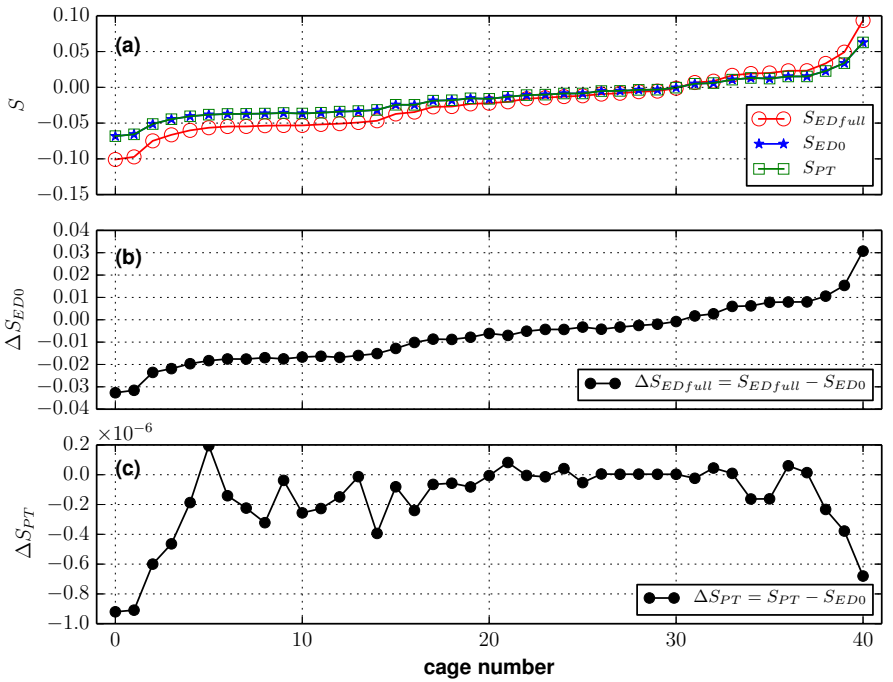
BASIS SIZE CONVERGENCE

- S_{EDfull} is the splitting calculated by exact diagonal in converged basis.
- S_{ED0} is calculated in converged rotational basis coupled with translational ground state.
- S_{PT} is the splitting calculated by first order degeneracy perturbation theory



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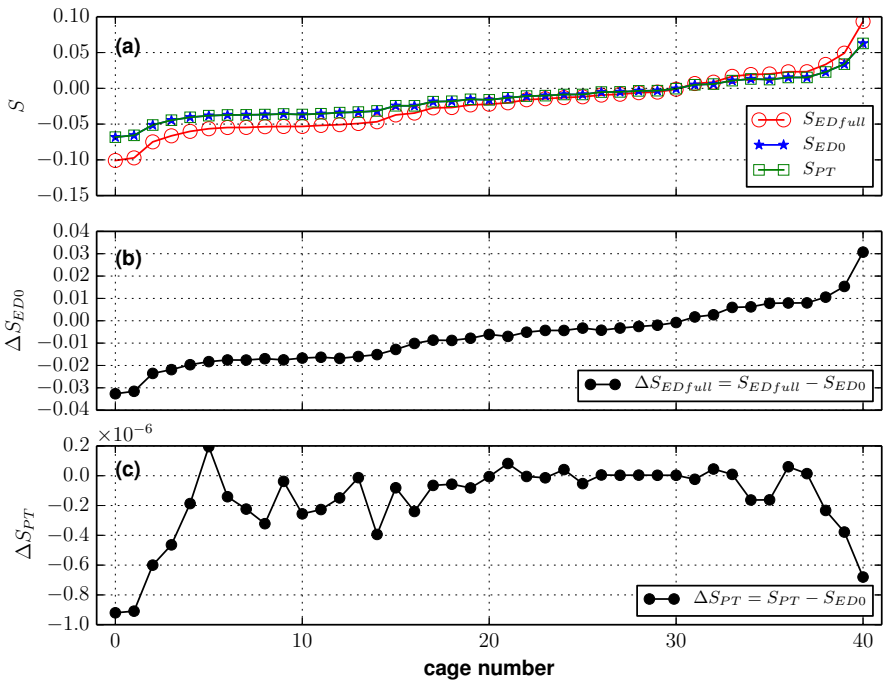

- Higher rotational level coupling is not important.
- the translational rotational coupling mostly comes from ortho ground state and translational ground state

- Deformation from perfect Ih C_{60} along gradient direction with fixed symmetry C_{3i}
  - $S = S(\vec{R_1}, \vec{R_2}, ..., \vec{R_{10}}) = S(R_{1x}, R_{1y}, R_{1z}, ..., R_{10x}, R_{10y}, R_{10z})$
  - Gradient of S is denoted as normalized $\vec{g}$
  - $\vec{R} = \vec{R_{Ih}} - \lambda\vec{g}$: λ is scale factor.
  - Apply C_{3i} operators on $\vec{R}$ to get one C_{60} cage

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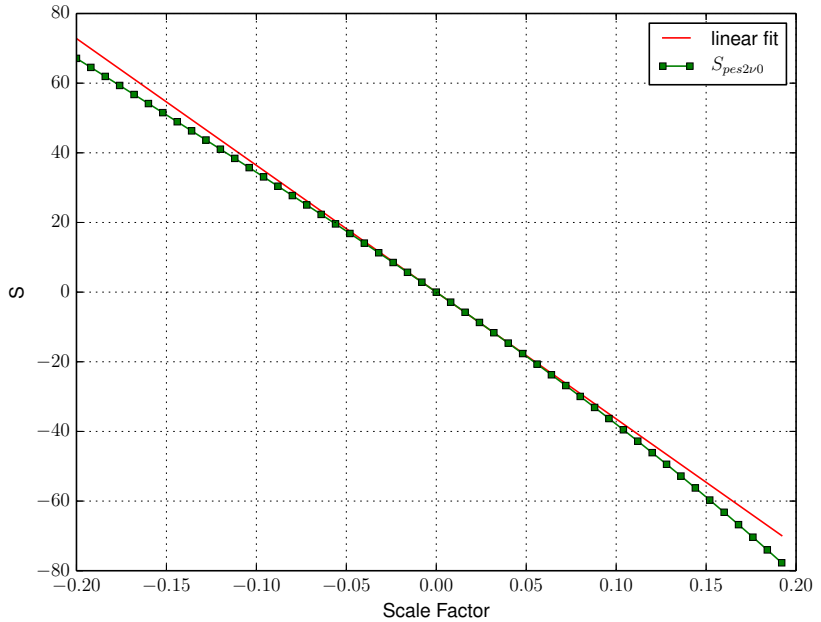

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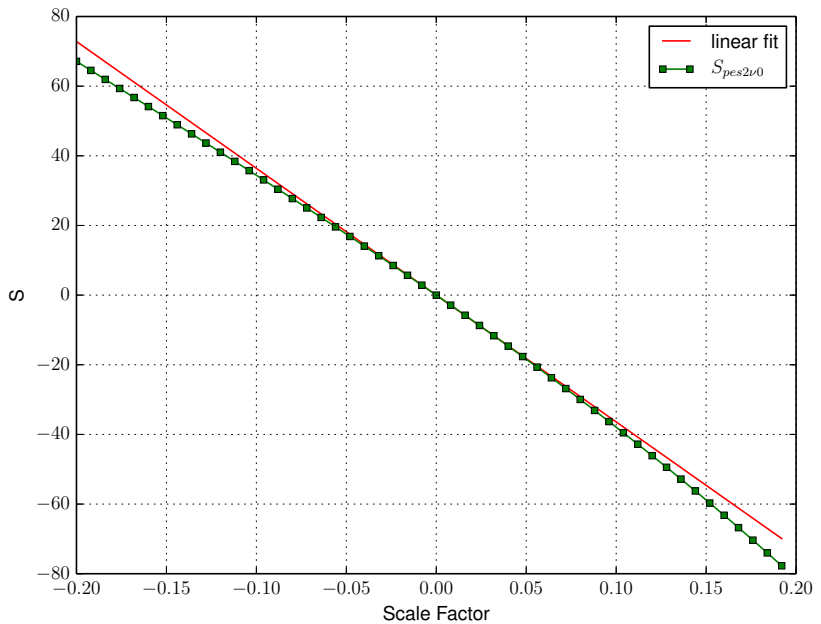

- linear regime is quite large:zero point motion of carbon atoms doesn't effect splitting

A video showing how carbon atoms moves along gradient direction: $\lambda > 0$

- $\lambda = 0$ gives no splitting
- $\lambda < 0$ gives positive splitting
- $\lambda > 0$ gives negative splitting

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- More potential energy surface:
  - Three more potential energy surfaces were tested, and all conclusions above holds.

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- Future direction
  - Add long range dipole-dipole interaction:lattice HF@C_{60} or H_2O@C_{60}

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