Study of the Si fullerene cage isomers

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Closed-cage structures
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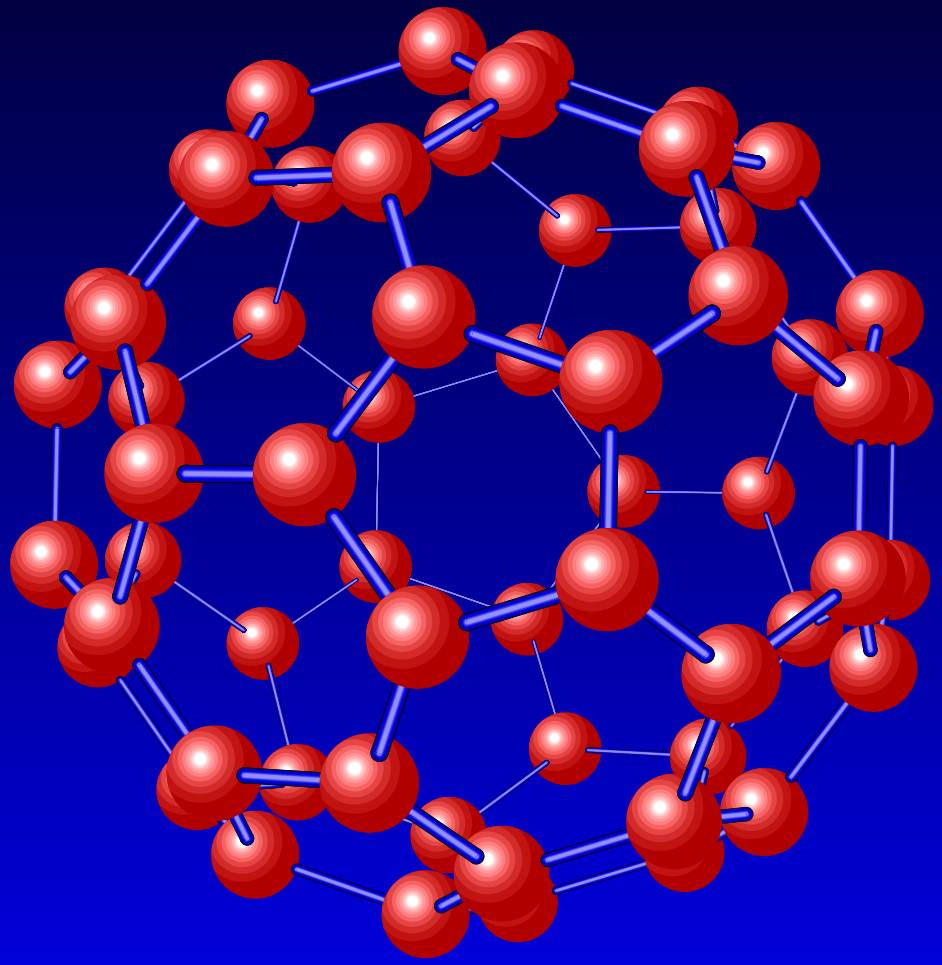
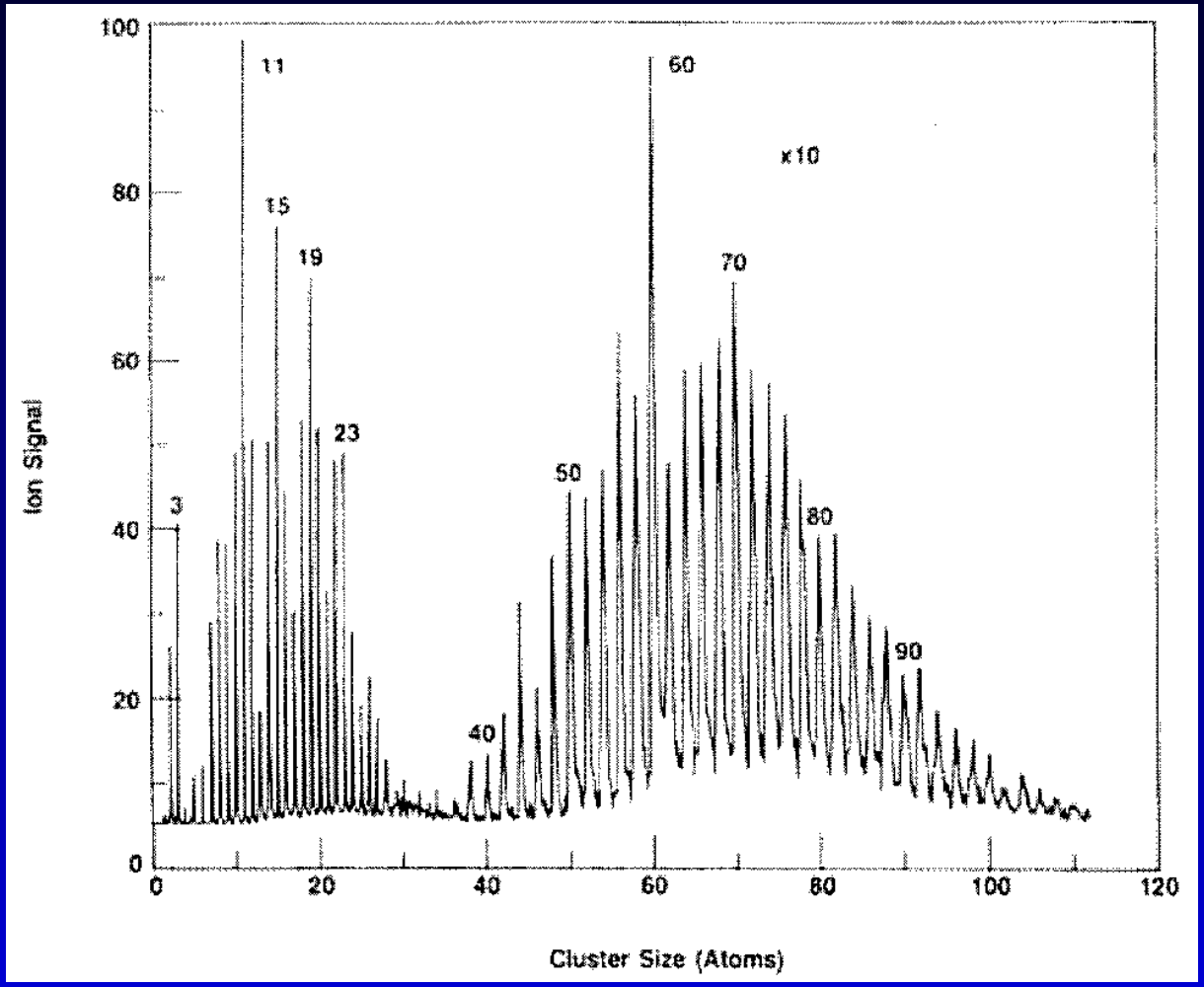
(All the atoms are three-fold co-ordinated
$\Longrightarrow$ sp^2-like bonding)

C_{60} Buckminsterfullerene



H.W.Kroto, J.R.Heath, S.C.O'Brien, R.F.Curl and R.E.Smalley, Nature, **318**, 162, (1985)

. . . but not only C_{60}



E.A.Rohlfing, D.M.Cox and A.Kaldor, J.Chem.Phys. **81**, 3322, (1984)

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- 12 pentagons
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Different arrangement of the pentagons and the hexagons gives different structures (isomers)

How many isomers are they ?

N	Isomers	N	Isomers	N	Isomers
20	1	42	45	62	2385
24	1	44	89	64	3465
26	1	46	116	66	4487
28	2	48	199	68	6332
30	3	50	271	70	8149
32	6	52	437	72	11190
34	6	54	580	74	14246
36	15	56	924	76	19151
38	17	58	1205	78	24109
40	40	60	1812	80	31924

P.W.Fowler and D.E.Manolopoulos, *An atlas of fullerenes*, (Oxford: Clarendon Press), 1995

What about Si fullerenes ?

Bonding:

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Si : mainly $\underline{sp^3}$ + dangling bonds

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However ...

Three-fold co-ordinated and/or fullerene-like Si systems

- Si surfaces

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Consequently: Si fullerenes are of interest

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- Focused on highly symmetric starting structures (for example I_h Si_{60})
- Studied structures:
  Si_N, $N = 20 - 32, 36, 44, 50, 60, 70$

The system under consideration

Si_{38}

all the 17 isomers

and

Si_{20}

for comparison

The method for Global Optimization I

- Molecular Dynamics At Constant Temperature

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i V - m\gamma\frac{E_K - E_T}{E_K}\frac{d\mathbf{r}_i}{dt}$$

$$E_K = \sum_{i=1}^{N}\frac{1}{2}m_i v_i^2 \qquad E_T = \frac{f}{2}k_B T$$

H.J.C.Berendsen, J.P.M.Postma, W.F. van Gunsteren, A.DiNola and J.R.Haak, J.Chem.Phys. **81**, 3684, (1984)

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- If first neigbour's distances > cut off distance then freezing the motions (i.e. $\mathbf{v}_i = 0$)
- Evolution of $V = V(t)$ in time under constant temperature

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- Configuration of the global energy minimum

In agreement with the Cambridge Cluster Database for the first 100 Lenard-Jones clusters (*http://www-wales.ch.cam.ac.uk/CCD.html*)

38-atom fullerene isomers

Table A.3. Fullerene isomers of C_{38}

Isomer	Ring spiral	Point group	NMR pattern	Vibrations	Pentagon indices	Band gap	Transformations
38:1	1 2 3 4 5 7 15 17 18 19 20 21	C_2	19×2	108, 108, 108	0 2 2 6 2 0	0.0312	3(2)
38:2	1 2 3 4 5 9 13 17 18 19 20 21	D_{3h}	1×2, 2×6, 2×12	28, 47, 19	0 0 6 0 6 0	0.0000	
38:3	1 2 3 4 5 12 13 15 17 19 20 21	C_1	38×1	108, 108, 108	0 3 3 5 1 0	0.0691	1, 3(2), 5, 10
38:4	1 2 3 4 5 13 14 15 17 18 19 21	C_1	38×1	108, 108, 108	0 1 5 5 1 0	0.1427	4, 5, 6, 7
38:5	1 2 3 4 7 11 12 15 17 19 20 21	C_1	38×1	108, 108, 108	0 3 4 5 0 0	0.1402	3, 4, 6, 8, 10, 11, 13
38:6	1 2 3 4 7 11 13 15 17 18 20 21	C_2	19×2	108, 108, 108	0 2 4 6 0 0	0.2069	4(2), 5(2), 10
38:7	1 2 3 4 7 11 13 16 17 19 20 21	C_1	38×1	108, 108, 108	0 1 6 5 0 0	0.0652	4, 7, 11
38:8	1 2 3 4 11 12 13 14 16 17 20 21	C_1	38×1	108, 108, 108	0 1 8 3 0 0	0.0982	5, 9, 11, 13, 14(2), 17
38:9	1 2 3 4 11 12 14 15 16 18 19 21	D_3	1×2, 6×6	53, 55, 36	0 0 6 6 0 0	0.1973	8(6)
38:10	1 2 3 5 7 10 12 15 17 19 20 21	C_2	19×2	108, 108, 108	0 4 4 4 0 0	0.0177	3(2), 5(2), 6, 10(2), 13(2)
38:11	1 2 3 5 7 10 14 16 17 18 19 20	C_1	38×1	108, 108, 108	0 1 8 3 0 0	0.1099	5, 7, 8, 14
38:12	1 2 3 5 7 11 14 16 17 18 20 21	C_{2v}	5×2, 7×4	83, 108, 83	0 0 8 4 0 0	0.0045	
38:13	1 2 3 5 10 11 13 15 16 19 20 21	C_2	19×2	108, 108, 108	0 2 8 2 0 0	0.1505	5(2), 8(2), 10(2), 13, 17(2)
38:14	1 2 3 5 10 12 14 15 16 17 19 20	C_1	38×1	108, 108, 108	0 1 10 1 0 0	0.1036	8(2), 11, 15, 16, 17
38:15	1 2 3 5 11 12 14 15 16 17 18 20	C_{2v}	7×2, 6×4	84, 108, 84	0 0 10 2 0 0	0.0311	14(4)
38:16	1 2 3 10 11 12 13 14 15 16 17 18	C_{3v}	2×1, 4×3, 4×6	57, 57, 57	0 0 12 0 0 0	0.0454	14(6)
38:17	1 2 4 7 9 10 12 13 15 18 20 21	C_2	19×2	108, 108, 108	0 2 10 0 0 0	0.3004	8(2), 13(2), 14(2), 17(2)

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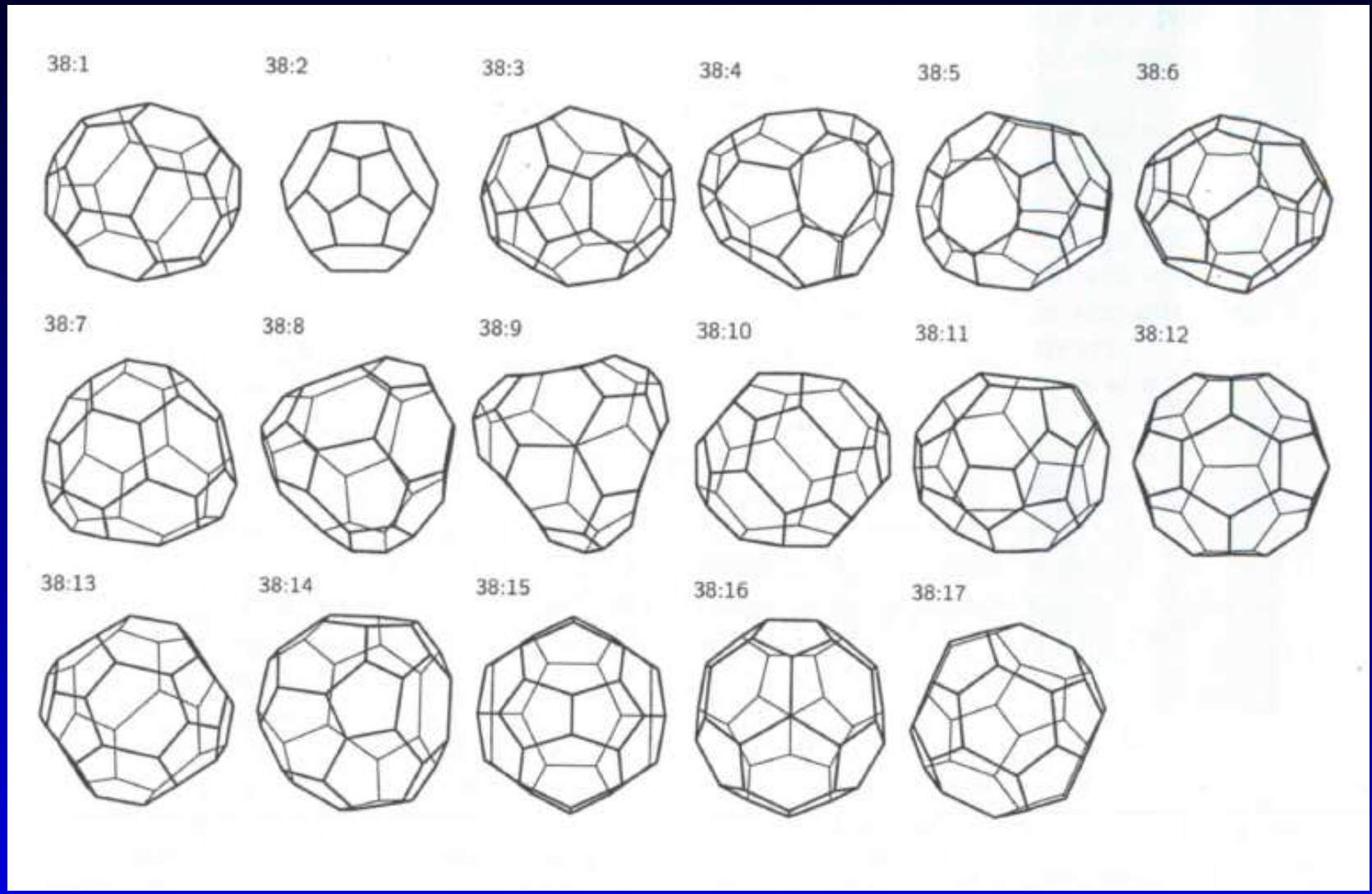
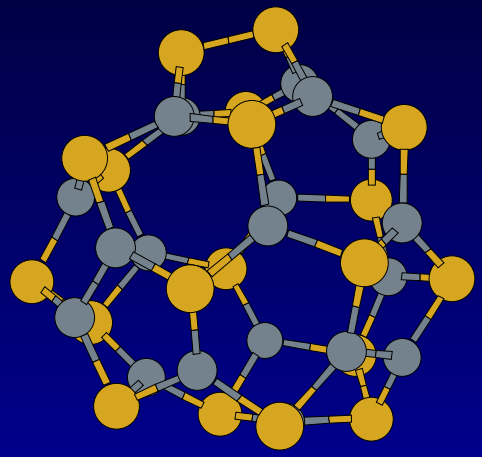
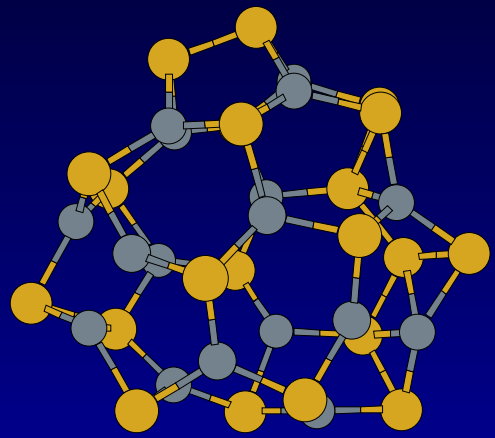
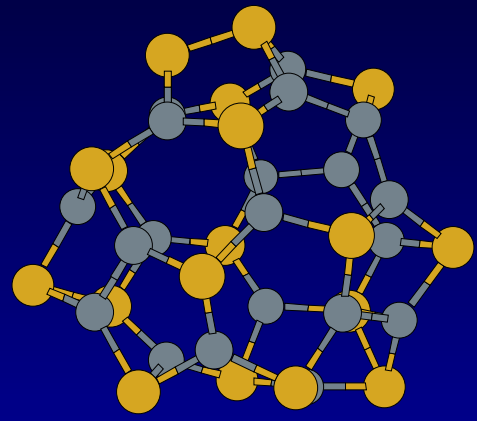
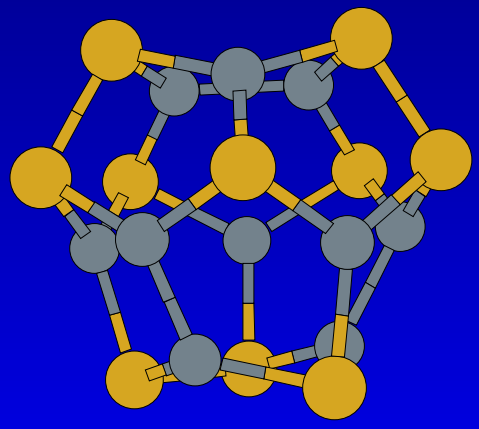
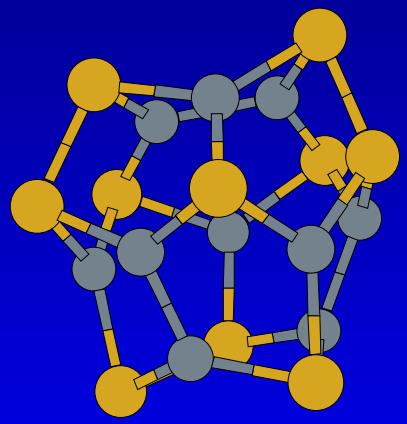
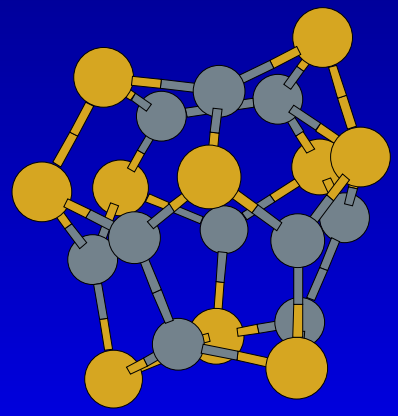
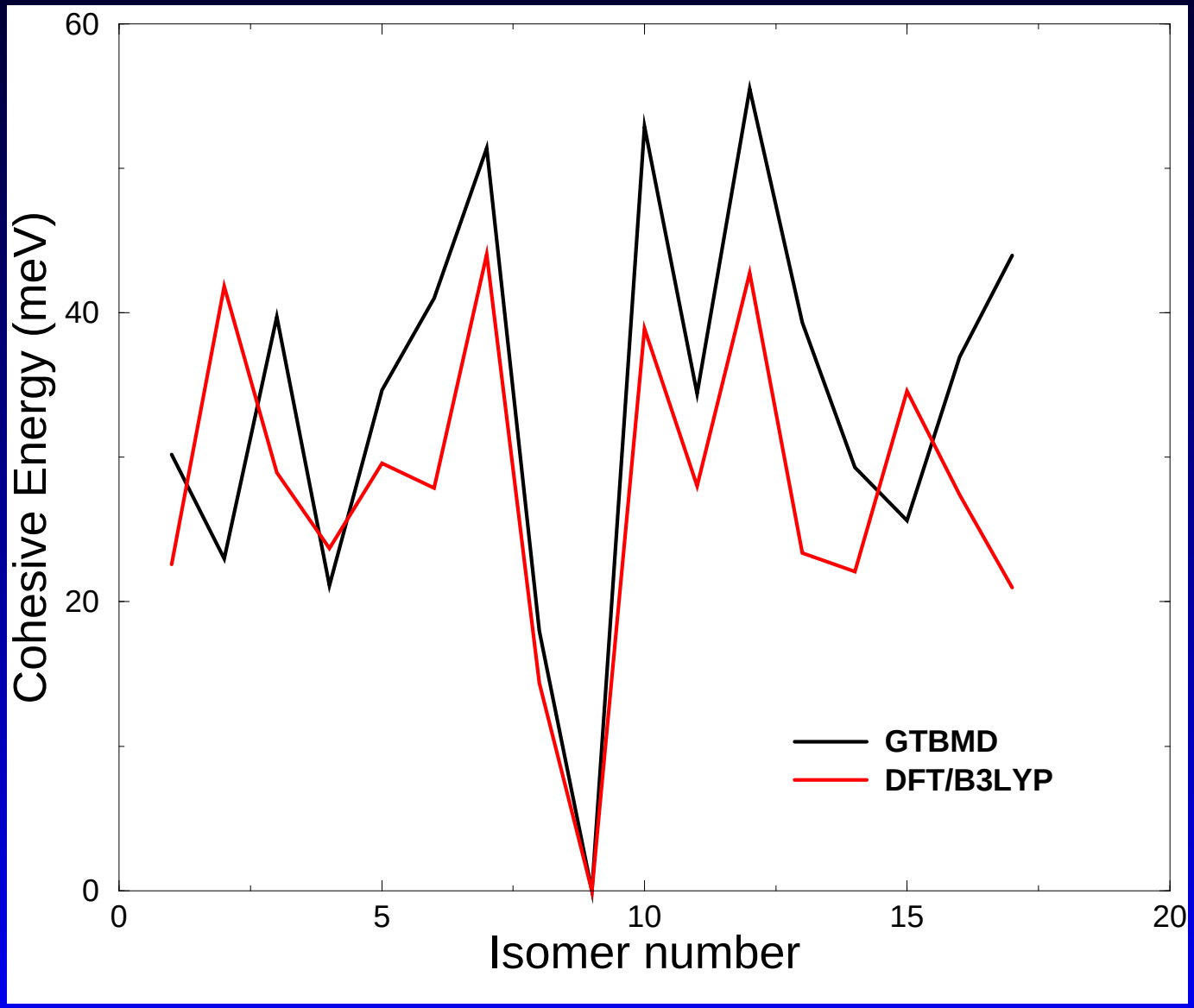


Optimized Structures

	OTBMD	GTBMD	DFT/B3LYP
Si_{38}			
Si_{20}			

Cohesive Energy



Comparison between Si_{38} and Si_{20}

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Method	Difference
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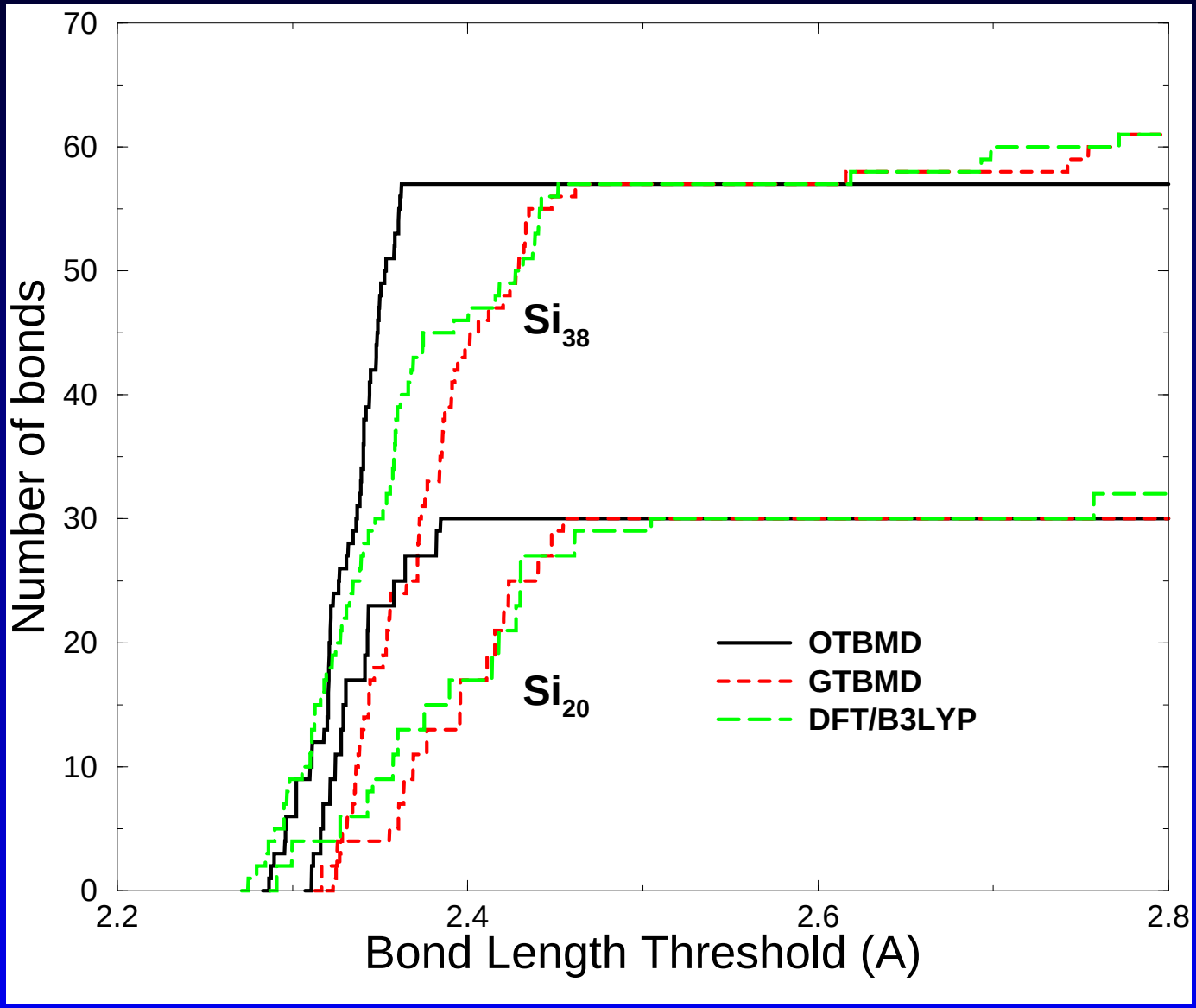
Marsen and Sattler assumptions:

- The smallest Si fullerenes are the most stable
- For Si a fused pentagon rule can replace the IPR of C fullerenes

B. Marsen and K. Sattler, Phys. Rev. B **60**, 11593, (1999)

Bond Lengths

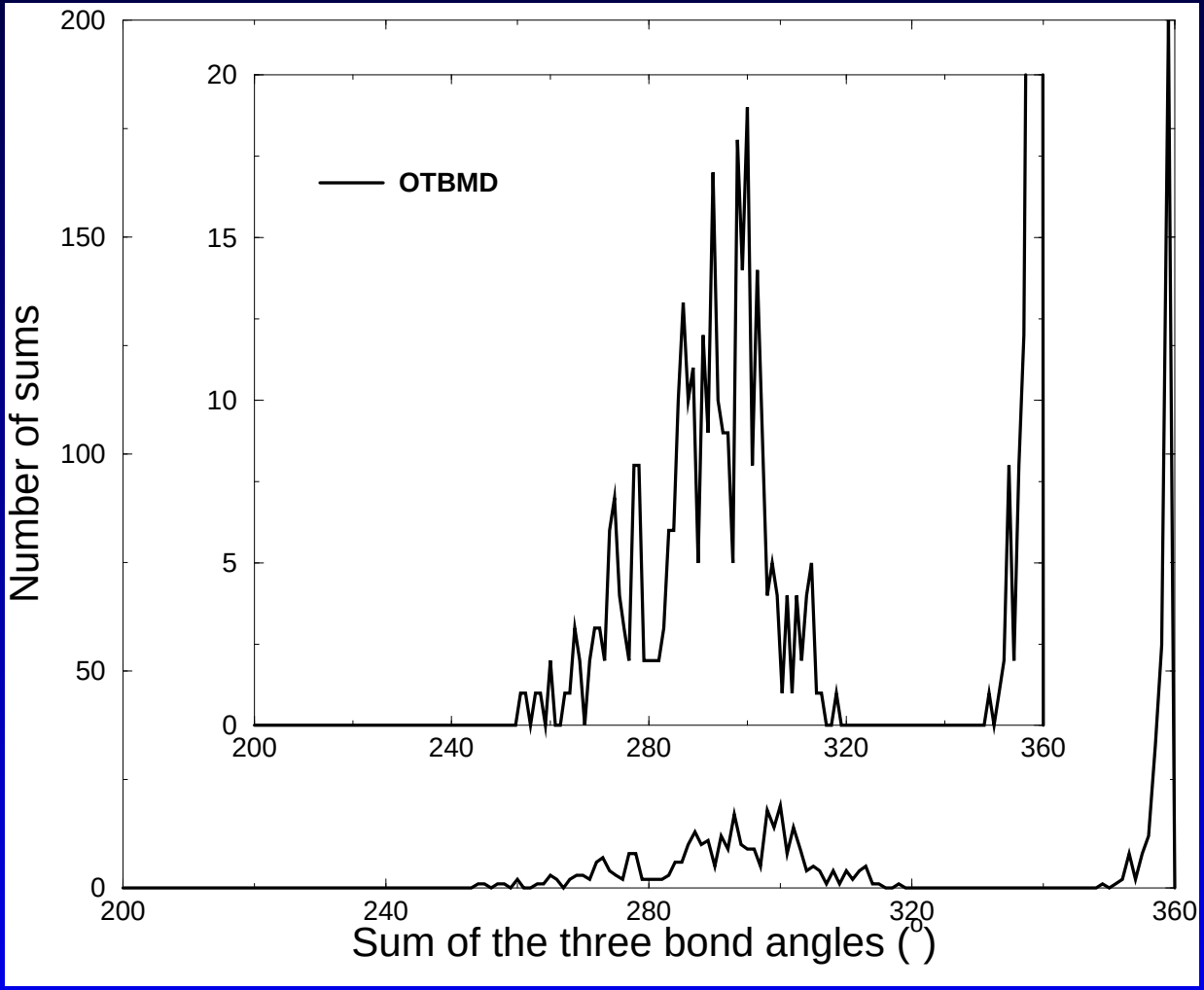


Sum of the three bond associated angles for ideal cases

For n_p pentagons ($n_p = 0, 1, 2, 3$)
sum = $360^o - 12^o n_p$

3 hexagons	360^o
2 hexagons + 1 pentagon	348^o
1 hexagon + 2 pentagons	336^o
3 pentagons	324^o
tetrahedral arrangement	328.41^o
not hybridized bonding	270^o

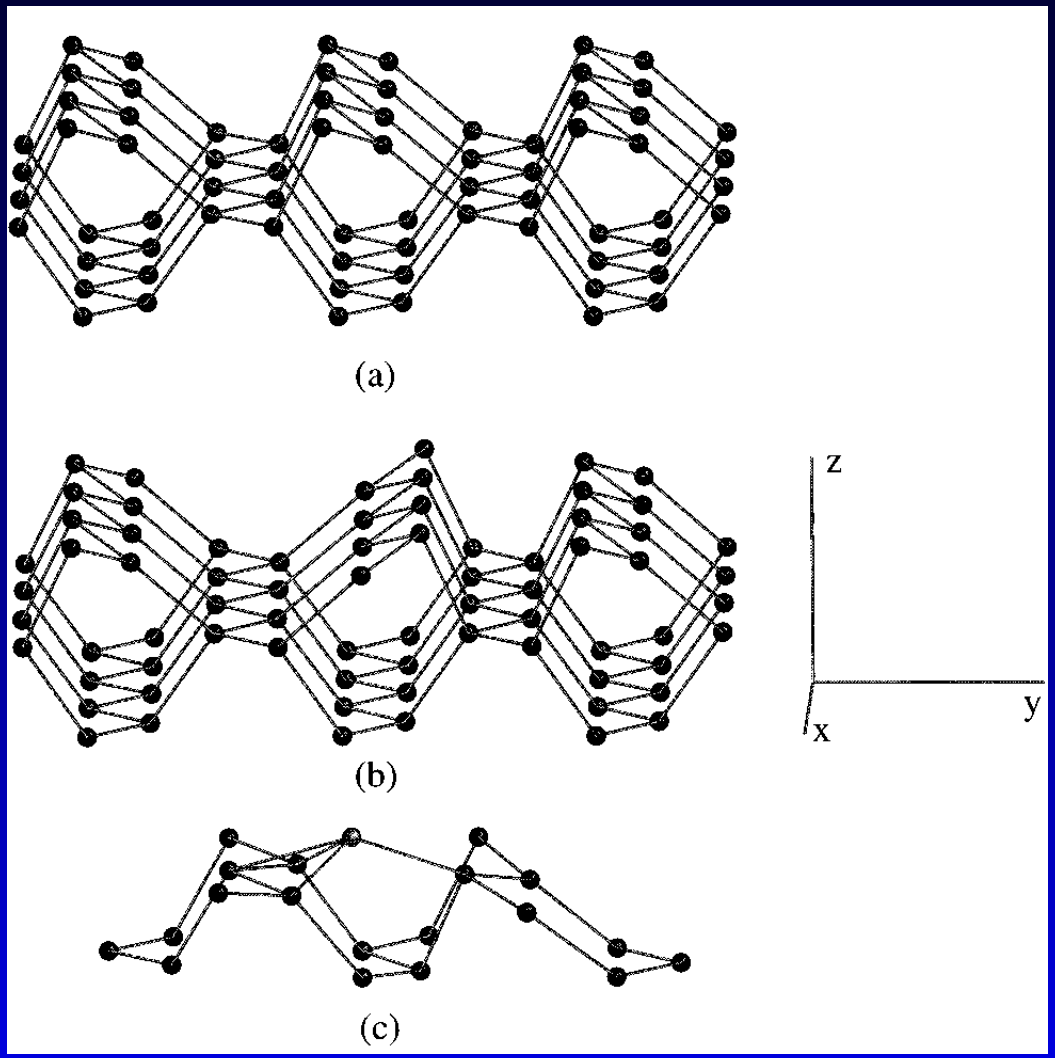
Distribution of the sum of the three bond associated angles



Acknowledgments

- Prof. A.N.Andriotis
- This work was partially supported by EU TMR Network "USEFULL"

The Si(110) surface



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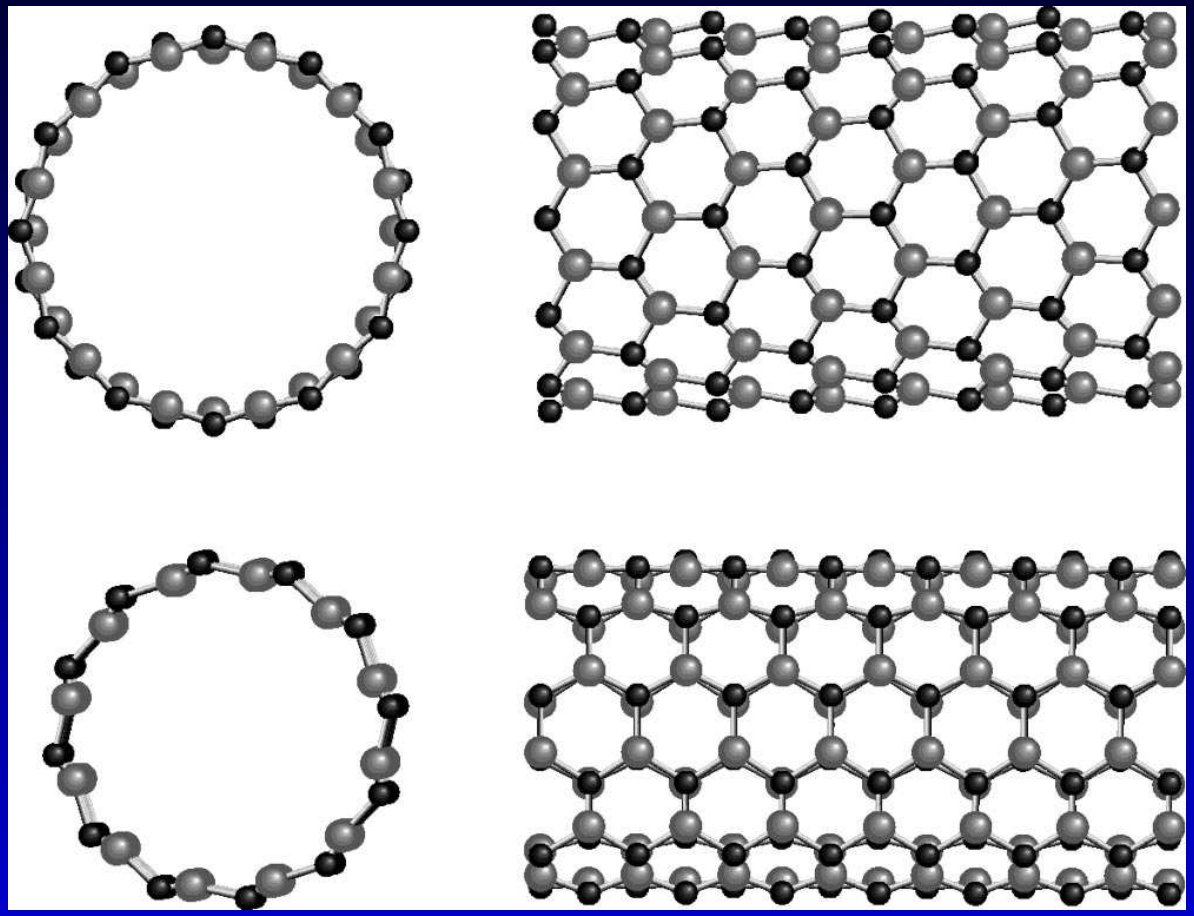
Back

Si-C nanotubes



Back

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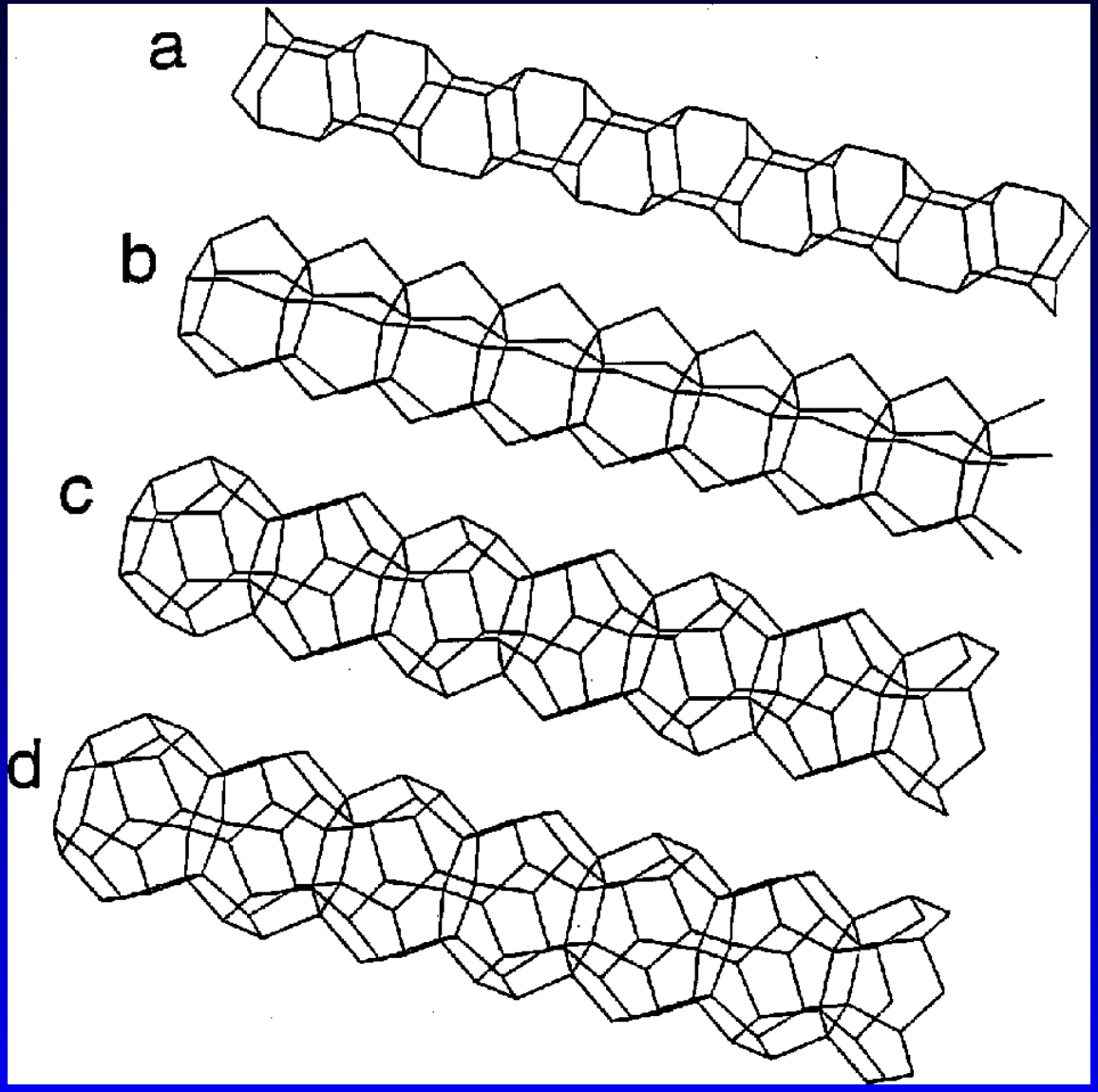
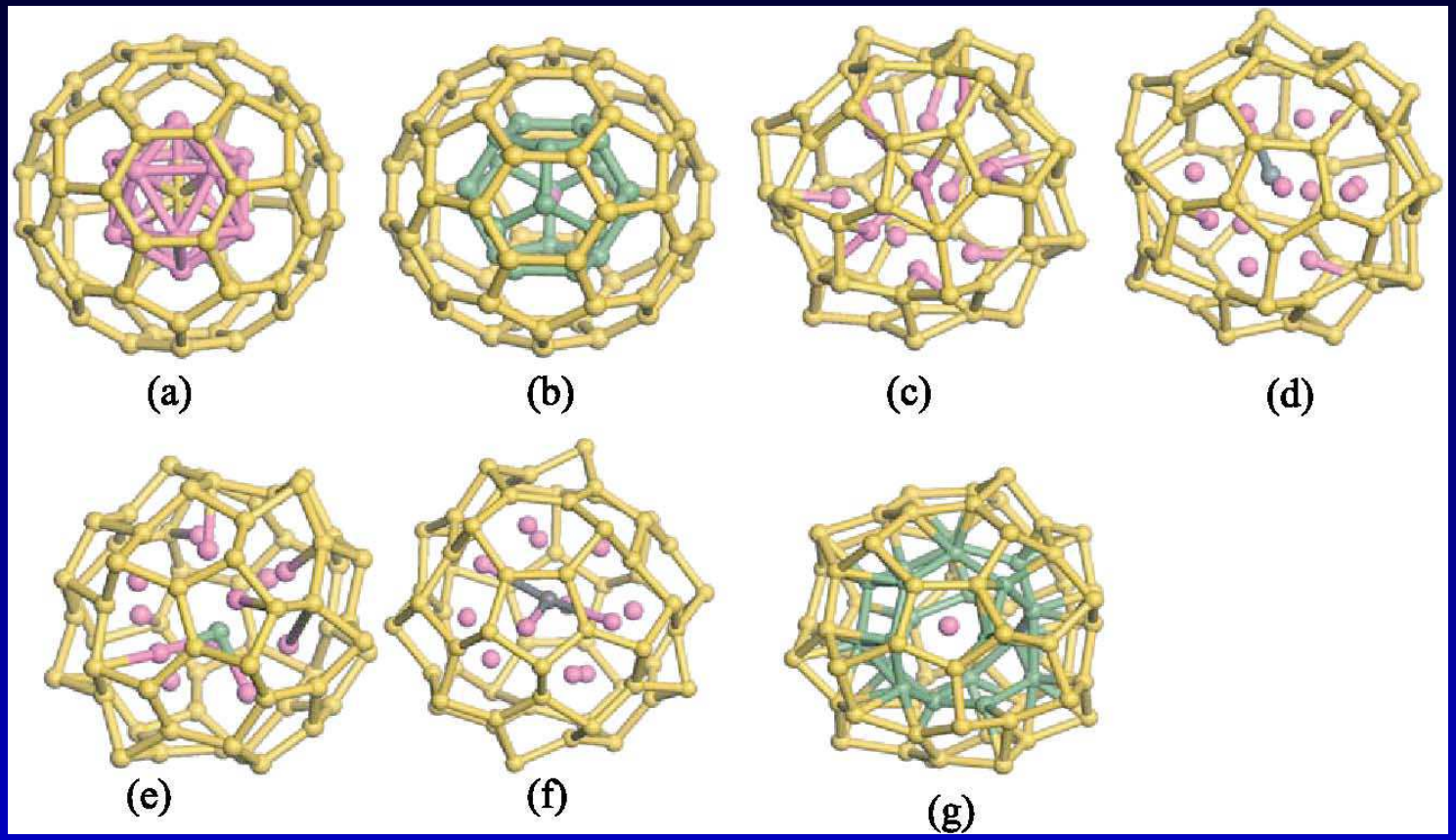
Si nanowires and nanotubes



B.Marsen and K.Sattler, Phys. Rev. B **60**, 11593, (1999)

Back

Si fullerene-like endohedral clusters



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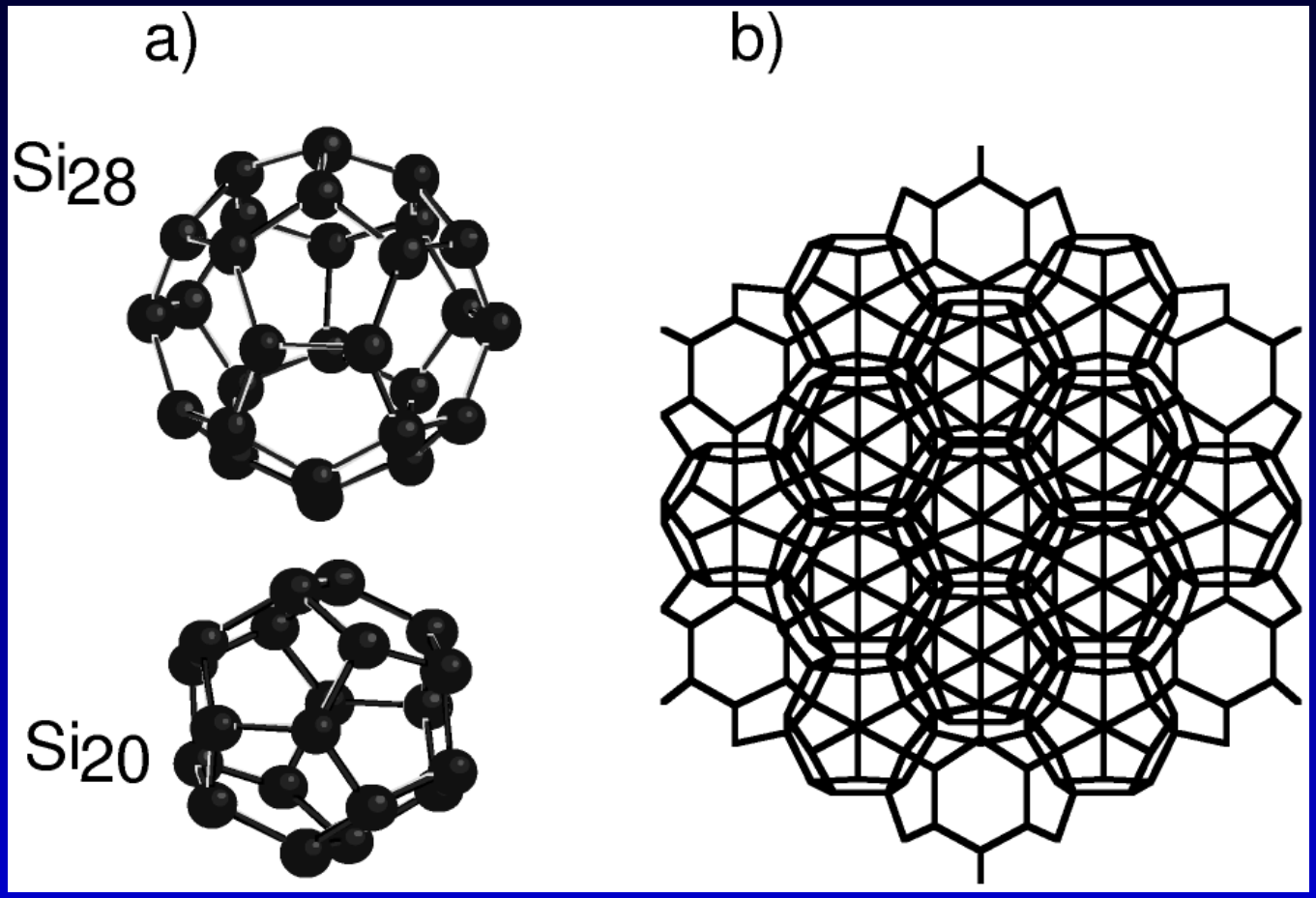
Phys. Rev. Lett. **90**, 135503, (2003)

Back

Si clathrates



Back

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Si20