Structure and internal dynamics of several 1,2-dicarba-closo-dodecaborane derivatives

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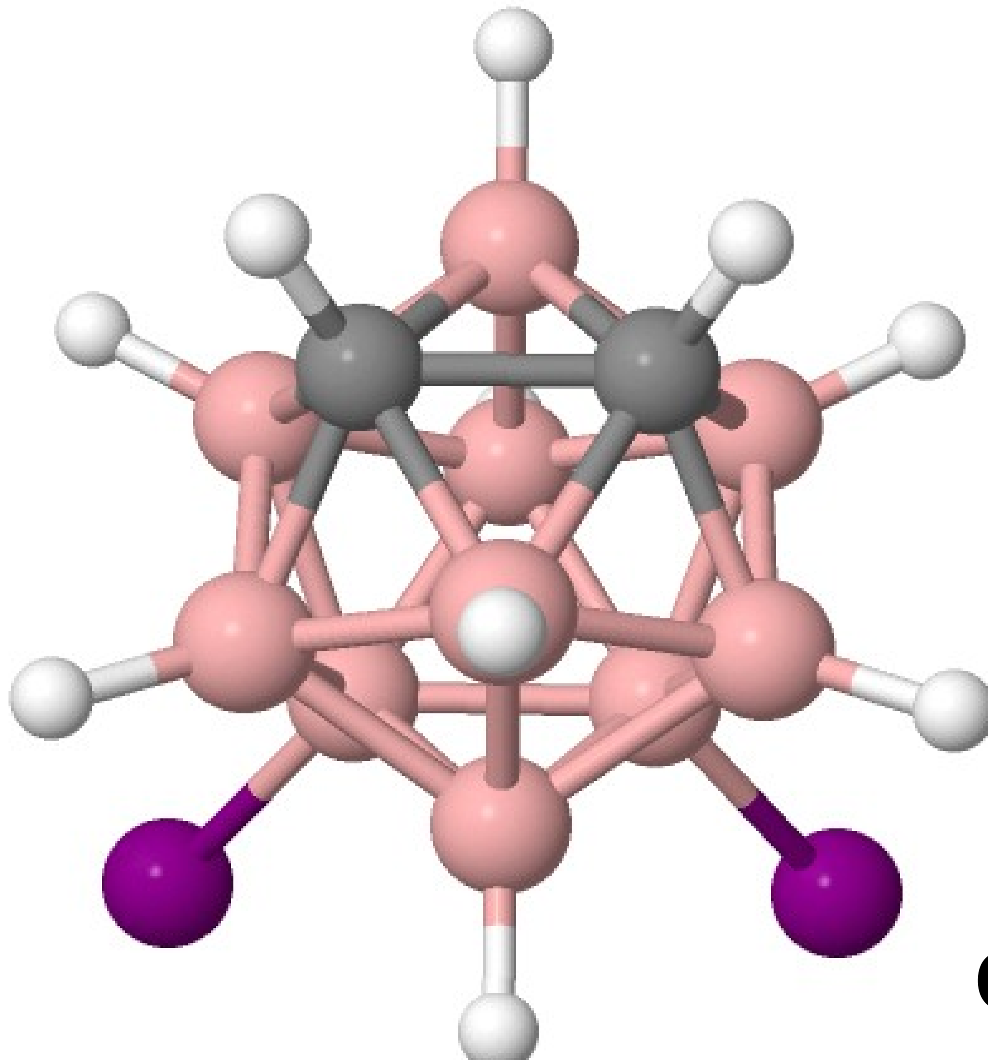
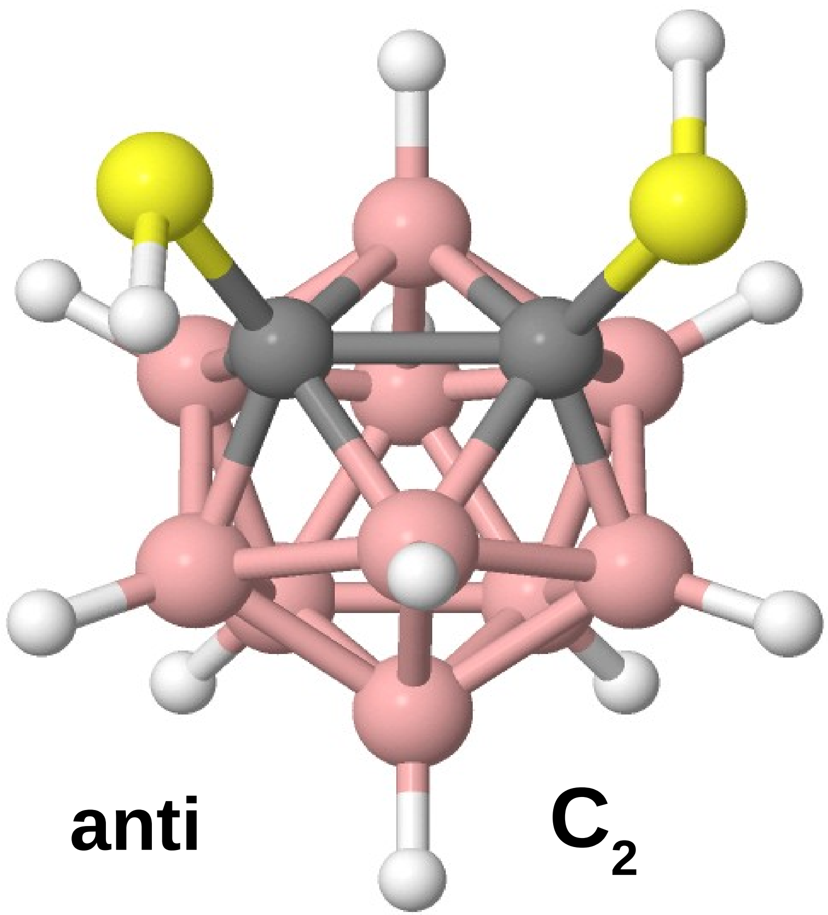
Skilizium, 2015

9,12-I_2-1,2-dicarba-closo-dodecaborane (“I”)

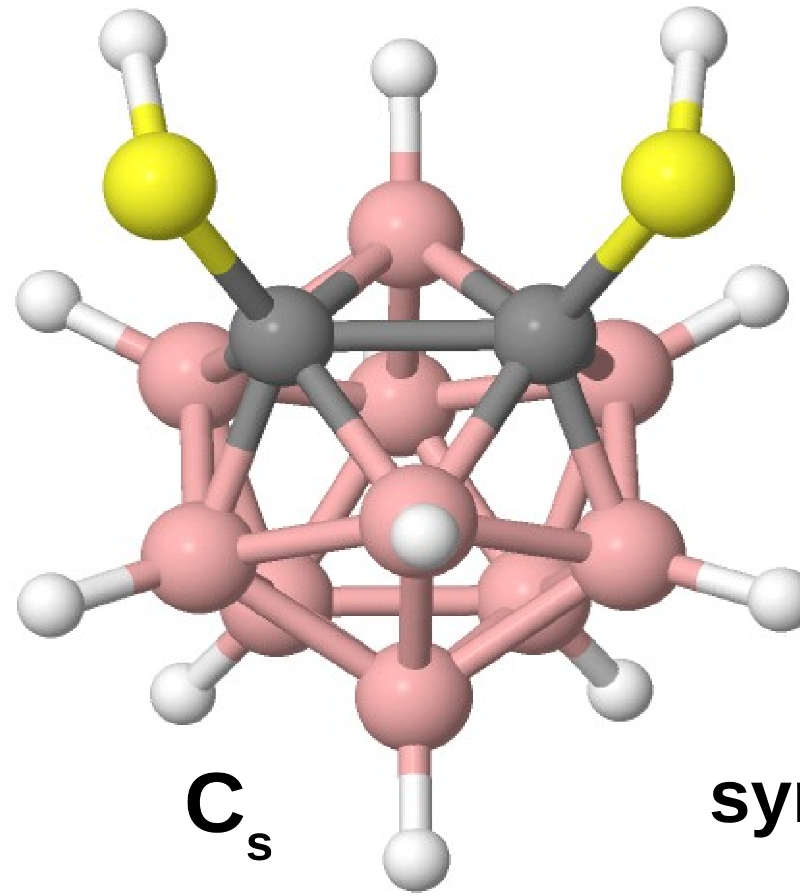


C_{2v}

1,2-$(SH)_2$-1,2-dicarba-closo-dodecaborane (“SH”)

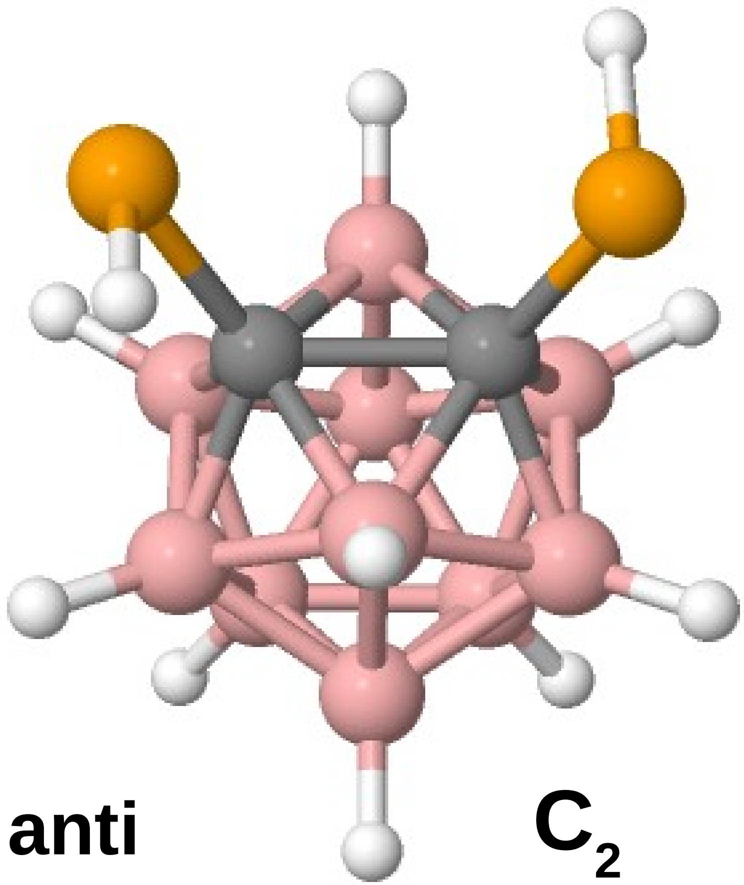


anti **C_2**

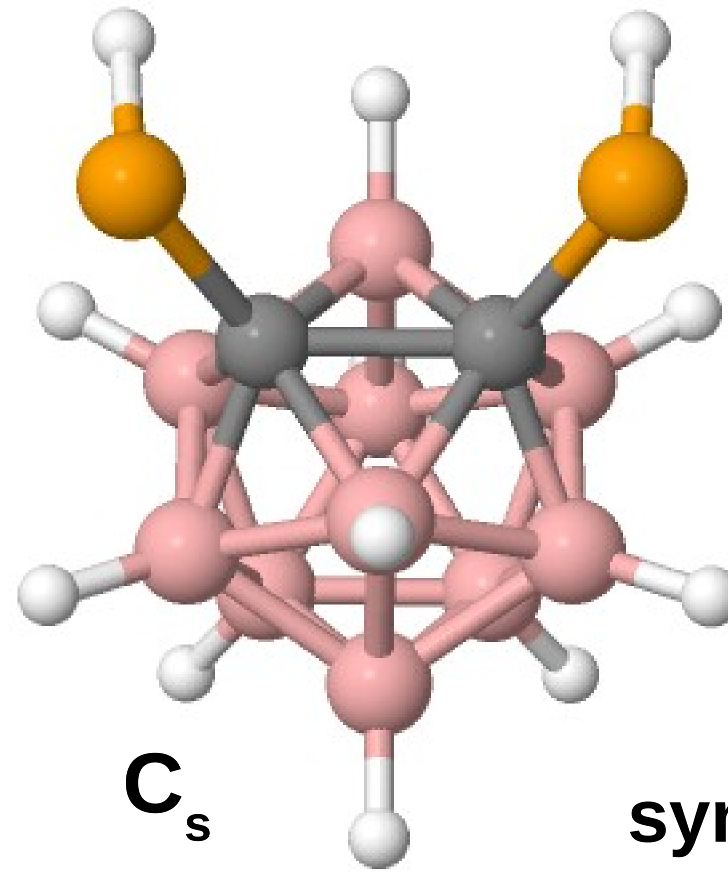


C_s **syn**

1,2-$(SeH)_2$-1,2-dicarba-closo-dodecaborane (“SeH”)

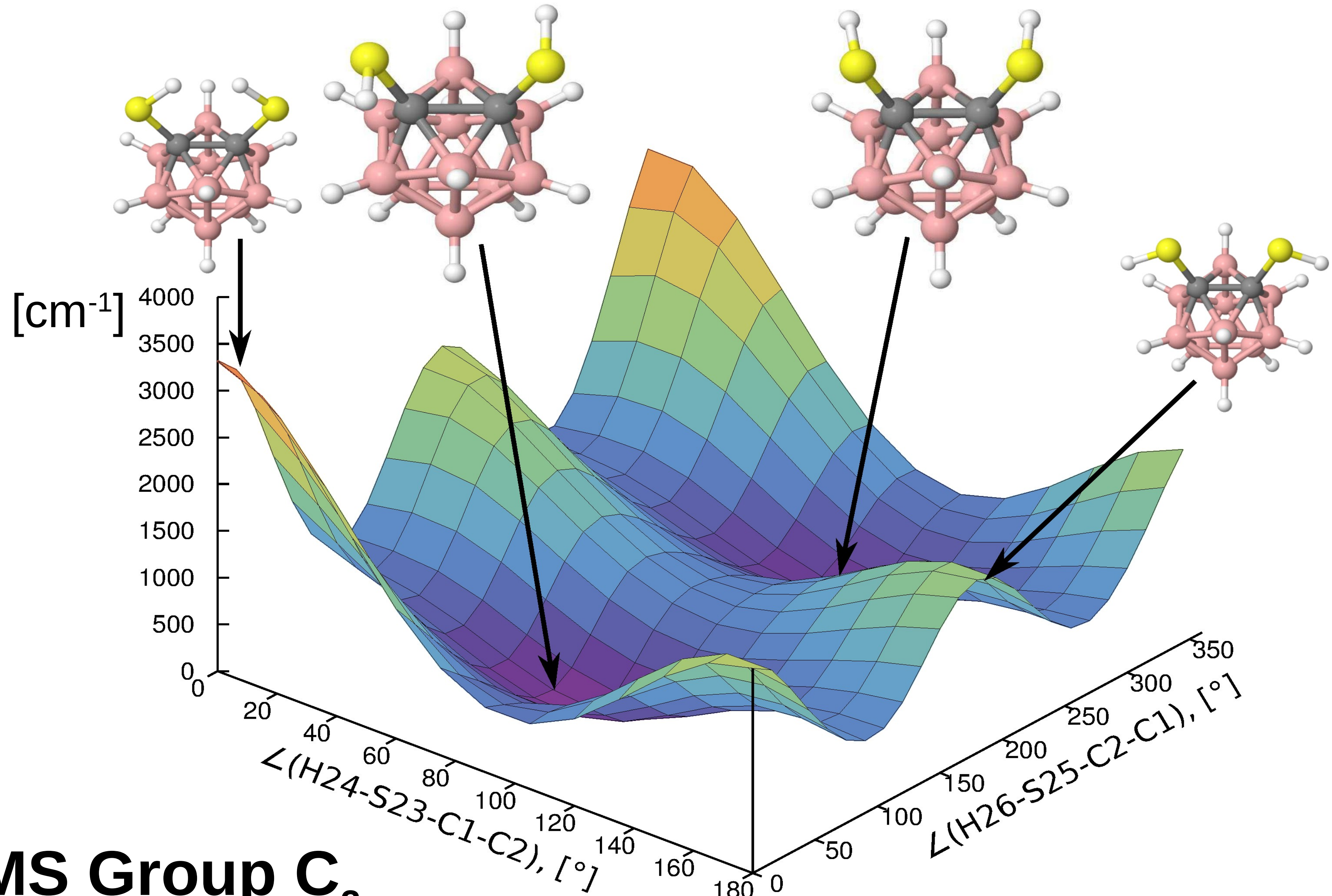


anti C_2



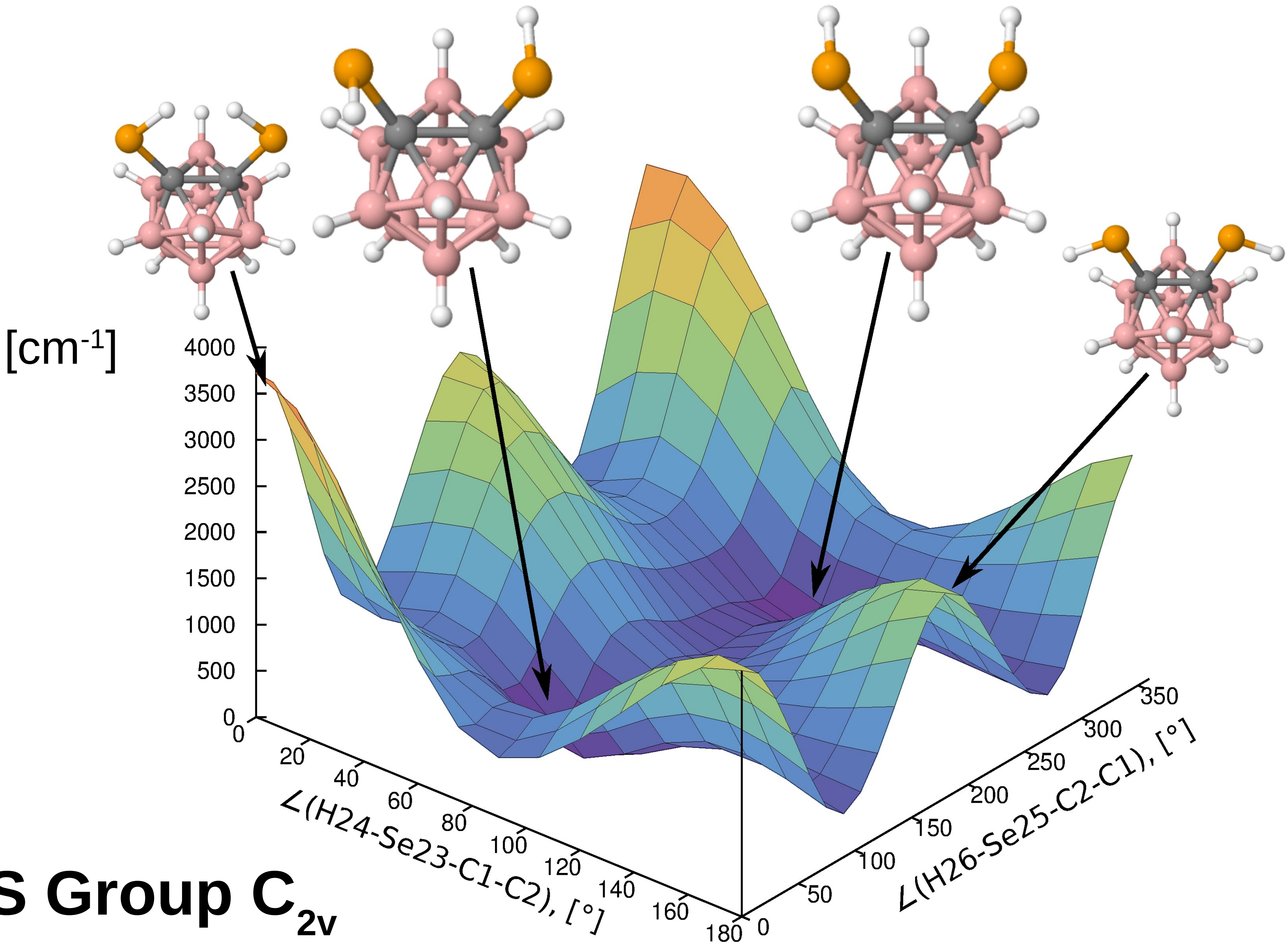
C_s syn

PES for "SH"



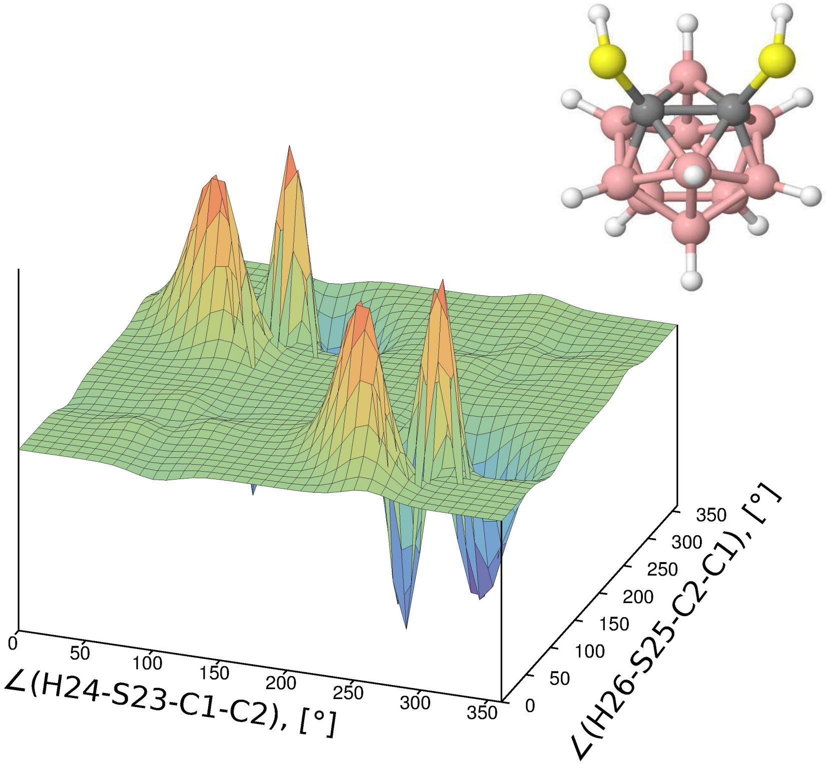
MS Group C_{2v}

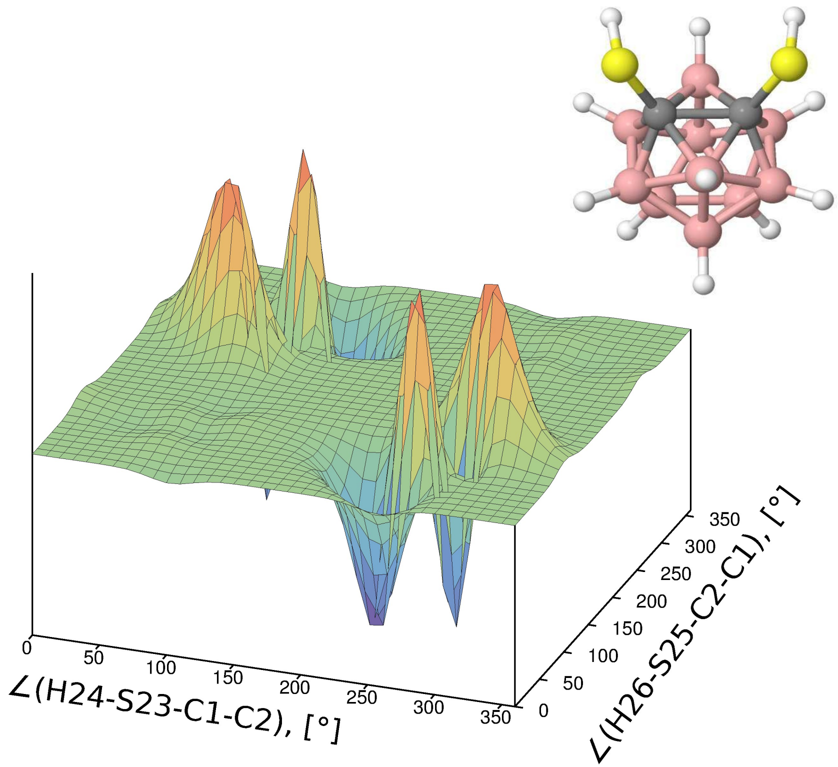
PES for “SeH”



MS Group C_{2v}

Wavefunctions for LAM vibrations in “SH”, syn





v=26

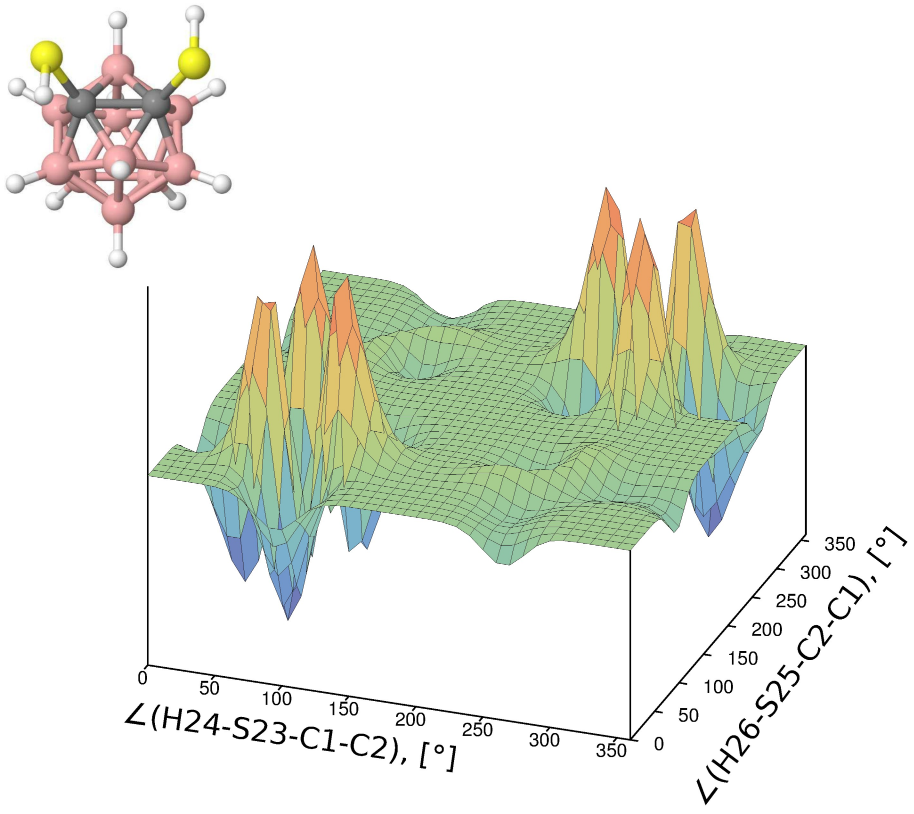
E_{av}=694.22 [cm^{-1}]

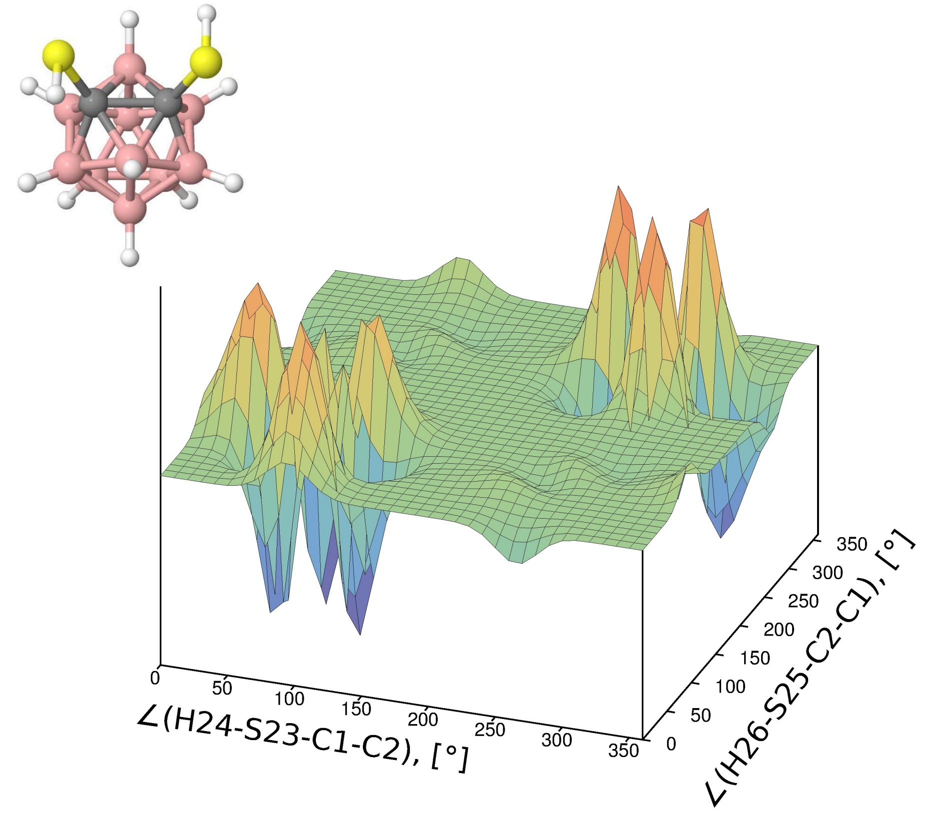
ΔE=0.031 [cm^{-1}]

$V_{A'}$=0 ; $v_{A''}$=4

v=27

Wavefunctions for LAM vibrations in “SH”, anti





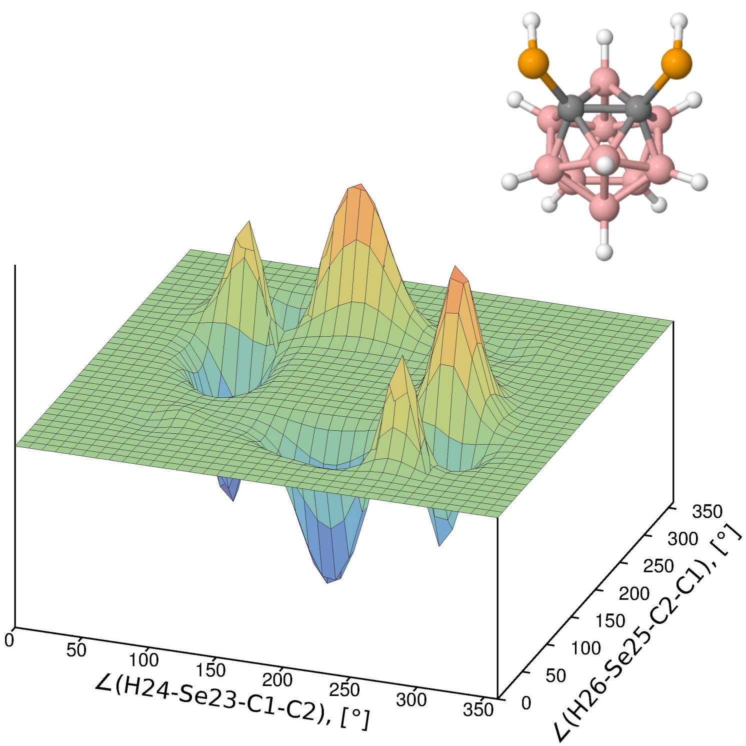
v=28

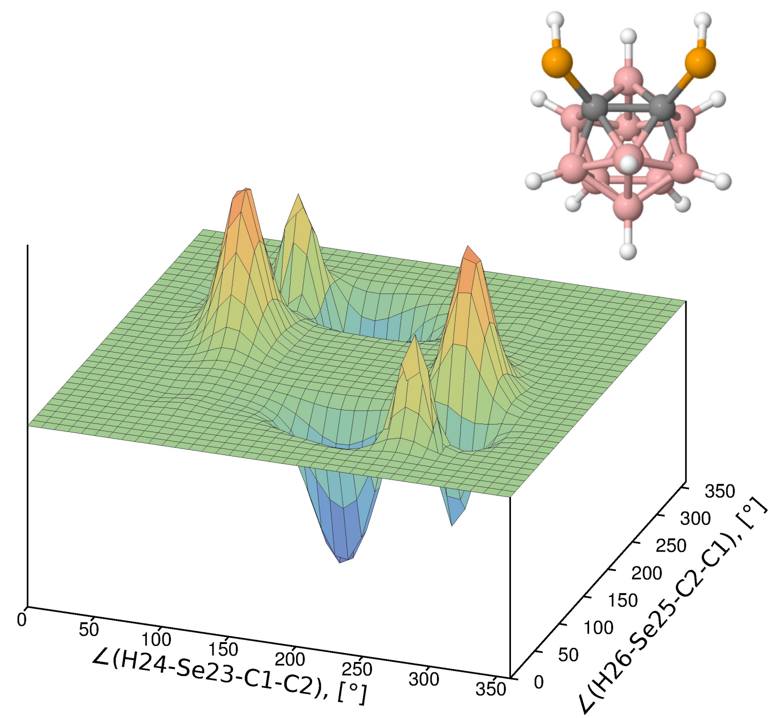
E_{av}=711.07 [cm^{-1}] v=29

ΔE=0.158 [cm^{-1}]

V_A=2 ; v_B=1

Wavefunctions for LAM vibrations in “SeH”, syn





v=12

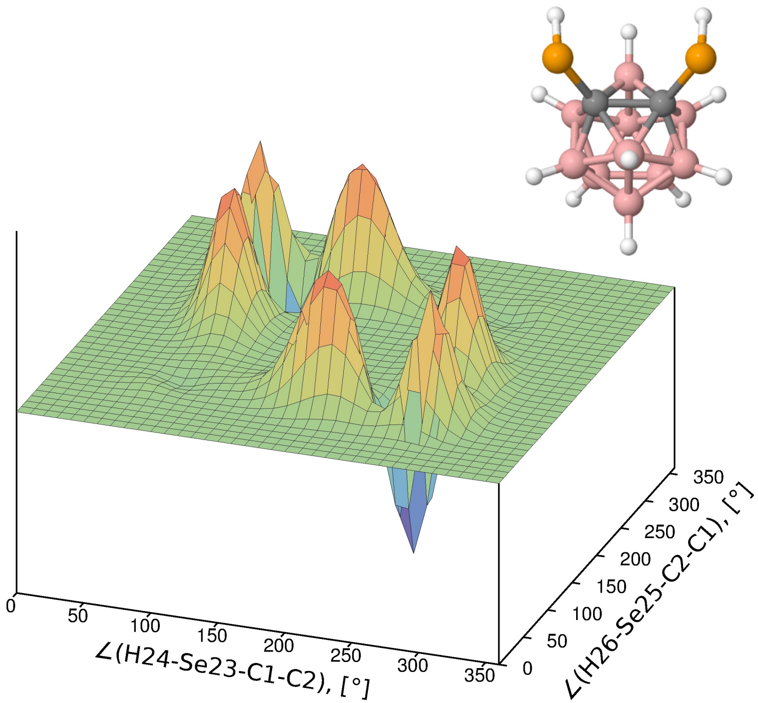
E_{av}=602.026 [cm^{-1}]

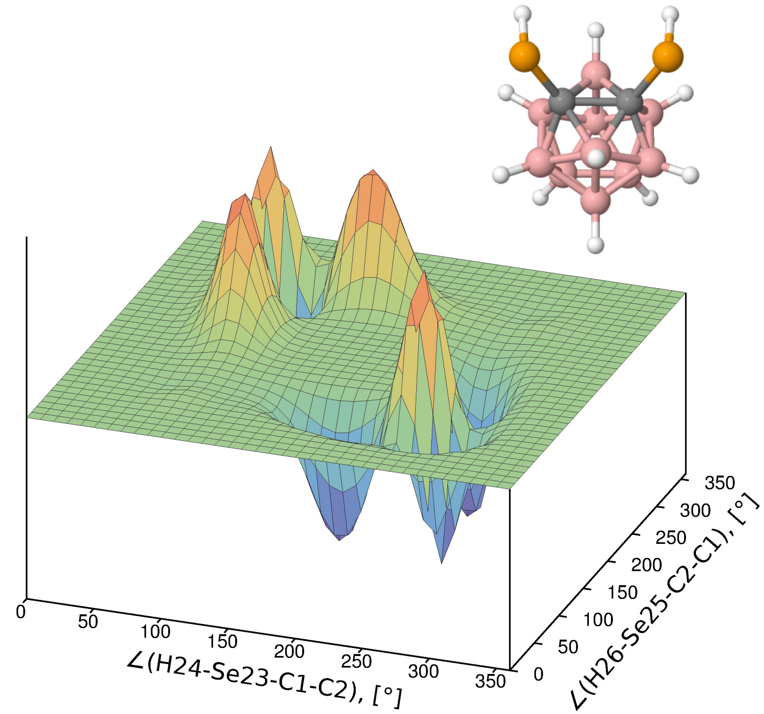
v=13

ΔE=0.02 [cm^{-1}]

$V_{A'}=0$; $v_{A''}=3$

Wavefunctions for LAM vibrations in "SeH", syn





v=14

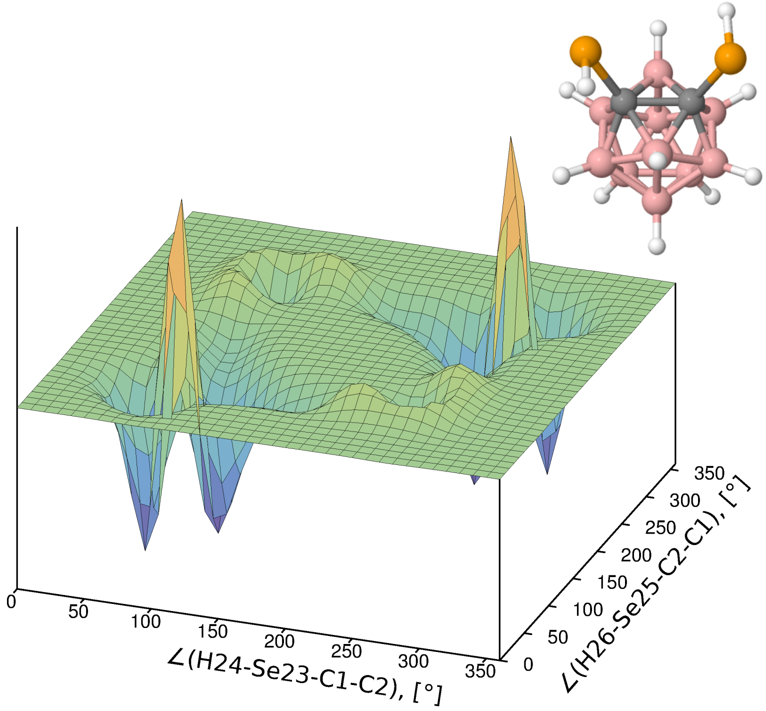
E_{av}=606.41 [cm^{-1}]

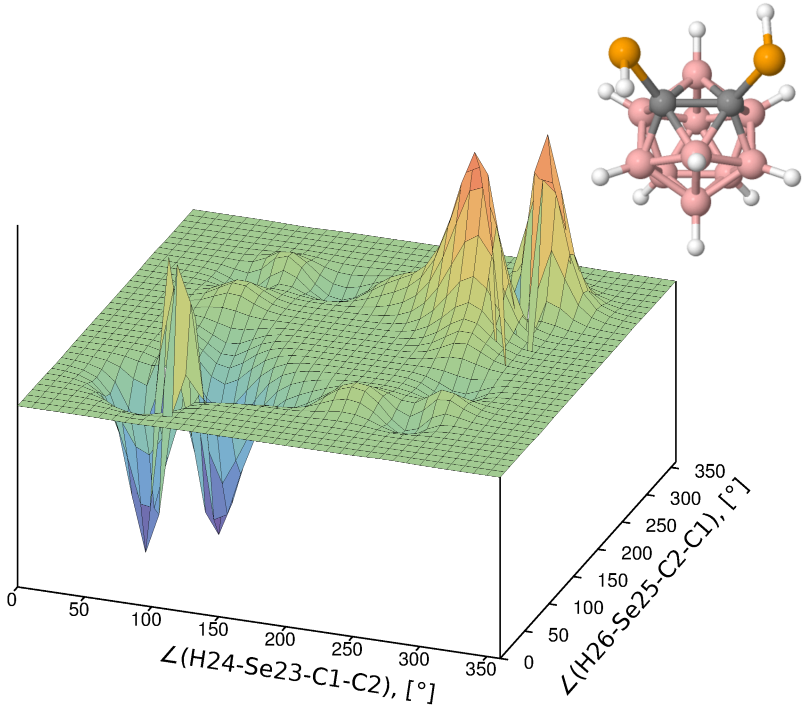
ΔE=0.02 [cm^{-1}]

$V_{A'}$=2 ; $v_{A''}$=1

v=15

Wavefunctions for LAM vibrations in “SeH”, anti





v=16

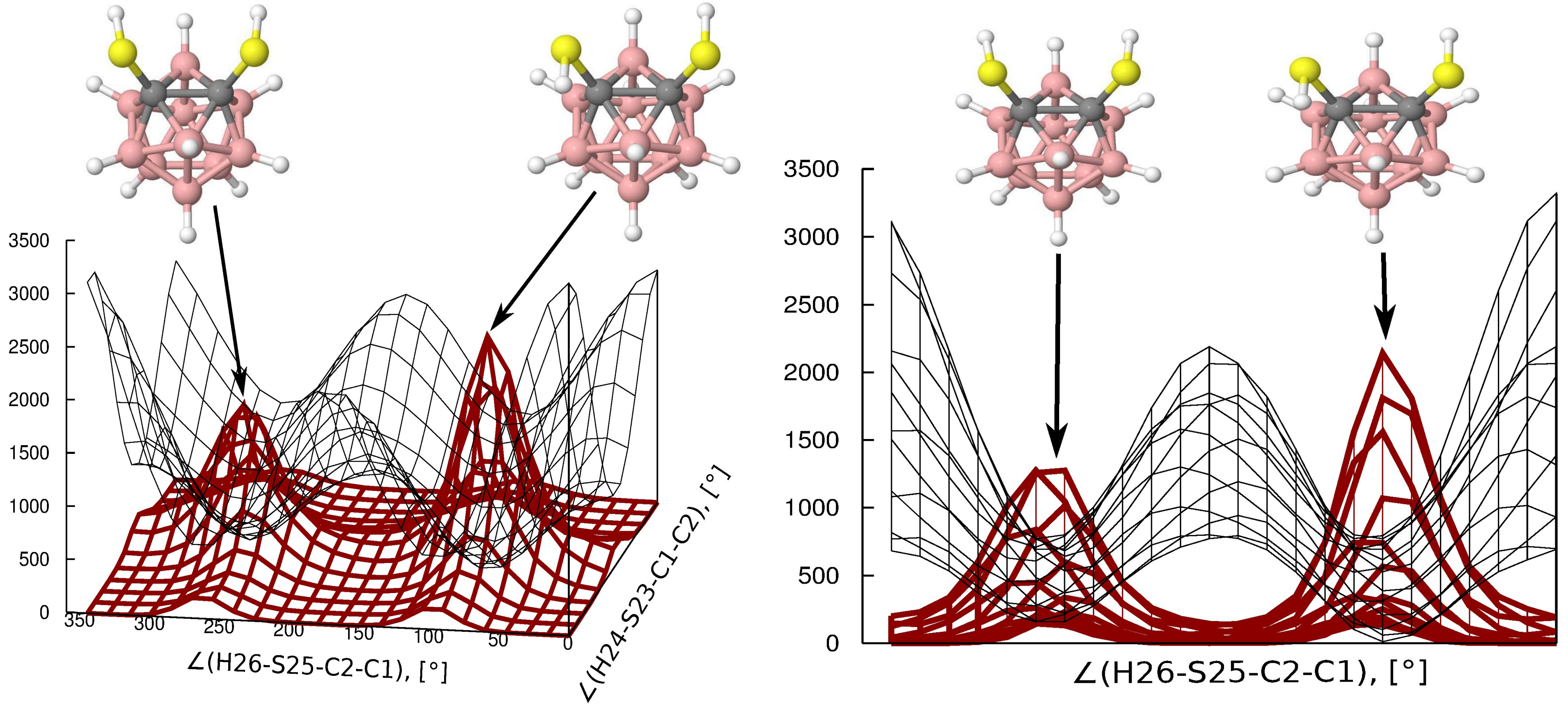
E_{av}=649.30 [cm^{-1}]

ΔE=0.25 [cm^{-1}]

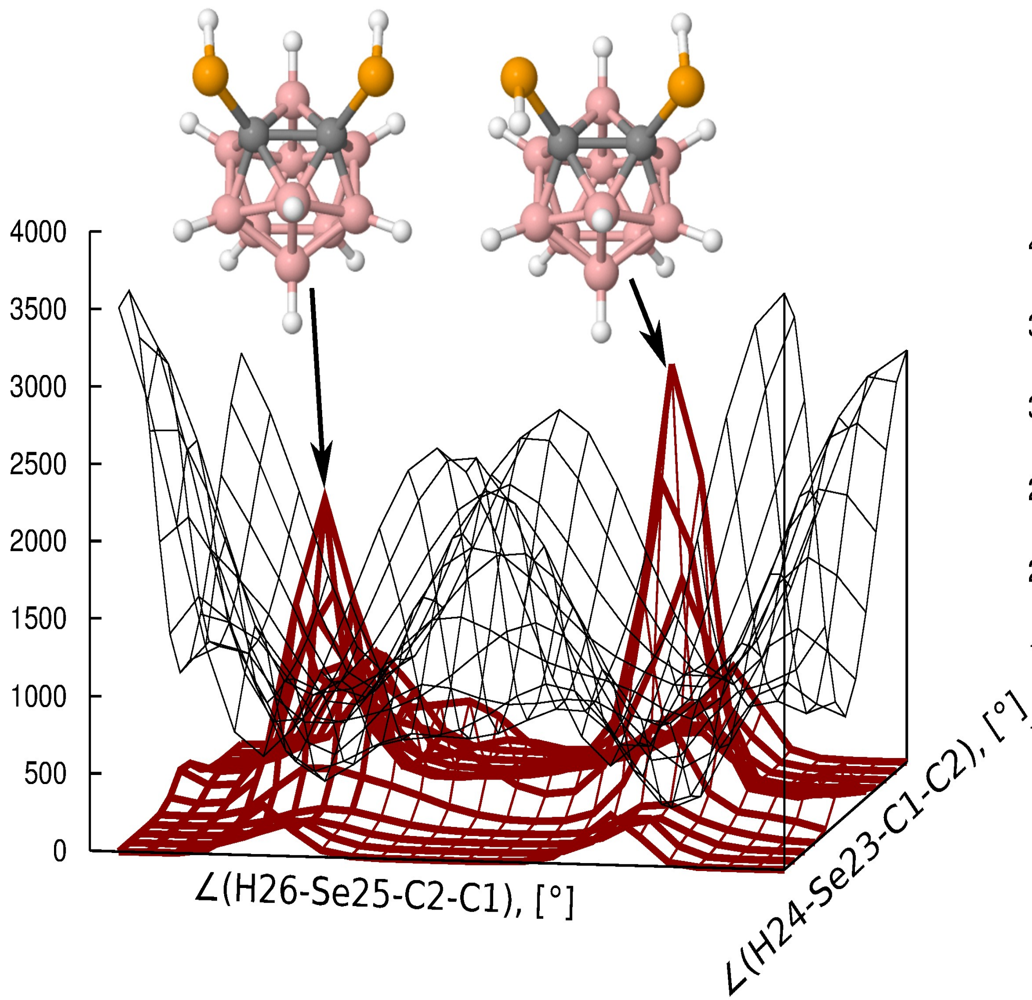
V_A=2 ; v_B=0

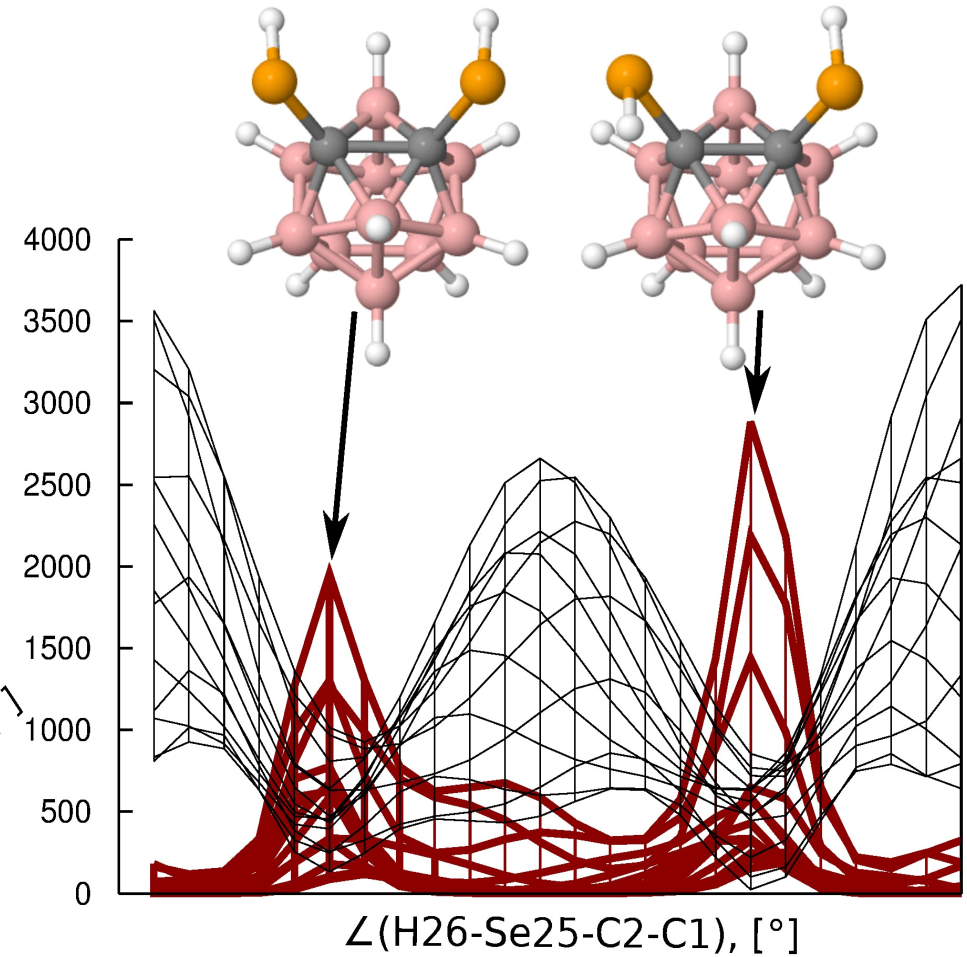
v=17

Classical conformer distribution for “SH”



Classical conformer distribution for “SeH”



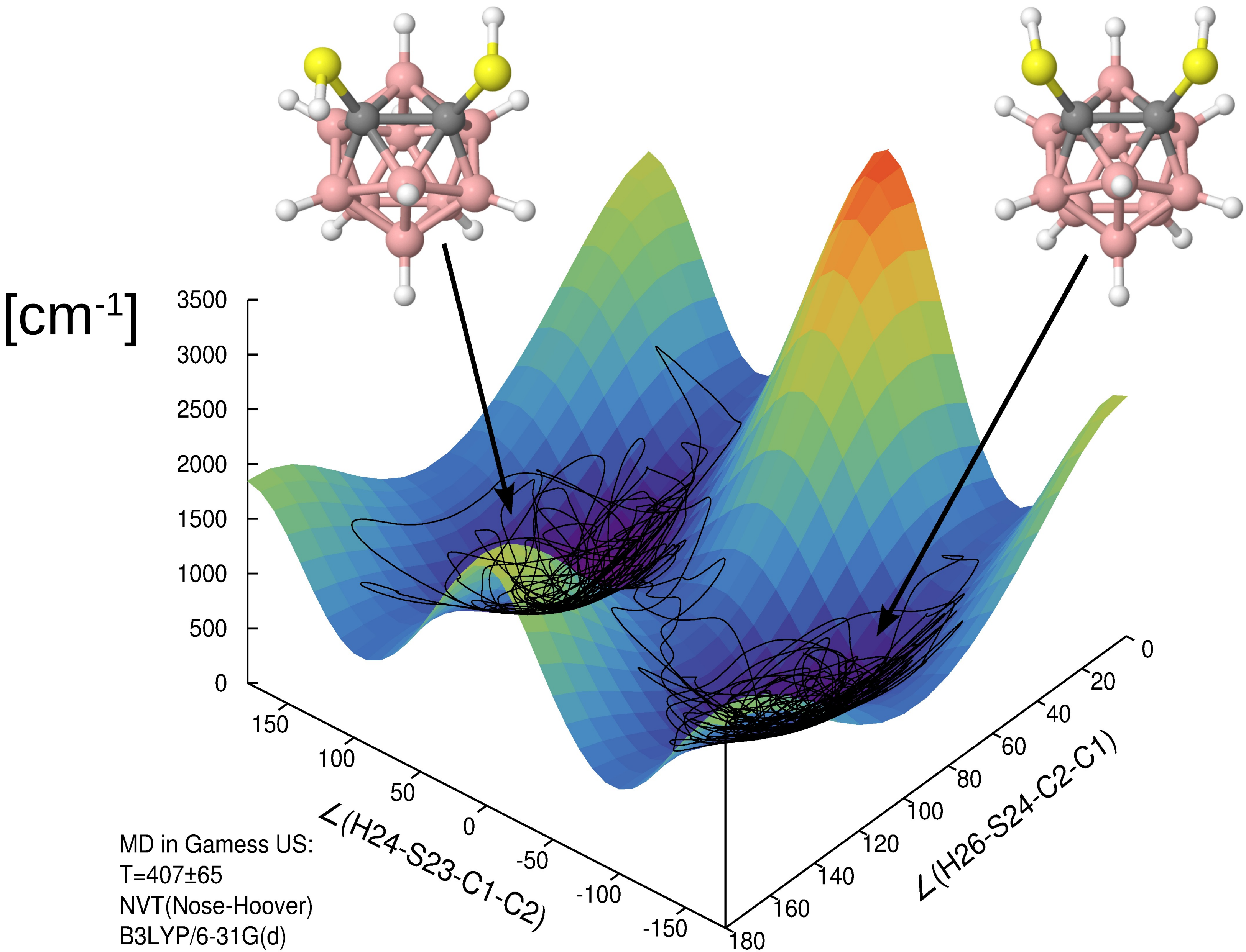


MD vs. Anharmonic Fields

$$1 < \frac{\tau_{MD}}{\tau_{cubic}} \approx \frac{ab\left(\omega_{max}/\omega_{min}\right)}{36\,N^2}$$

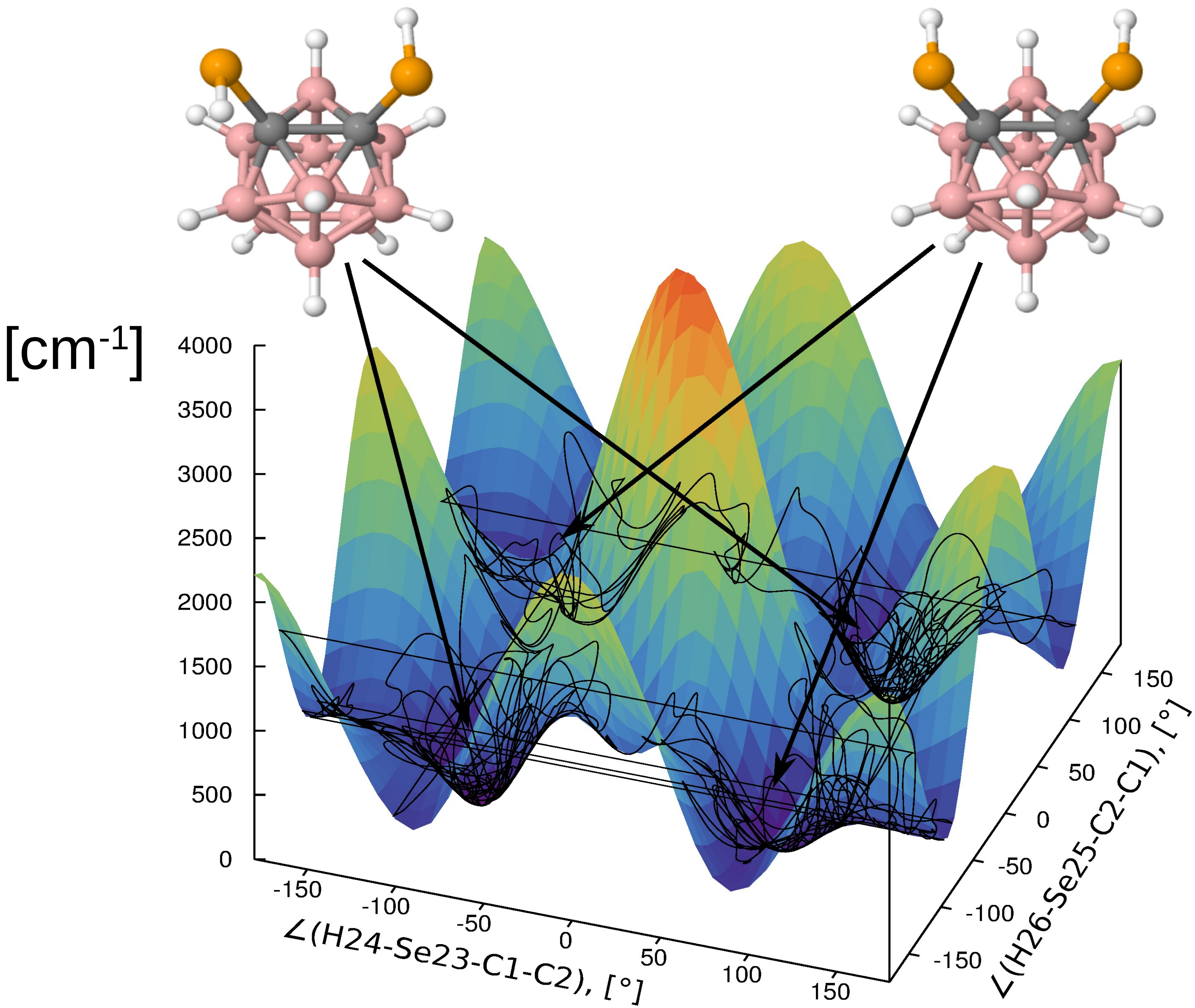
$a, \; b > 1$

MD simulation



MD in Gamess US:
T=407±65
NVT(Nose-Hoover)
B3LYP/6-31G(d)

MD simulation



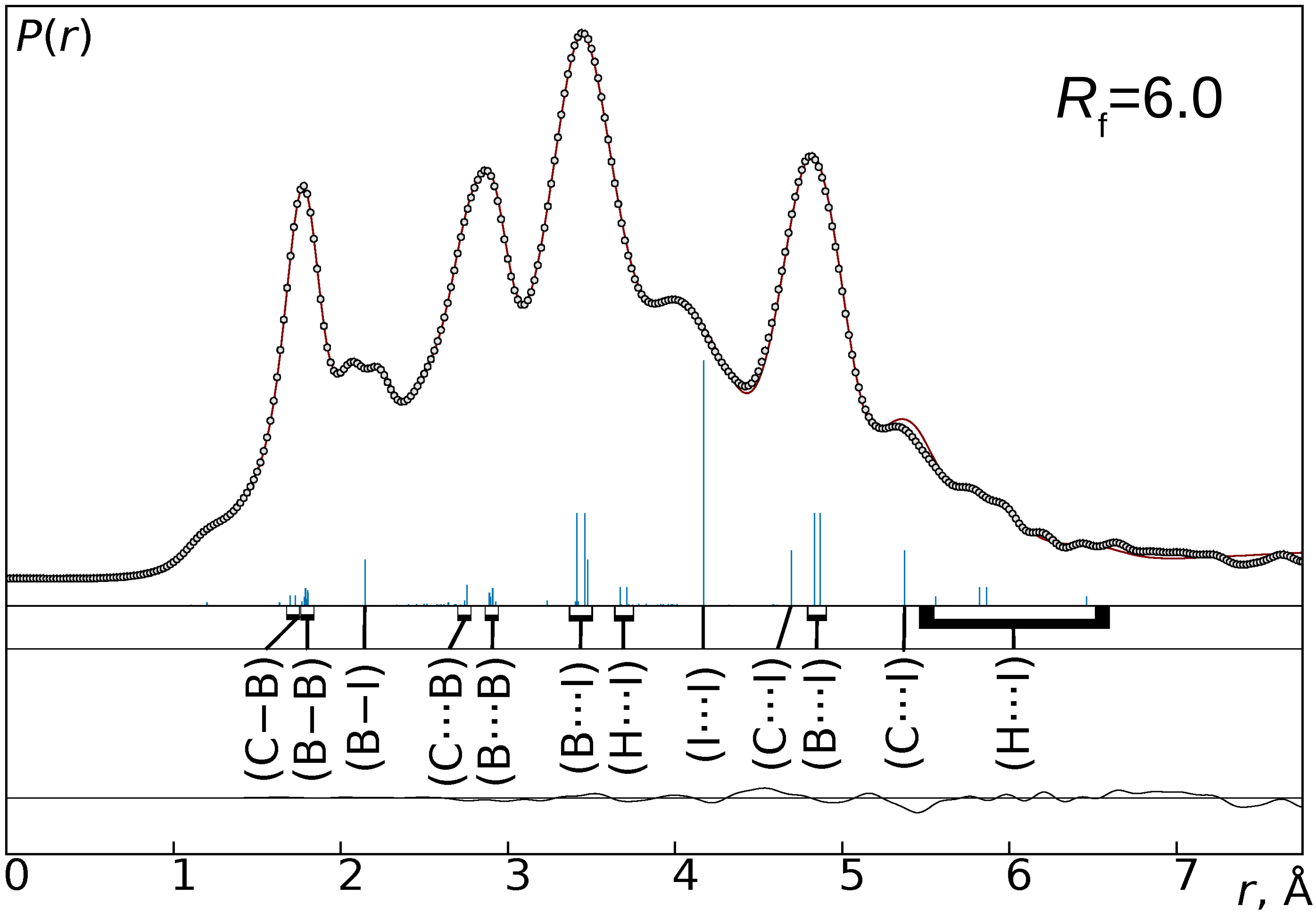
Problems of MD usage in GED

Absence of nuclei in classically forbidden zones

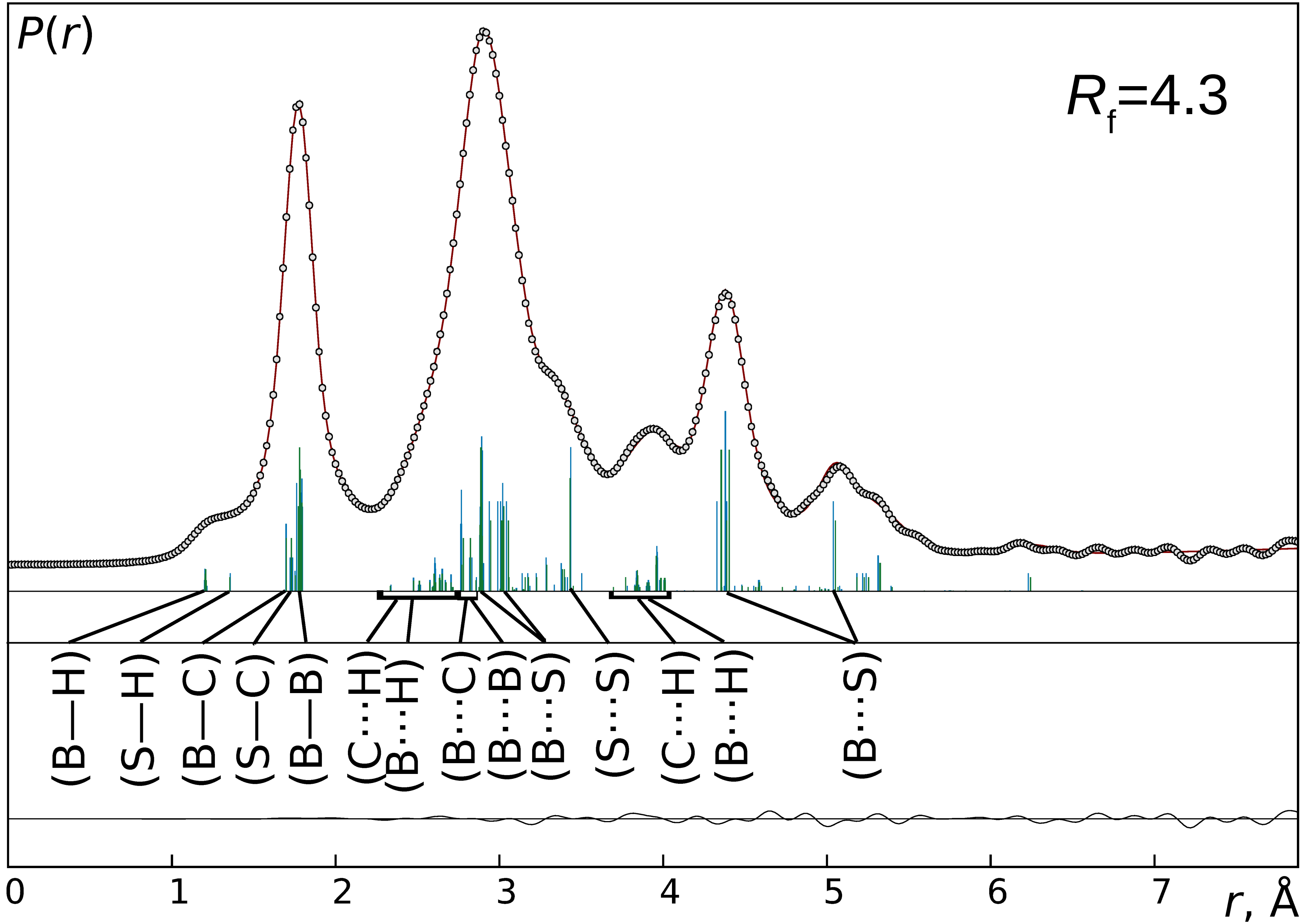
Problems of MD usage in GED

“Flying Ice Cube Effect”

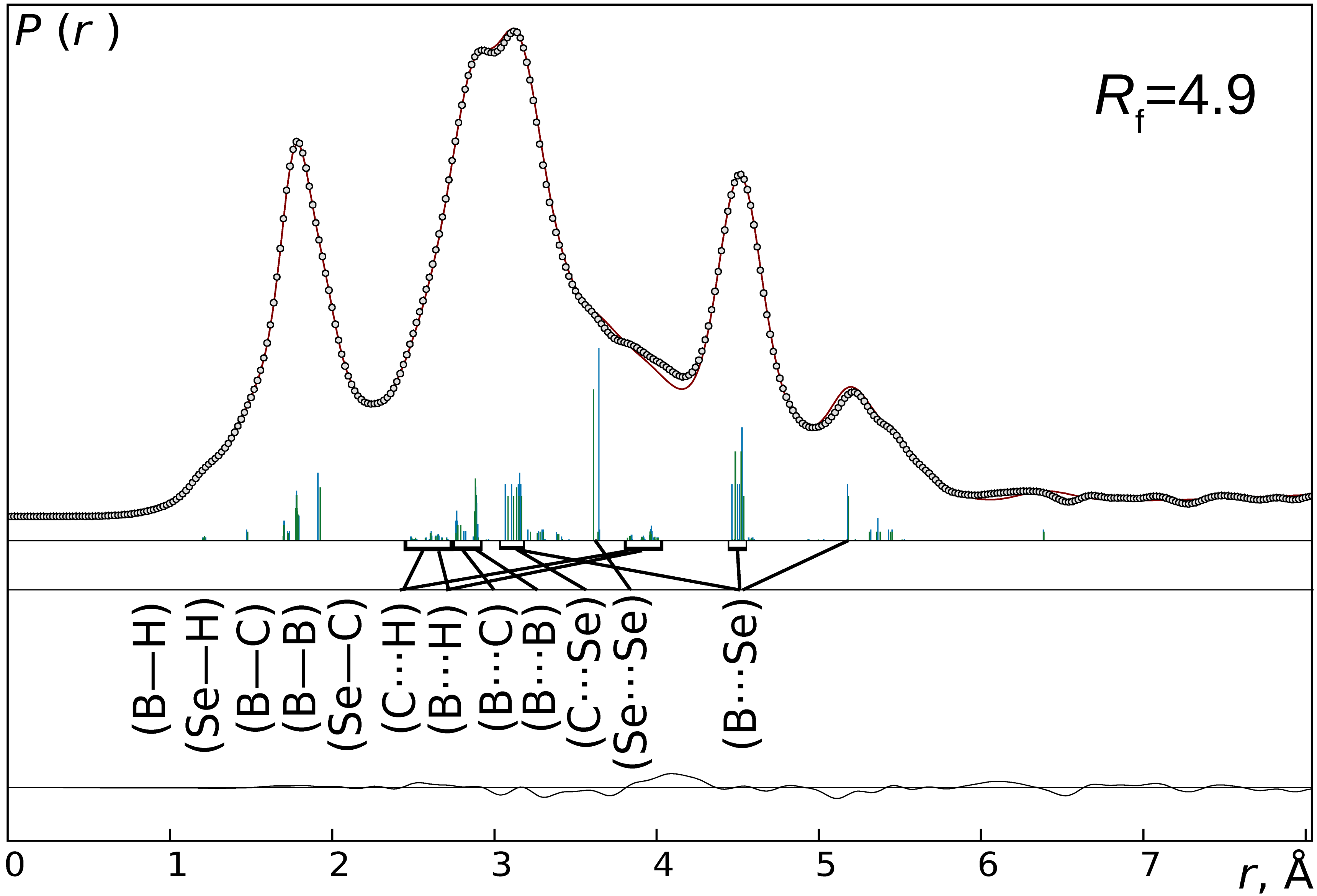
GED for “I”



GED for “SH”



GED for “SeH”



Average B—B bond lengths in 1,2-dicarba-closo-dodecaboranes

[Å]	**“ - “[a]**	**“I”**	**“SH”**	**“SeH”**
$\mathbf{r_g}$	1.791(8)	1.793(4)	1.789(11)	1.786(8)

[a] – A.R. Turner, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, M. A. Fox, Dalton Trans., 2005, 1310 – 1318

Average B—C bond lengths in 1,2-dicarba-closo-dodecaboranes

[Å]	**“ - “**[a]	**“I”**	**“SH”**	**“SeH”**
$\mathbf{r_g}$	1.717(7)	1.715(3)	1.718(11)	1.718(8)

[a] – A.R. Turner, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, M. A. Fox, Dalton Trans., 2005, 1310 – 1318

C—C bond length in 1,2-dicarba-closo-dodecaboranes

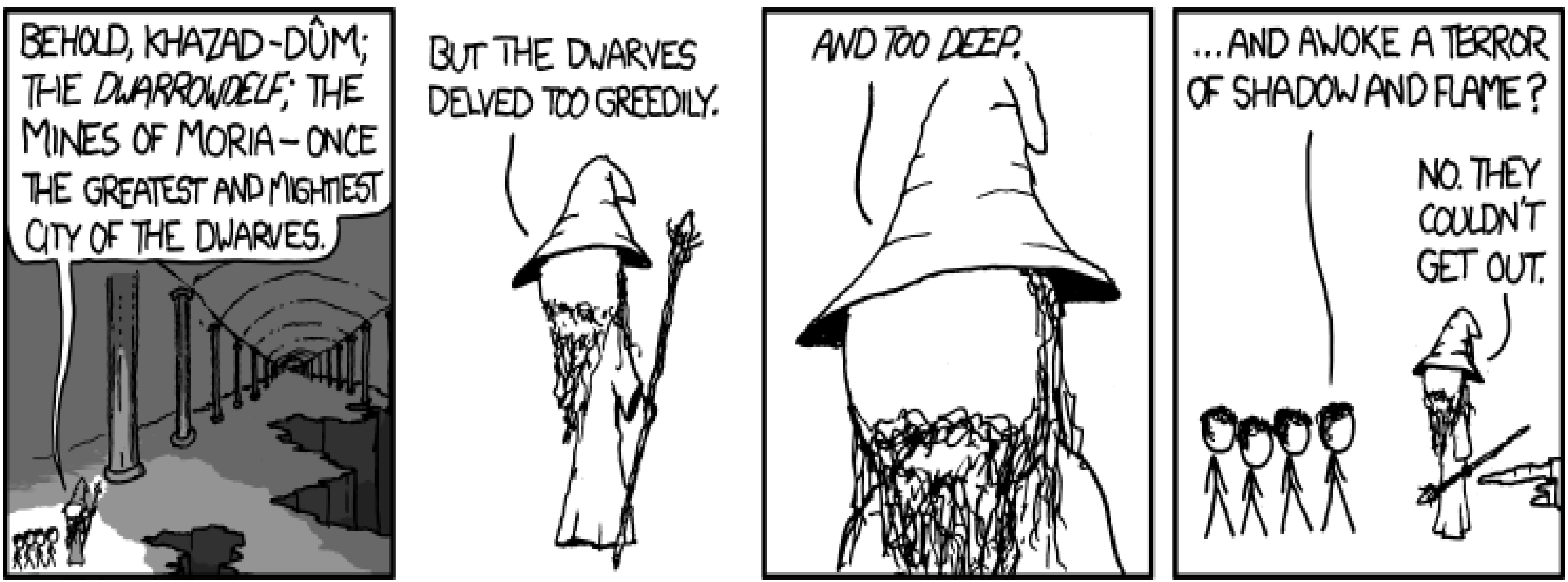
[Å]	**“ - “[a]**	**“I”**	**“SH”**	**“SeH”**
$\mathbf{r_g}$	1.624(8)	1.637(6)	1.763(16)	1.722(11)

[a] – A.R. Turner, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, M. A. Fox, Dalton Trans., 2005, 1310 – 1318

Core Facility
GED @ Bi
Gas-Electron-Diffraction &
Small Molecule Structures Centre

Mitzel Group
inorganic & structural chemistry

Thank You For Your Attention!



B—B bond in 1,2-dicarba-closo-dodecaboranes

	" - "	**"I"**	**"SH"**	**"SeH"**
$\mathbf{r_g}$	1.791(8)	1.793(12)	1.789(34)	1.786(23)
$\mathbf{r_e}$	—	1.778(12)	1.773(34)	1.771(23)

B—C bond in 1,2-dicarba-closo-dodecaboranes

	“ - “	**“I”**	**“SH”**	**“SeH”**
$\mathbf{r_g}$	1.717(7)	1.715(10)	1.718(33)	1.718(23)
$\mathbf{r_e}$	—	1.699(10)	1.698(33)	1.698(23)

C—C bond in 1,2-dicarba-closo-dodecaboranes

	“ - “	**“I”**	**“SH”**	**“SeH”**
$\mathbf{r_g}$	1.624(8)	1.637(18)	1.763(49)	1.722(34)
$\mathbf{r_e}$	—	1.621(18)	1.753(49)	1.723(34)

[Å / °]	**Anti-S**	**Syn-S**	**Anti-Se**	**Syn-Se**
B-B(av)	1.773(35)	1.773(33)	1.771(24)	1.771(23)
B-C(av)	1.697(34)	1.698(33)	1.701(23)	1.695(22)
C-C	1.750(49)	1.756(50)	1.723(33)	1.723(34)
B-H(av)	1.189(35)	1.190(35)	1.195(24)	1.195(24)
X-H	1.341(36)	1.340(32)	1.466(24)	1.463(22)
C-X	1.749(25)	1.758(30)	1.898(17)	1.908(19)
φ	-90(3)	95(2)	-85(2)	93(1)
χ	0.56	0.44	0.56	0.44
R_f, [%]	4.3		4.9	

[Å / °]	**re**	**rg**
B-B(av)	1.778(12)	1.793(12)
B-C(av)	1.699(10)	1.715(10)
C-C	1.621(18)	1.637(18)
B-H(av)	1.183(13)	1.205(13)
C-H	1.088(12)	1.108(12)
B-I	2.139(8)	2.148(8)
R_f, [%]	4.3	

MD formulas for GED usage

$$r_a = 1/\langle \frac{1}{r} \rangle$$

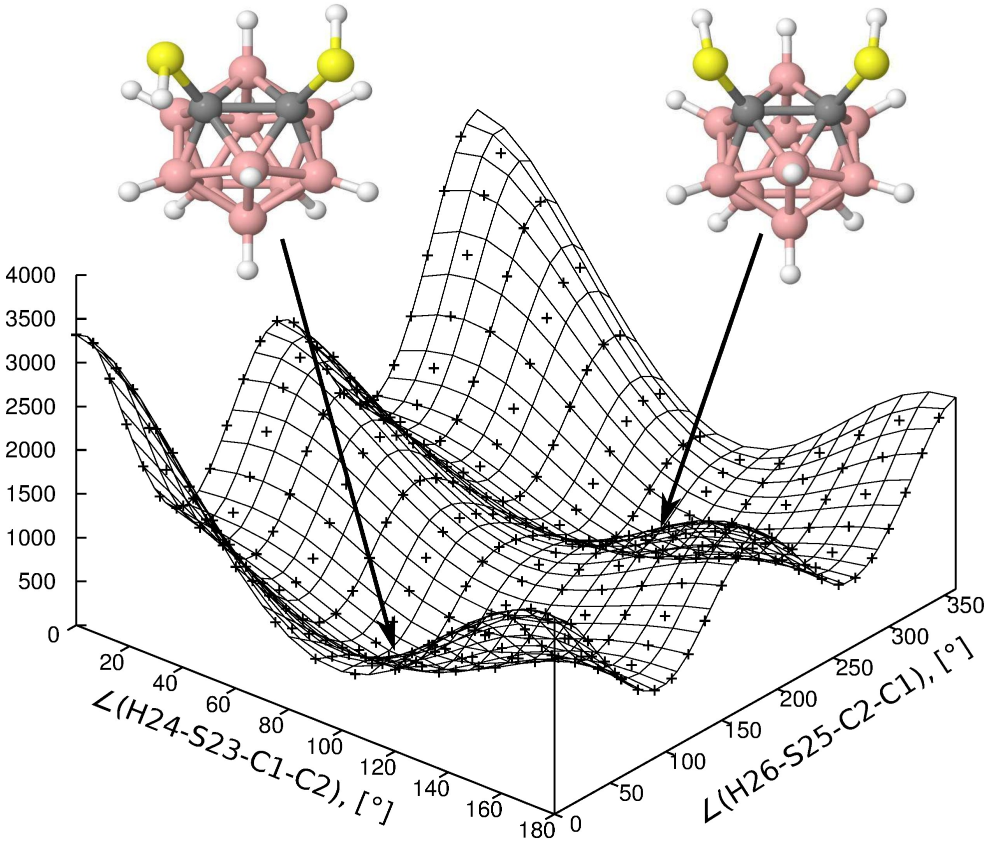
$$r_g = \langle r \rangle$$

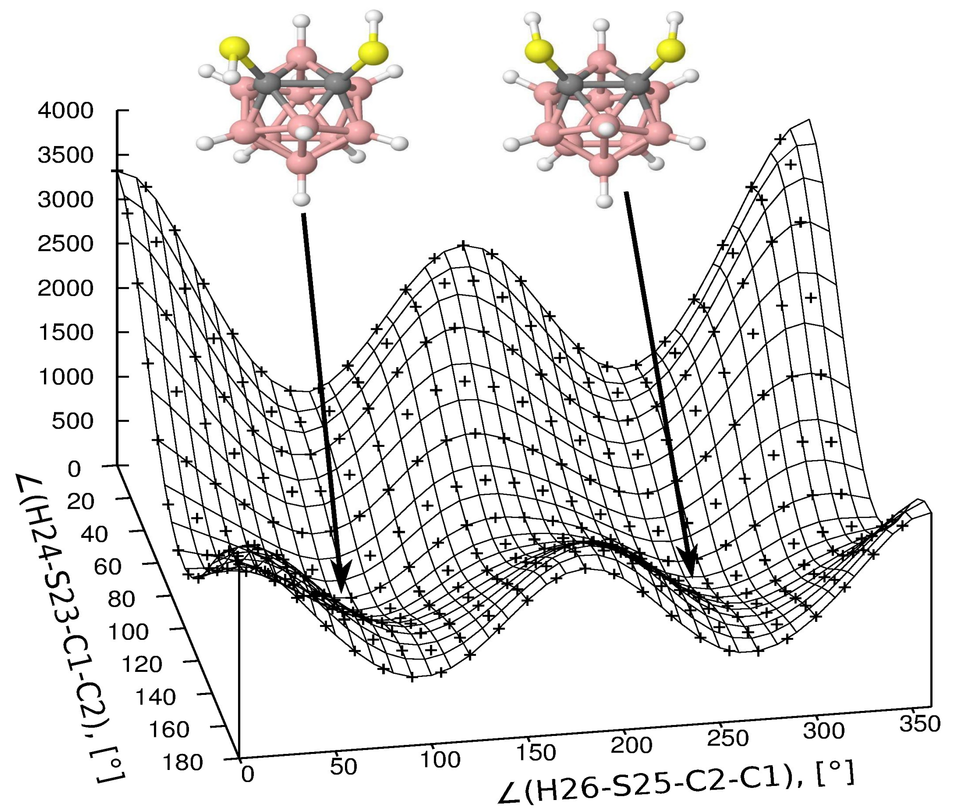
$$l^2 = \langle r^2 \rangle - \langle r \rangle^2$$

$$\kappa = \langle r^3 \rangle - 3 \langle r \rangle \langle r^2 \rangle + 2 \langle r \rangle^2$$

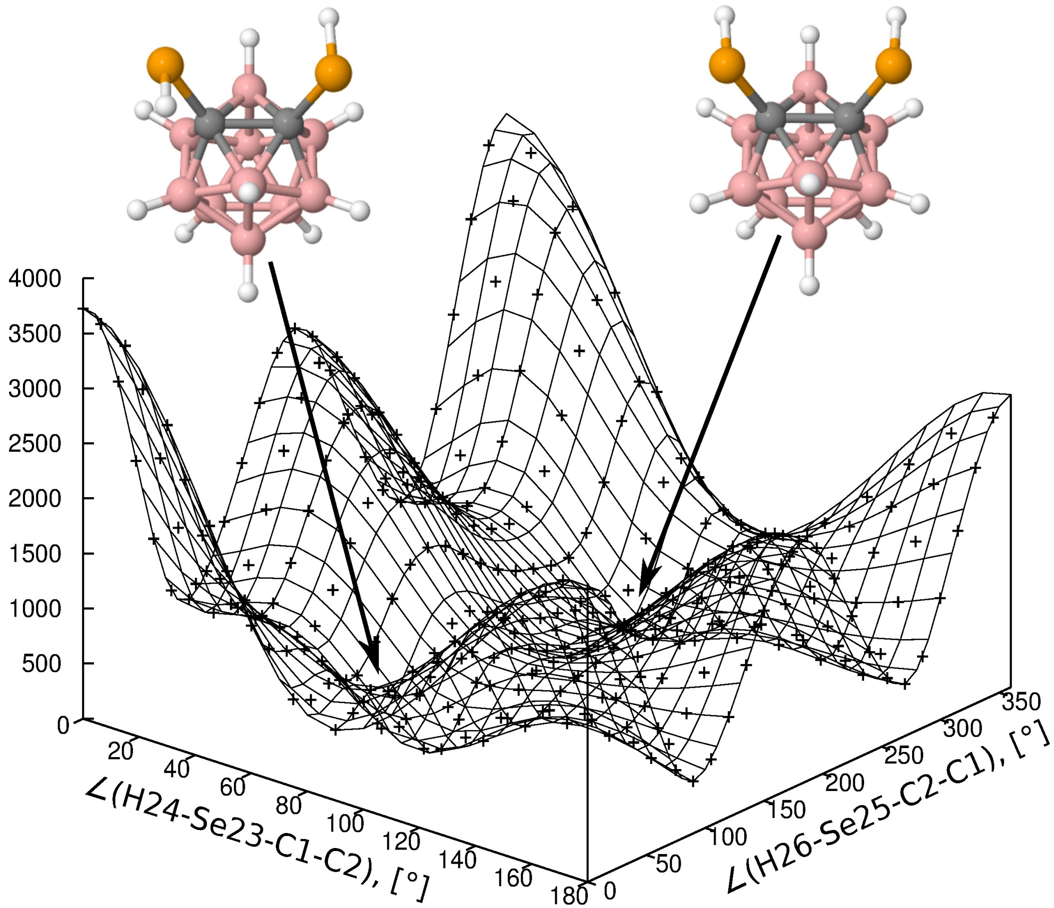
$$\langle x \rangle = \frac{1}{\tau} \int_0^\tau x(t)\, dt \approx \frac{1}{N} \sum_{i=1}^{N} x_i$$

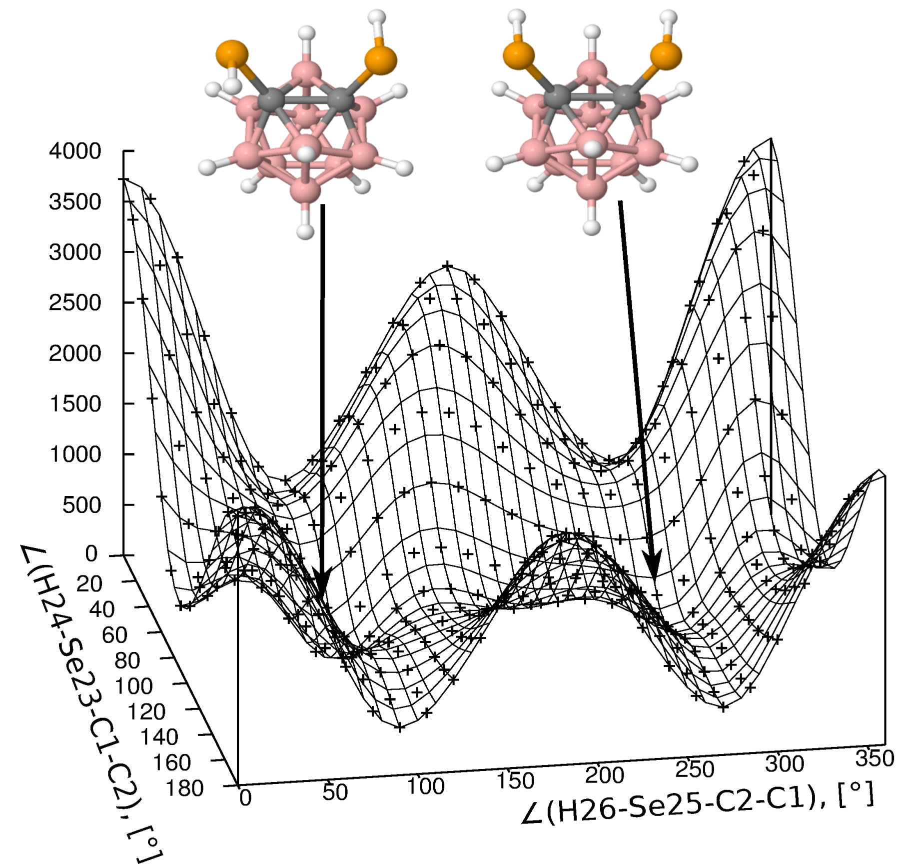
Quality of PES potential approximation for “SH”



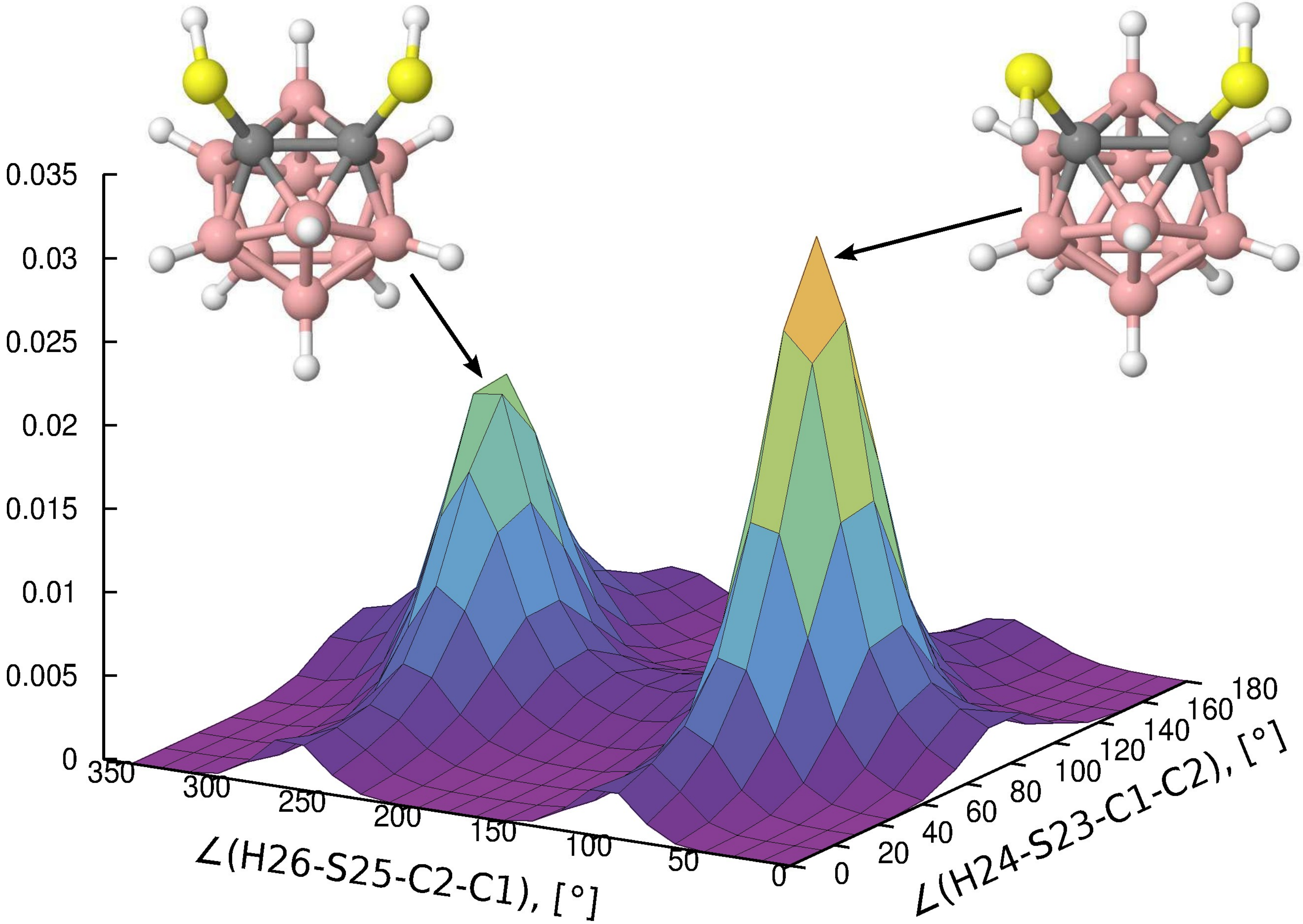


Quality of PES potential approximation for “SeH”

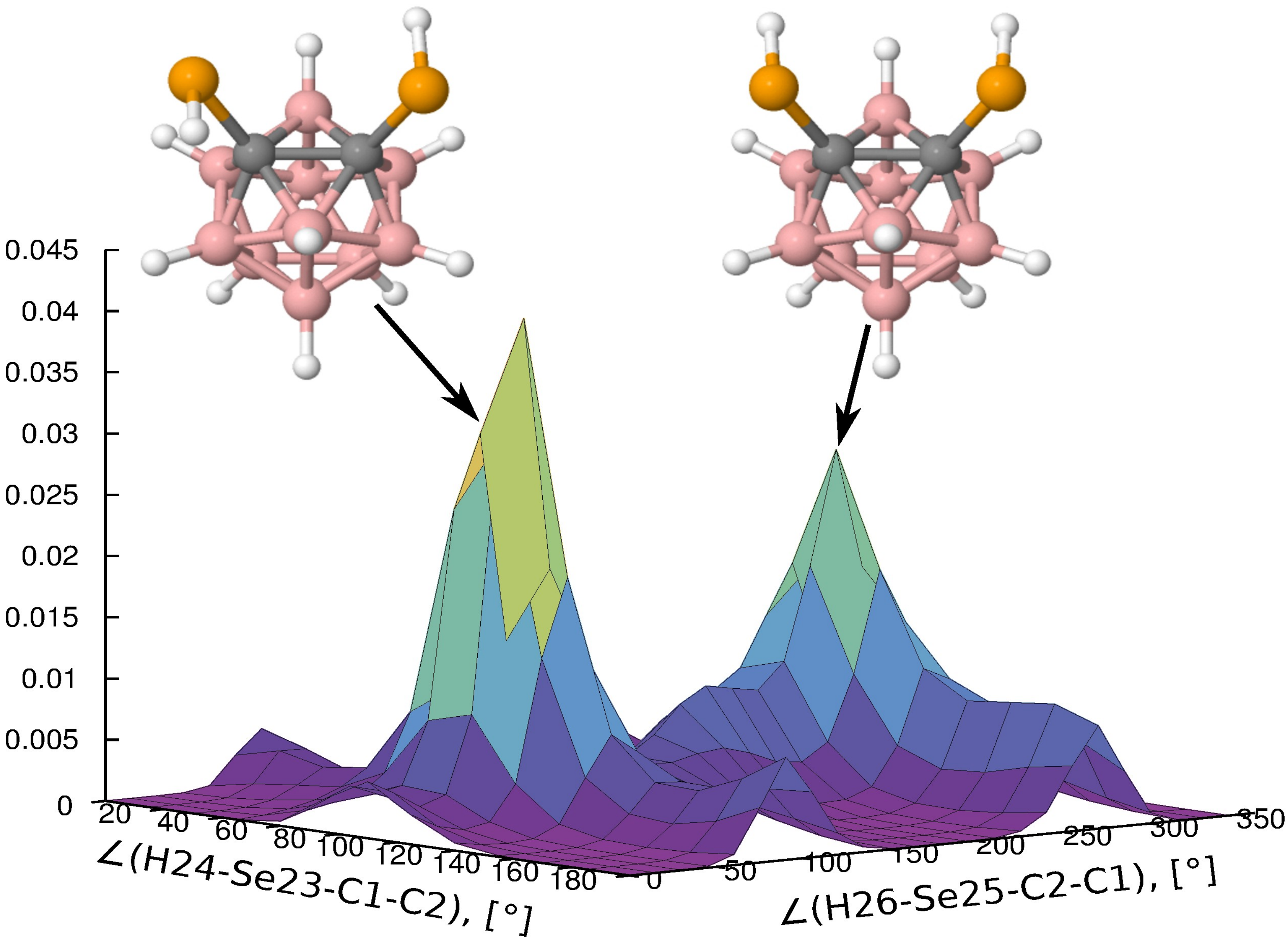




Classical Distribution for "SH"



Classical Distribution for “SeH”



Barrier Heights for “SH” and “SeH”

[cm^{-1}]	“SH”	“SeH”
BH1	681	626
BH2	773	423

Equilibrium torsion angles values for “SH” and “SeH”

[°]	“SH”	“SeH”
anti	87.3 / 90(3)	85.7 / 95(2)
syn	95.4 / 95(2)	88.7 / 93(1)