TECHNISCHE UNIVERSITÄT DRESDEN

Institut für Physikalische Chemie und Elektrochemie, Fakultät Mathematik und Naturwissenschaften

Electron delocalisation and weak interactions: Implications to chemistry, material sciences and physics

Thomas Heine

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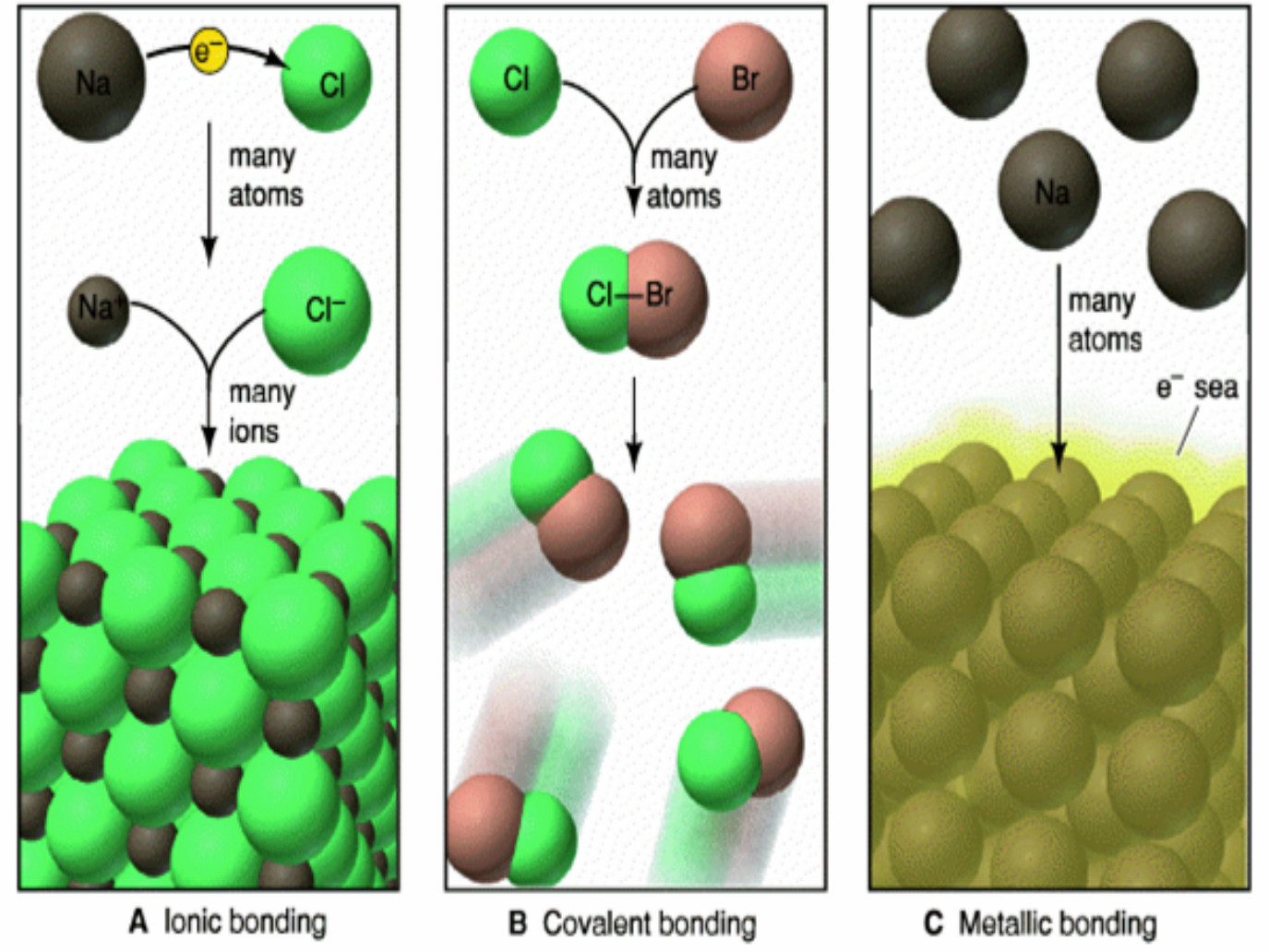
Bonding types in chemistry



displaced electrons **localised electrons** **delocalised electrons**

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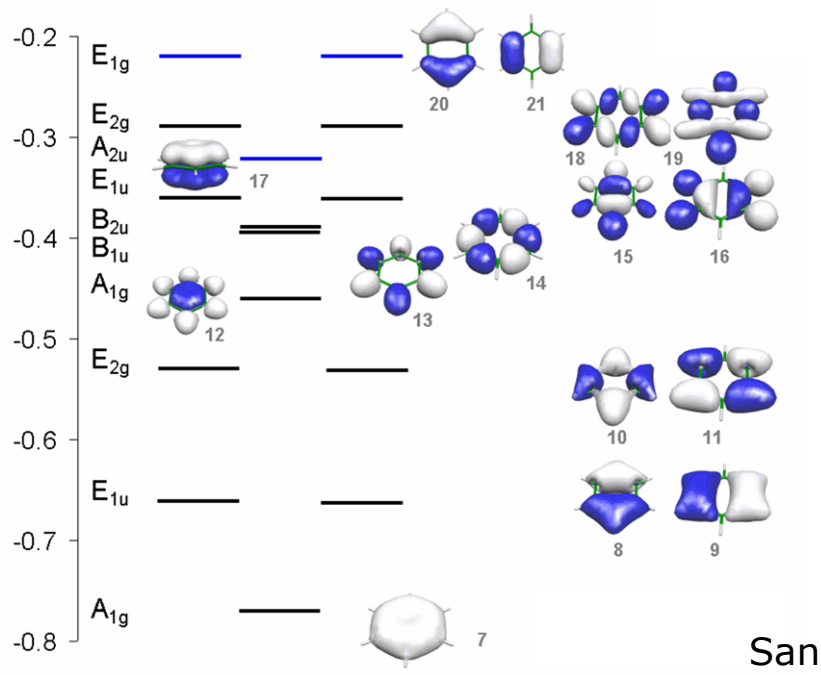
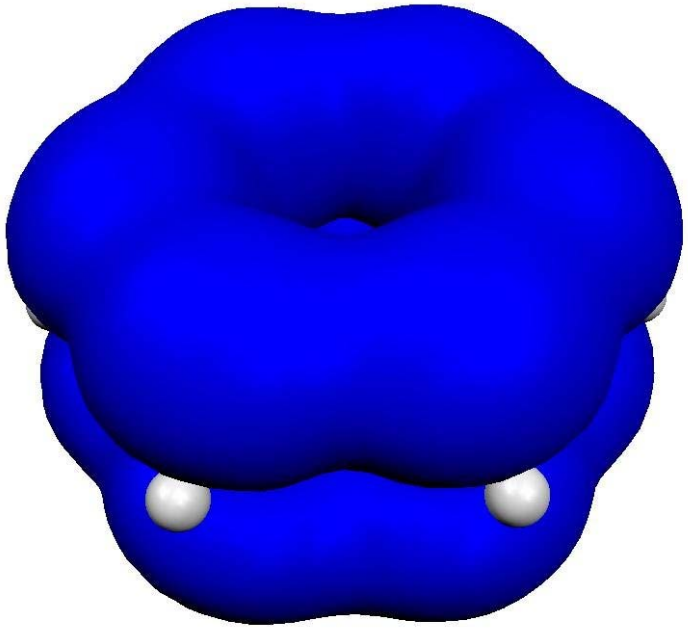
What about aromatic molecules

Molecular Orbitals of benzene



The ELF clearly shows delocalised clouds of π electrons



Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentealba, P. J. Chem. Phys. 2004, 120, 1670.

For Review:

Chem. Rev. 2005, 105, 3889-3910

Chem. Rev. 2005, 105, 3812-3841

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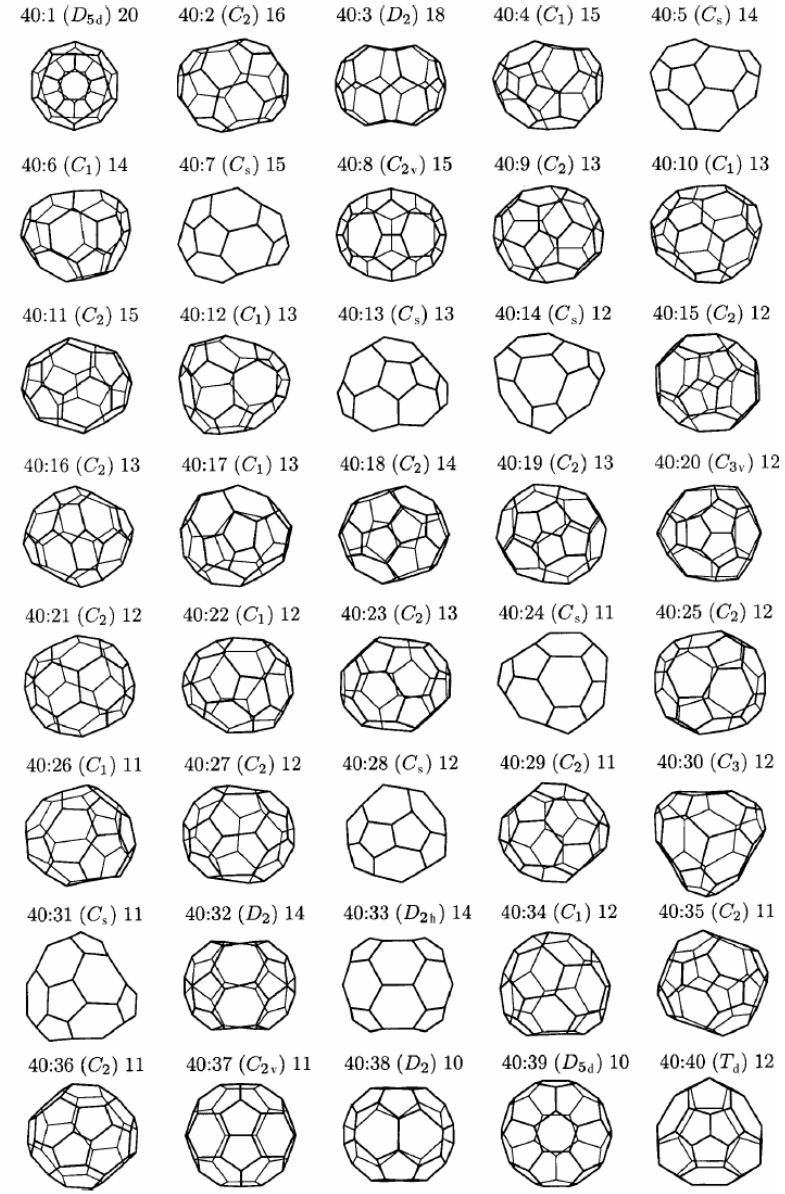
Pi system determines stability of sp^2 carbon structures



Fullerene isomers of C_{40}

- Contain 10-20 fused pentagons
- Nomenclature, (point group), number of pentagon adjacencies

Phys. Chem. Chem. Phys., 1999, 1, 2913-2918

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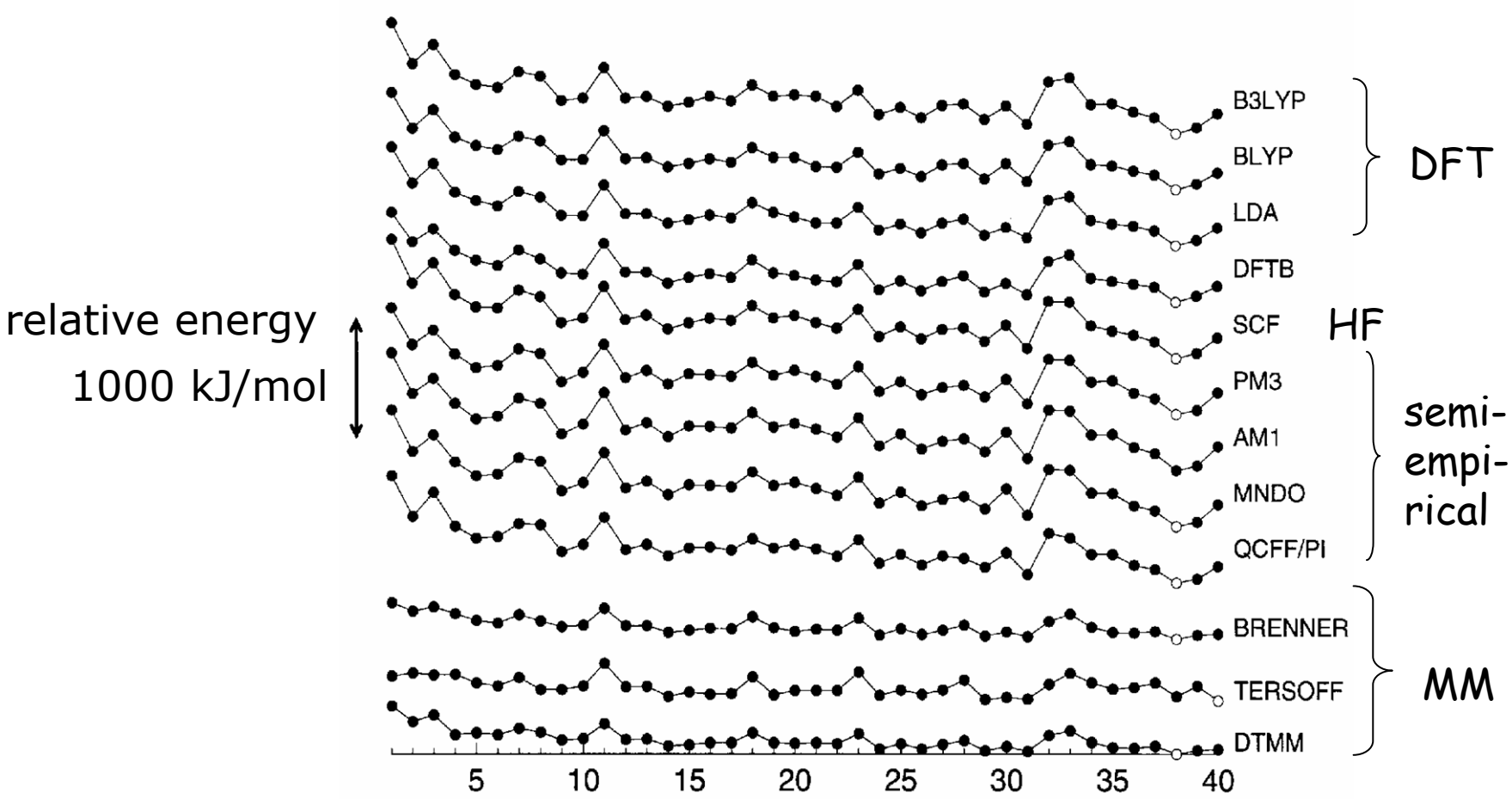
Relative energies of C_{40}



Phys. Chem. Chem. Phys., 1999, 1, 2913-2918

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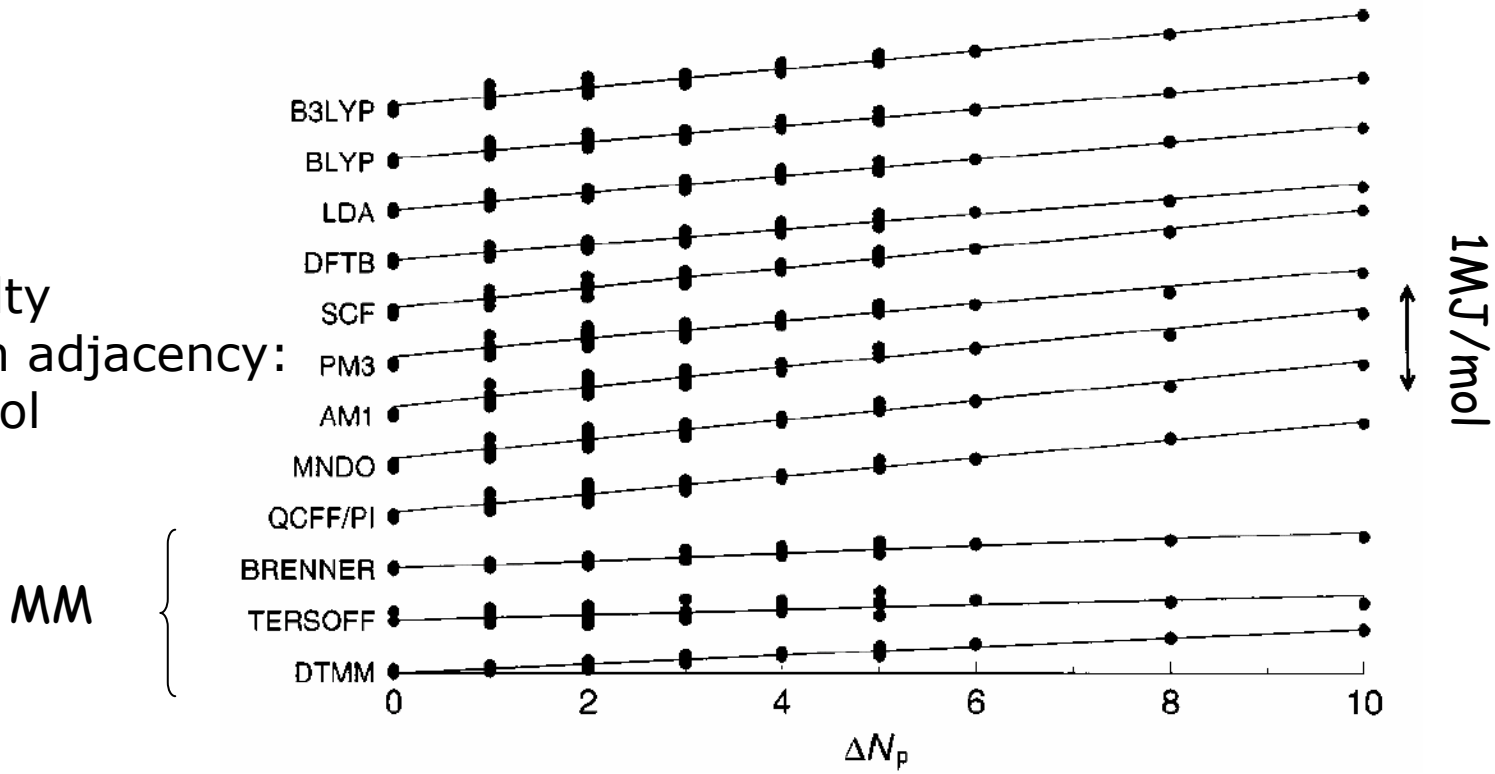
Rule of minimal number of pentagon adjacencies

Energy penalty
per pentagon adjacency:
70-120 kJ/mol



change in number of pentagon adjacencies

Pi system determines stability!

Phys. Chem. Chem. Phys.,
1999, 1, 2913-2918

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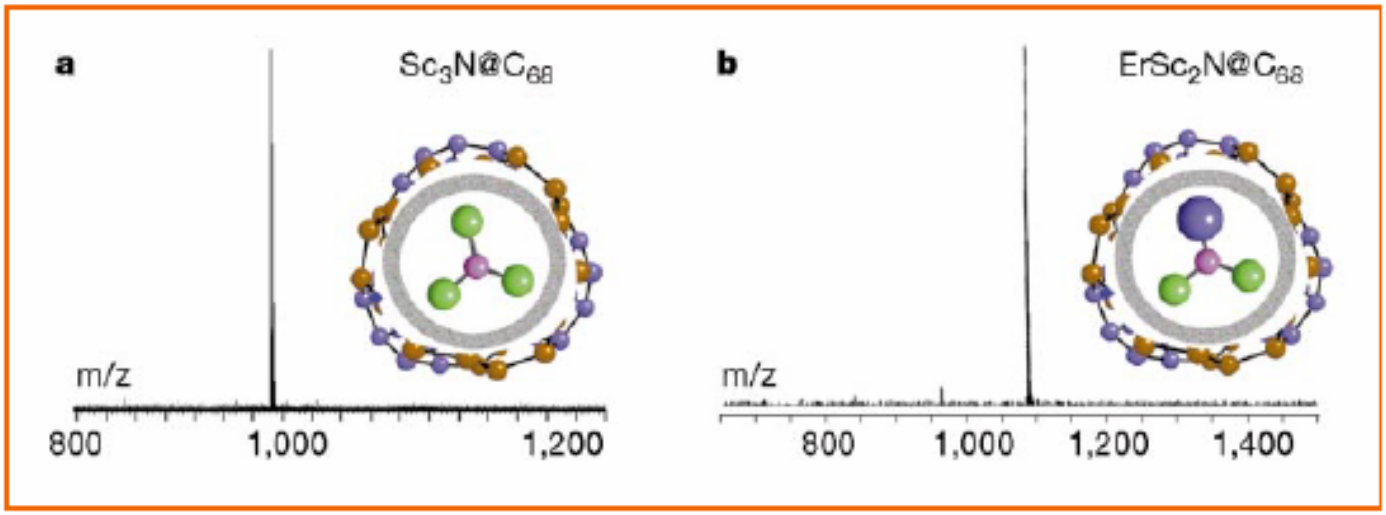
$Sc_3N@C_{68}$: The first fullerene with adjacent pentagons

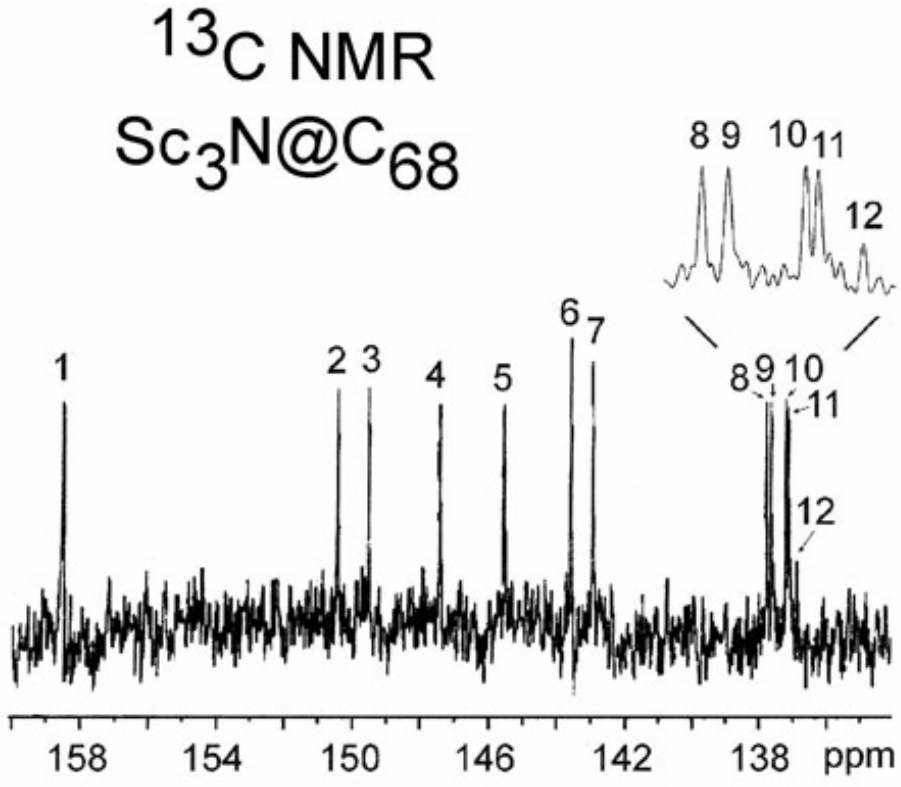
- mass spectrum: $Sc_3N@C_{68}$
- graph theory: C_{68} must have adjacent pentagons
- earlier calculations: adjacent pentagons energetically unfavoured
- assumption: stabilisation by endohedral Sc_3N molecule

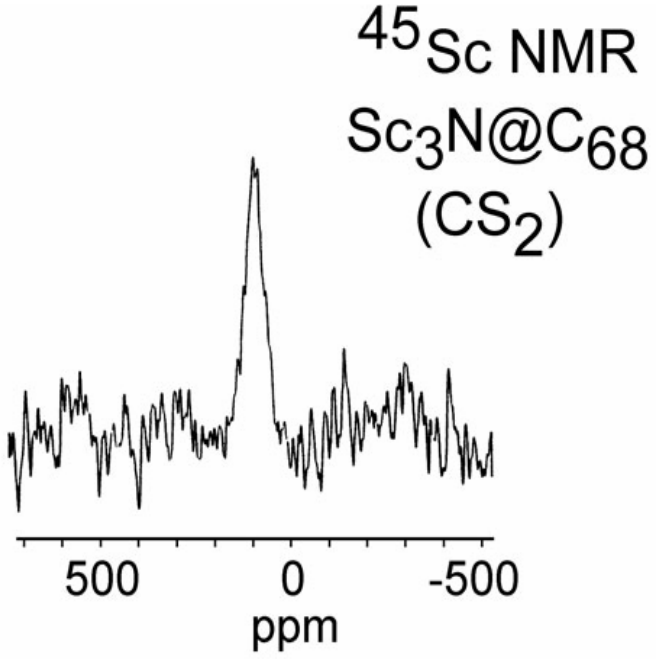


Nature 408 (2000) 427-428

Email: thomas.heine@chemie.tu-dresden.de

^{13}C and ^{45}Sc NMR gives information on symmetry





Nature 408 (2000) 427-428

Graph theory: 11 isomers (point groups D_3 and S_6) out of 6332 are compatible with one ^{45}Sc and 11+1 ^{13}C signals

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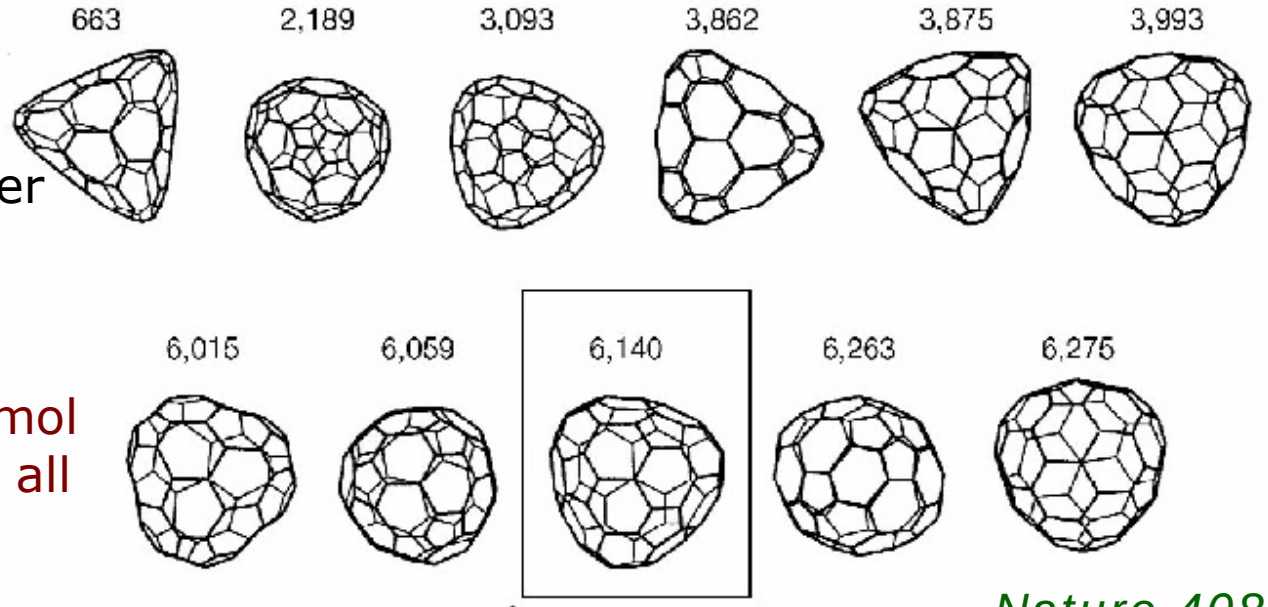
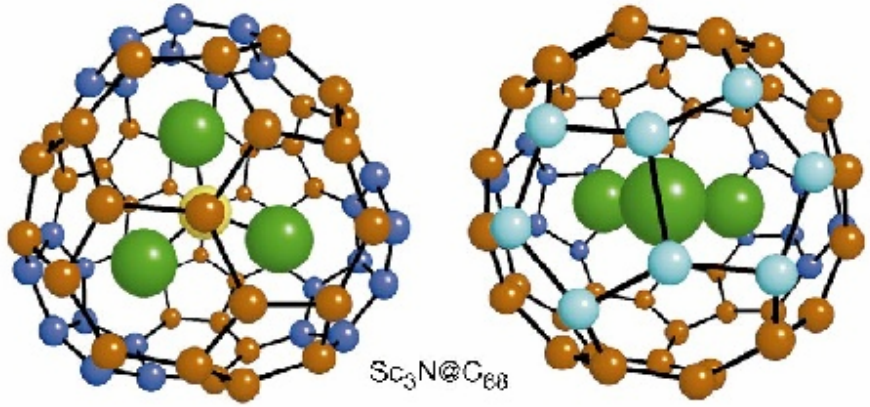
Which $Sc_3N@C_{68}$ isomer has been found?

- minimum number of pentagon adjacencies: 6140 and 6275.
- 6140 is 120 kJ/mol more stable than all other isomers.
- Added excess electrons (2, 4, 6) to simulate charge transfer increase the energy gap





Nature 408 (2000) 427-428

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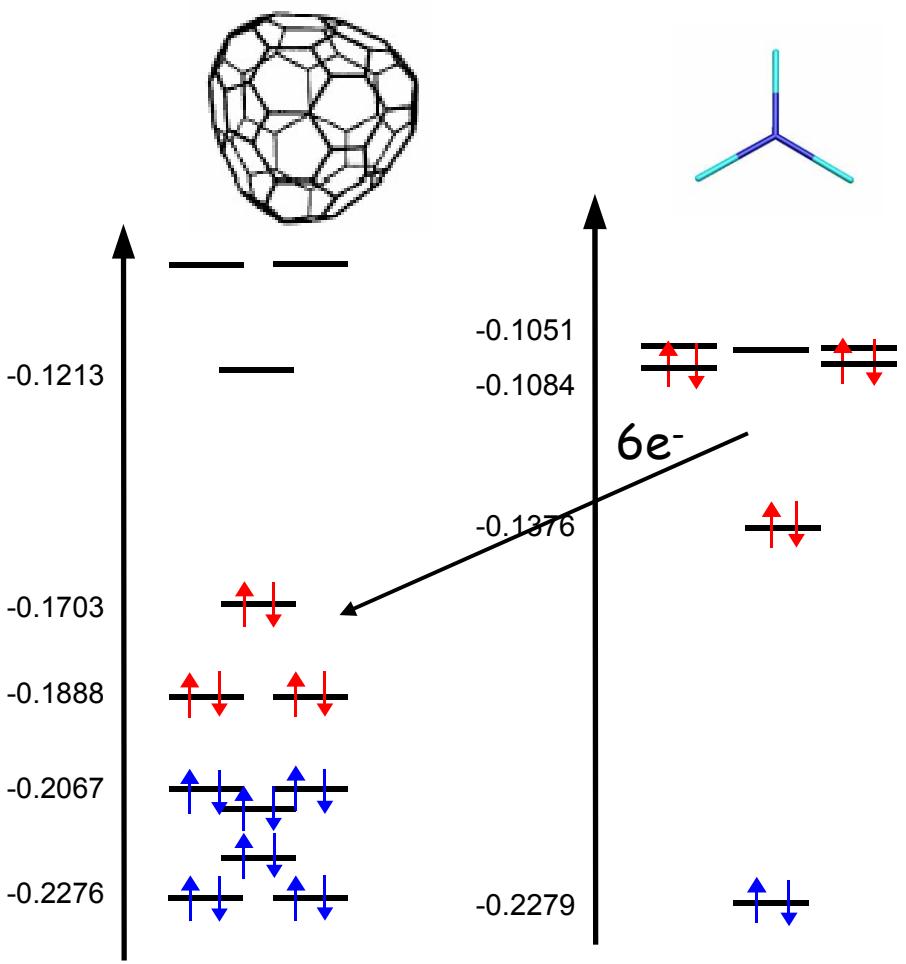
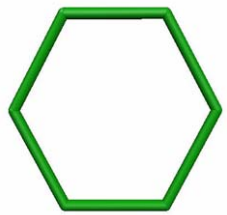
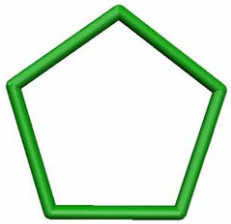
Simple explanation using Hückel and MO theory

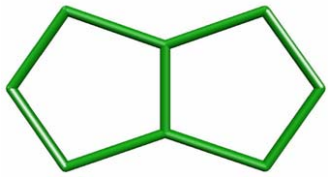




aromatic (4N+2 rule)



not aromatic (hole in π system)



antiaromatic (8 membered ring)

- $Sc_3N@C_{68}$: 3 adjacent pentagons connected to Sc
- ~2 electrons per adjacent pentagon →
- isoelectronic with 10 membered ring (aromatic)

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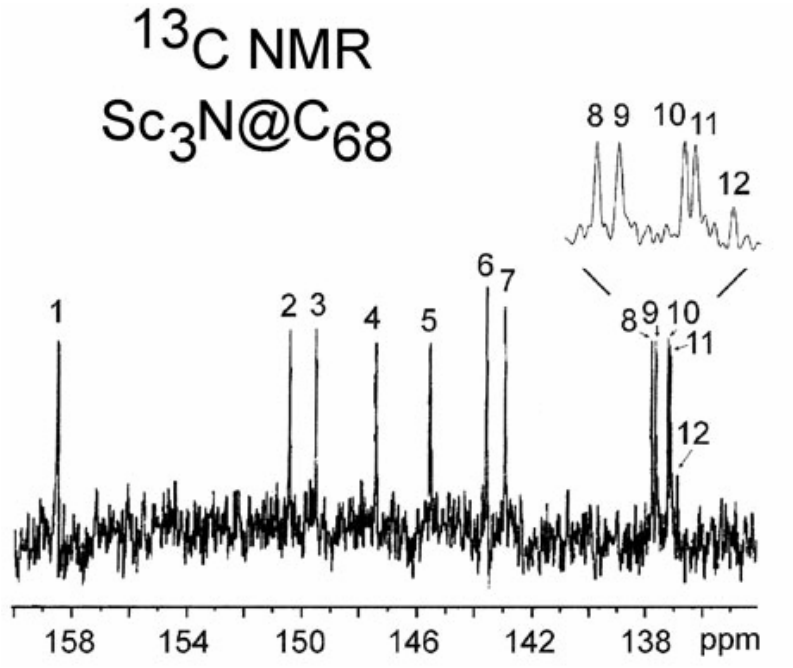
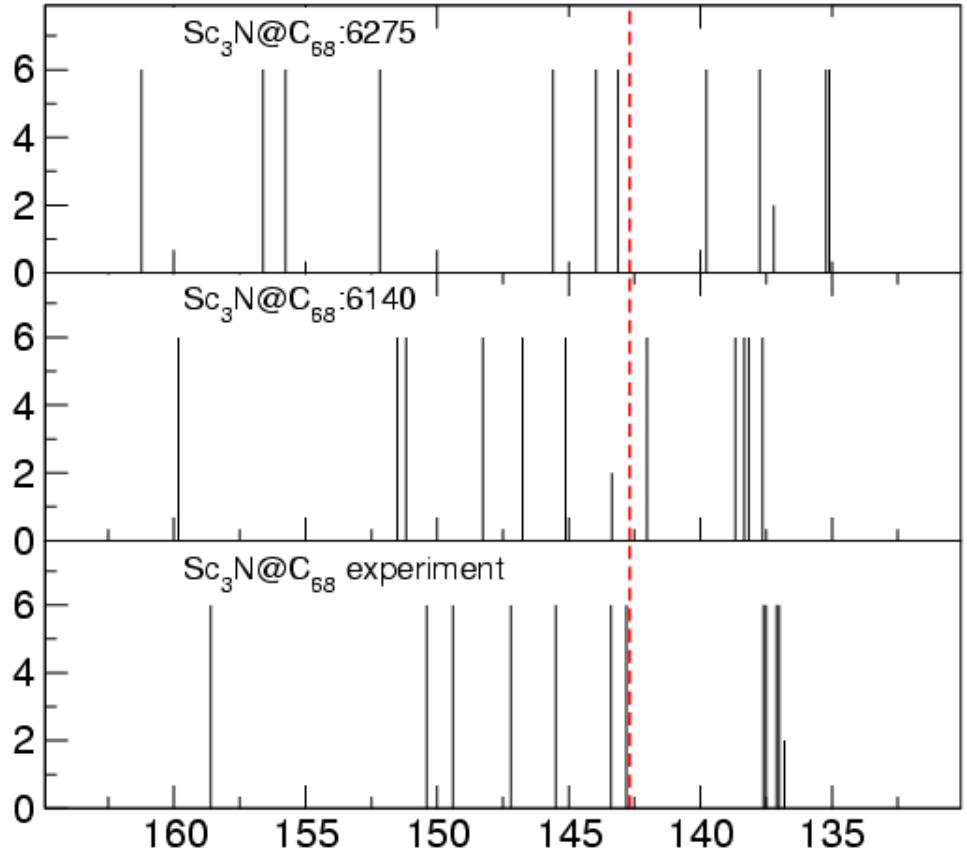
Confirmation by ^{13}C NMR fingerprint



Nature 408 (2000) 427-428



J. Phys. Chem. A 2005, 109, 7068-7072

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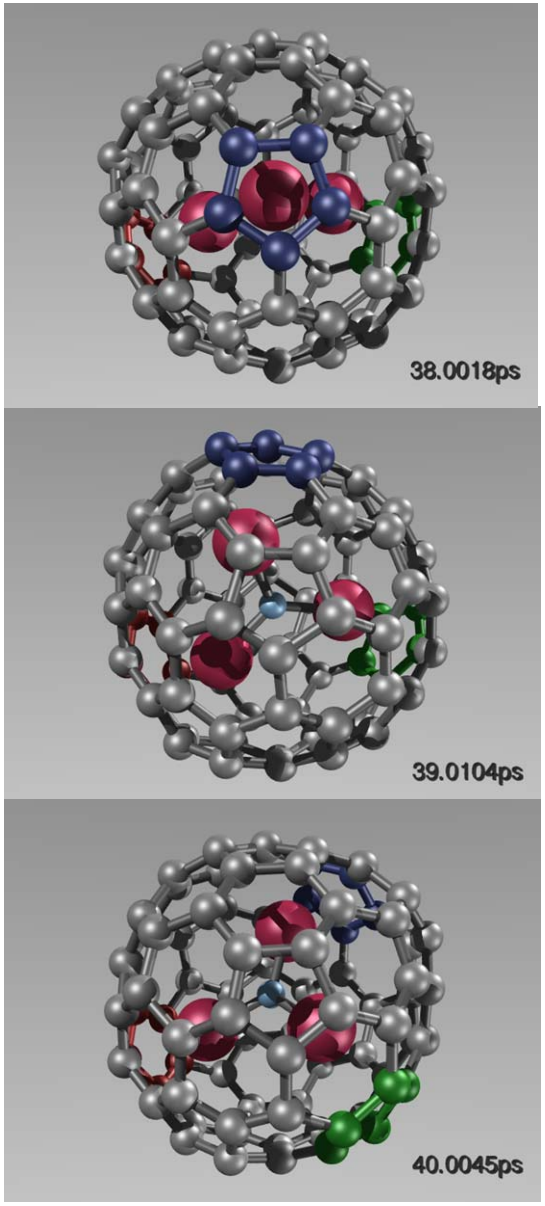
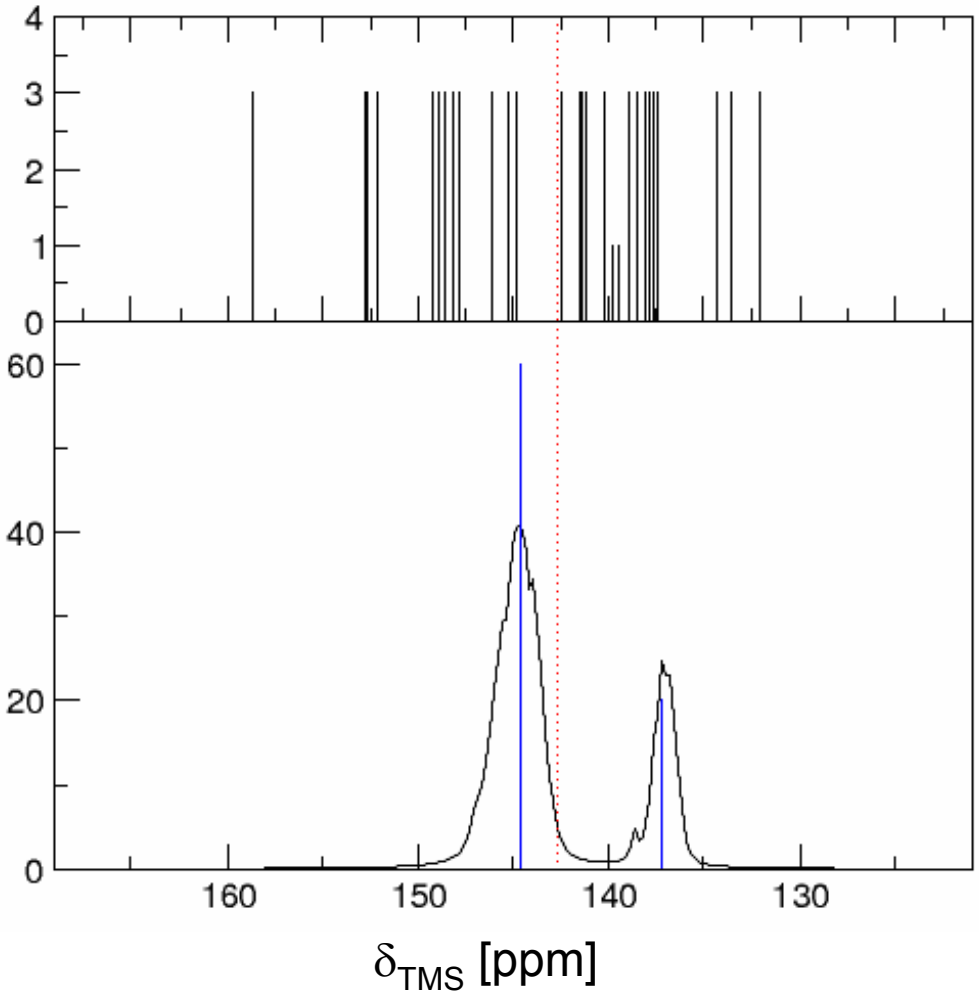
^{13}C NMR in $Sc_3N@C_{80}$





Magn. Res. Chem. 2004, 42,199

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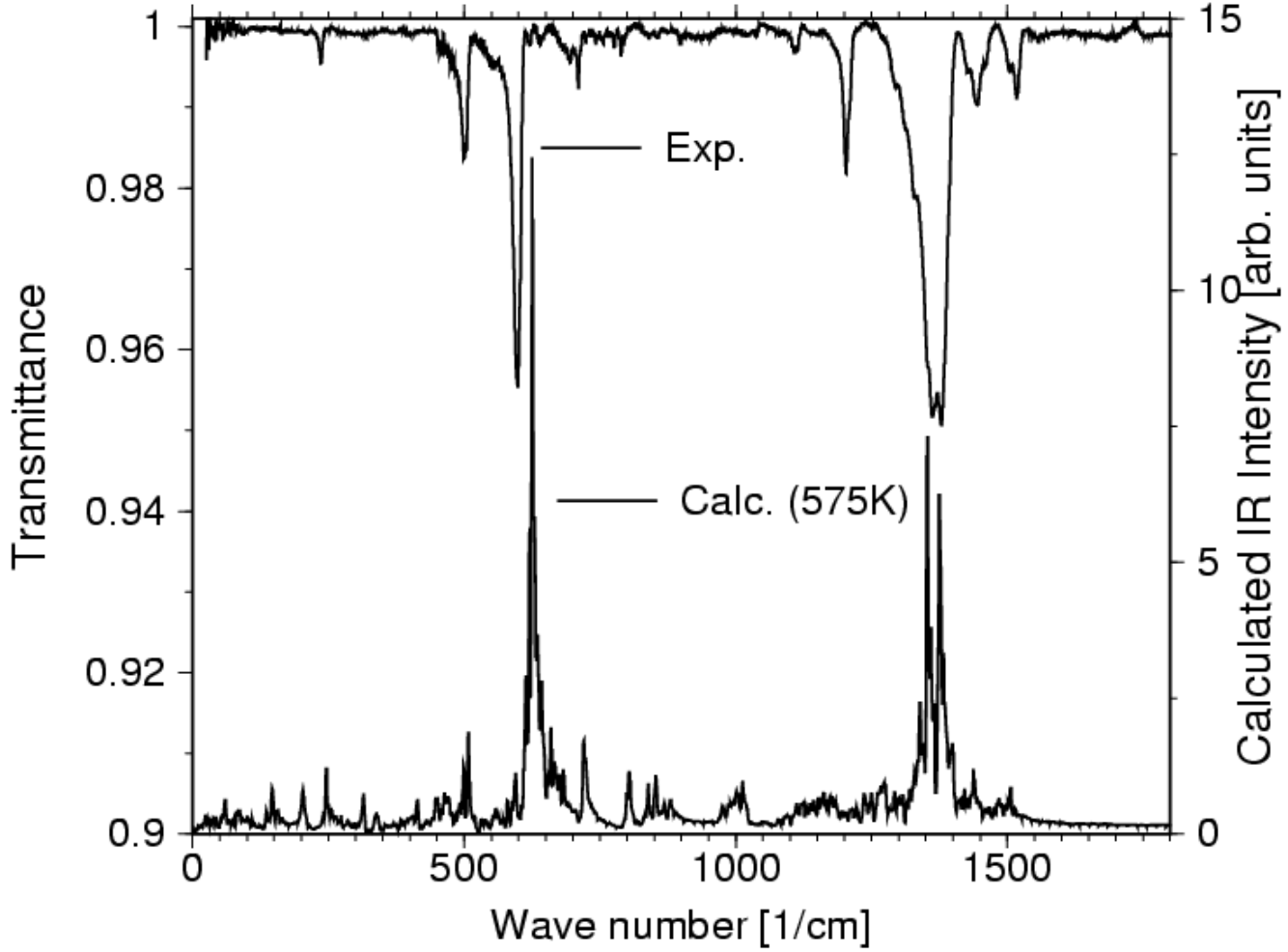
IR spectrum of $Sc_3N@C_{80}$



unpublished

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Mechanical and electromechanical properties of carbon and inorganic nanotubes

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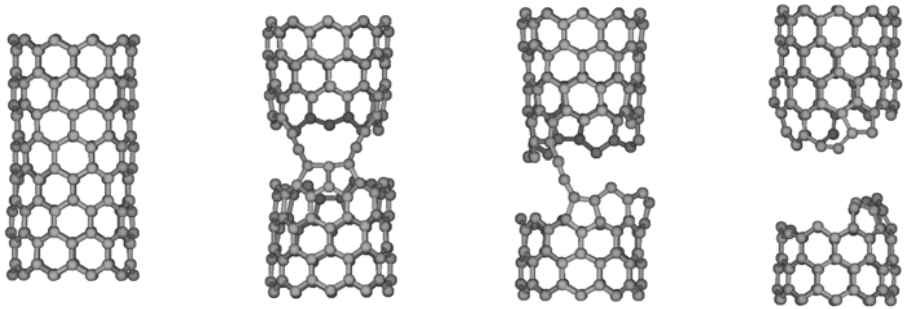
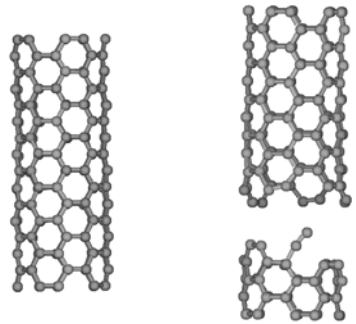
Electromechanical properties of single-walled carbon nanotubes

Rupture of CNTs at different temperatures: DFTB-based Born-Oppenheimer MD with successive iterations of pulling the tubes until rupture

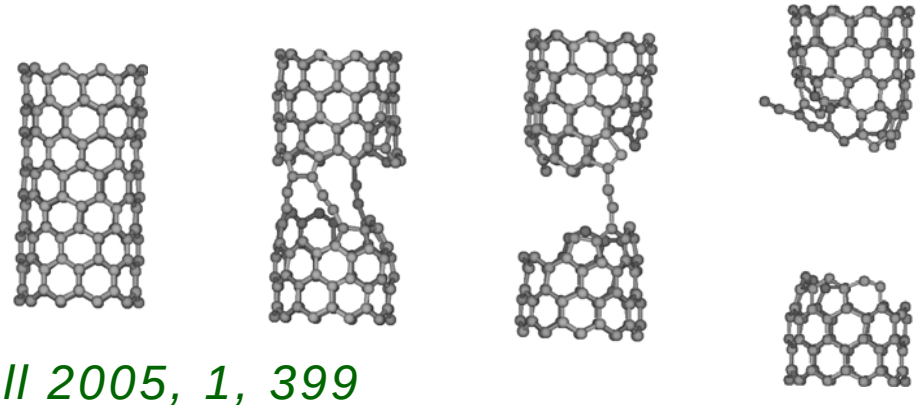
Zigzag 600K



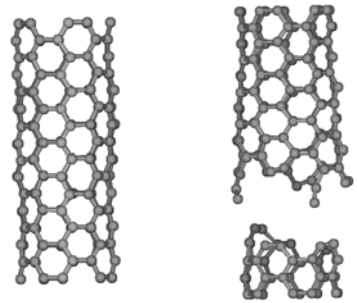
Armchair 600K



Zigzag 1000K



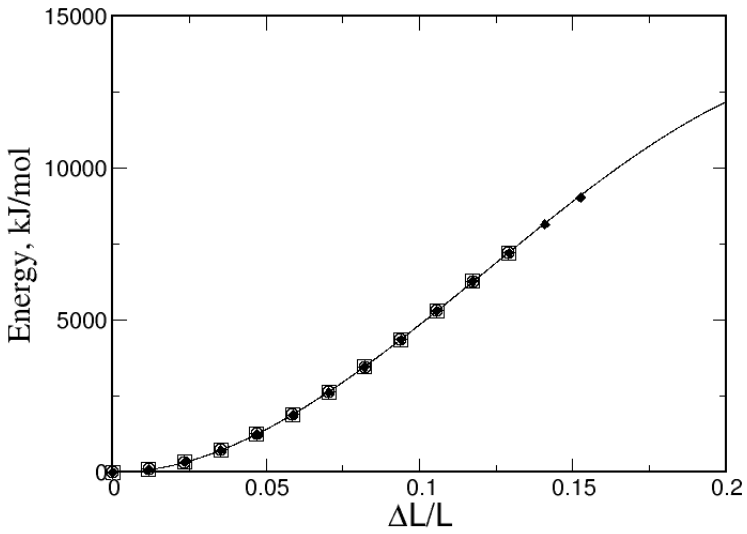
Armchair 1000K



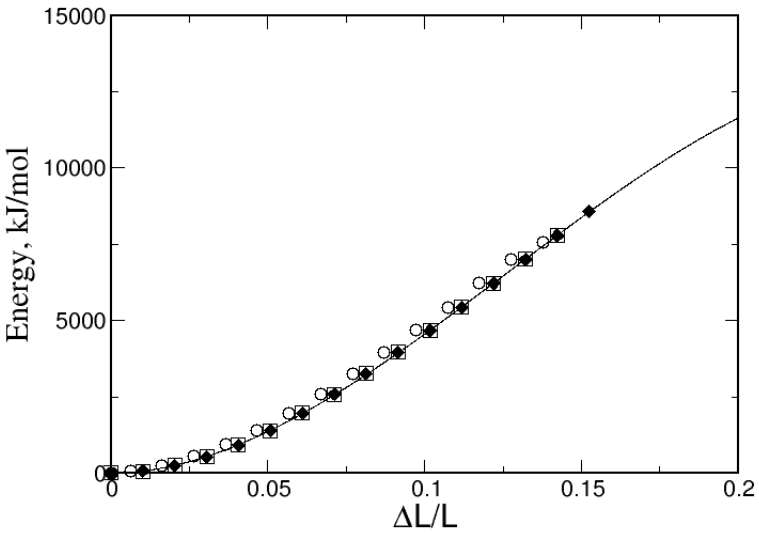
Small 2005, 1, 399

Email: thomas.heine@chemie.tu-dresden.de

Elastic properties of SWCNT's



zigzag



armchair

300K: full circles
600K: squares
1000K: empty circles

- Independent on temperature
- Rupture at $\Delta L/L \approx 0.15$
- Hooke-like behaviour up to $DL/L \approx 0.1$

Small 2005, 1, 399

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Mechanical properties of nanotubes

Thanks to Sibylle Gemming

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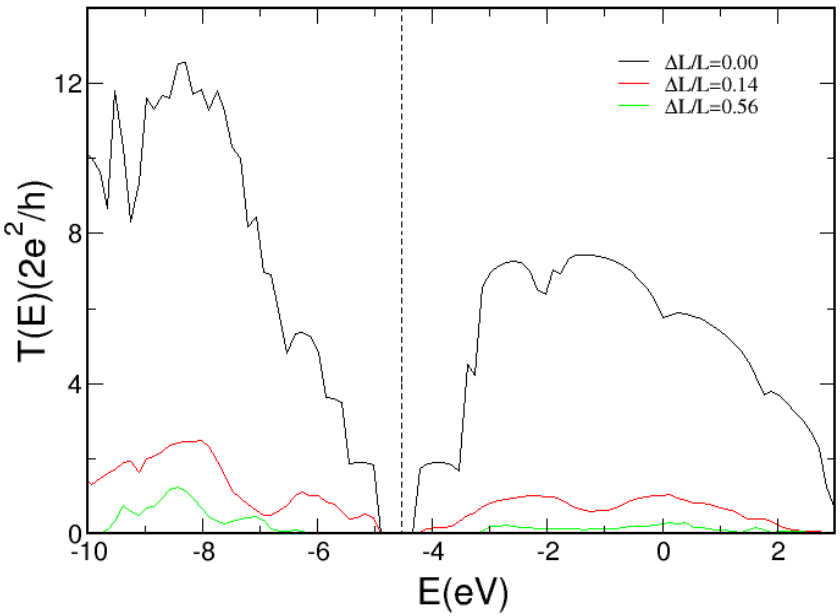
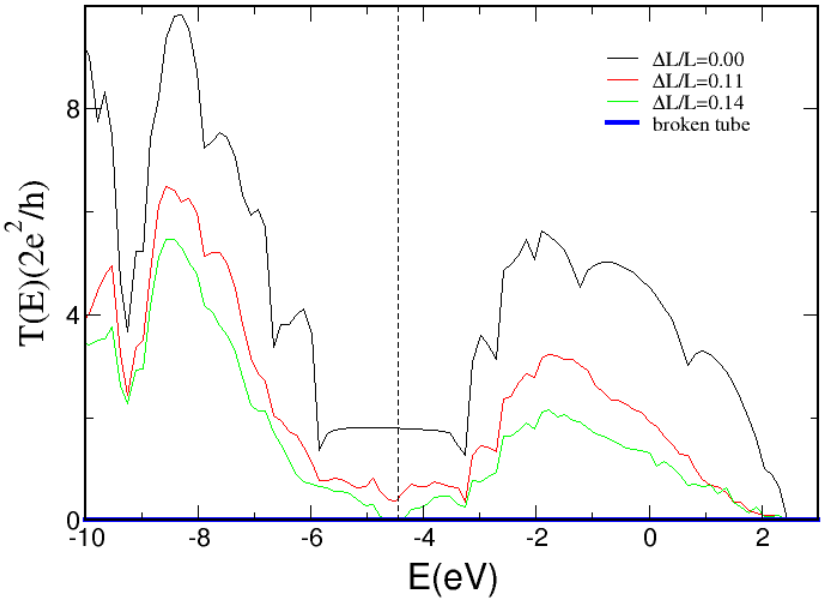
Electromechanical properties of CNTs



zigzag



armchair

Electronic transmission probability T(E) depends strongly on ΔL/L!

Small 2005, 1, 399

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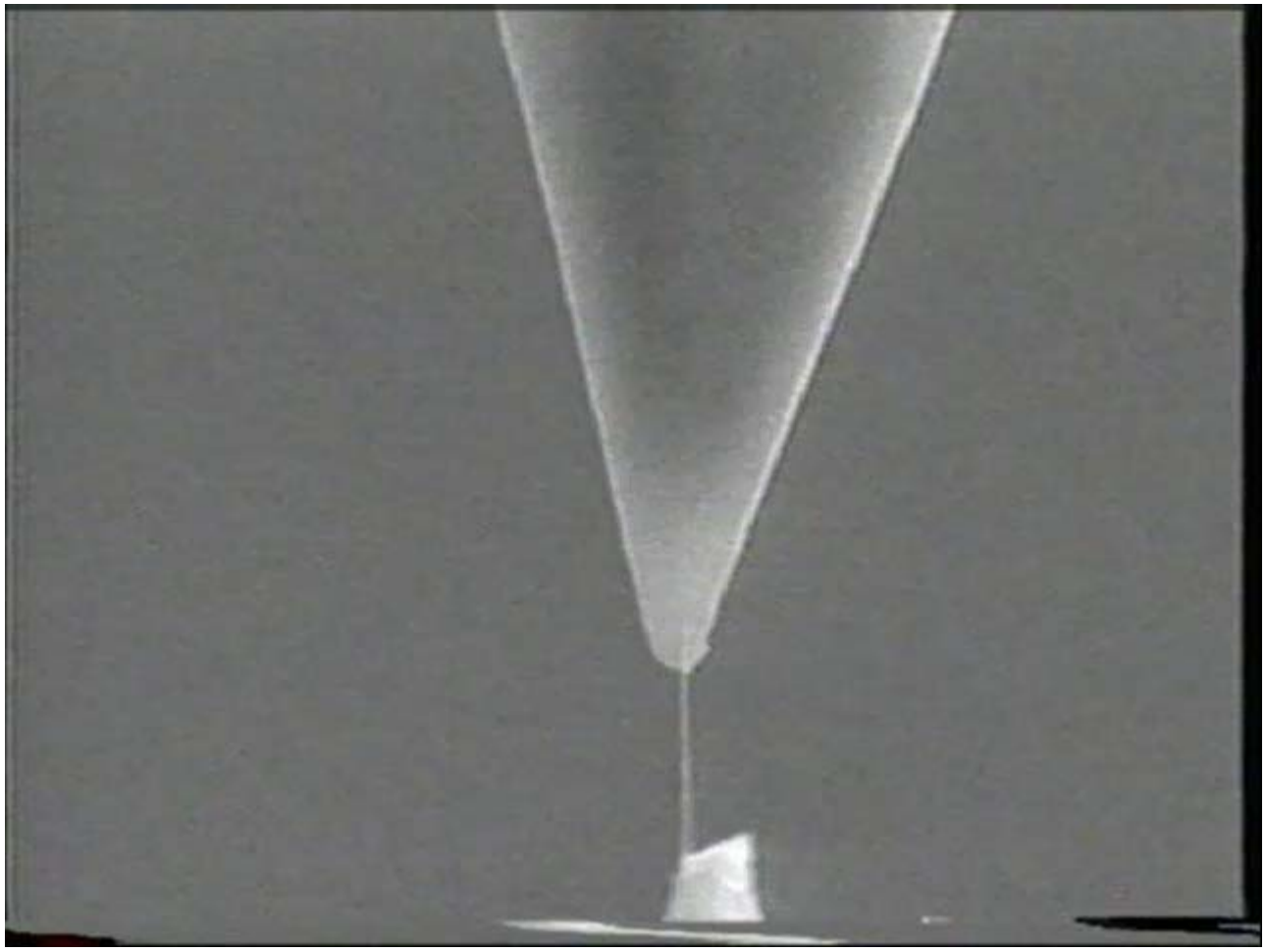
Axial tension of WS_2 and MoS_2 nanotubes

- In standard materials: mechanical properties are determined by defects (Griffith theory)
- Nanotubes: almost defect free → mechanical properties of almost ideal structure can be studied, and superior mechanical properties can be achieved
- Special structure of WS_2/MoS_2 particularly interesting regarding the axial tension

Email: thomas.heine@chemie.tu-dresden.de

Mechanical properties of MoS_2 nanotubes - experiment



Breaking a WS_2 nanotube with an AFM, in-situ SEM

Proc. Natl. Acad. Sci. USA 2006, 103, 523.

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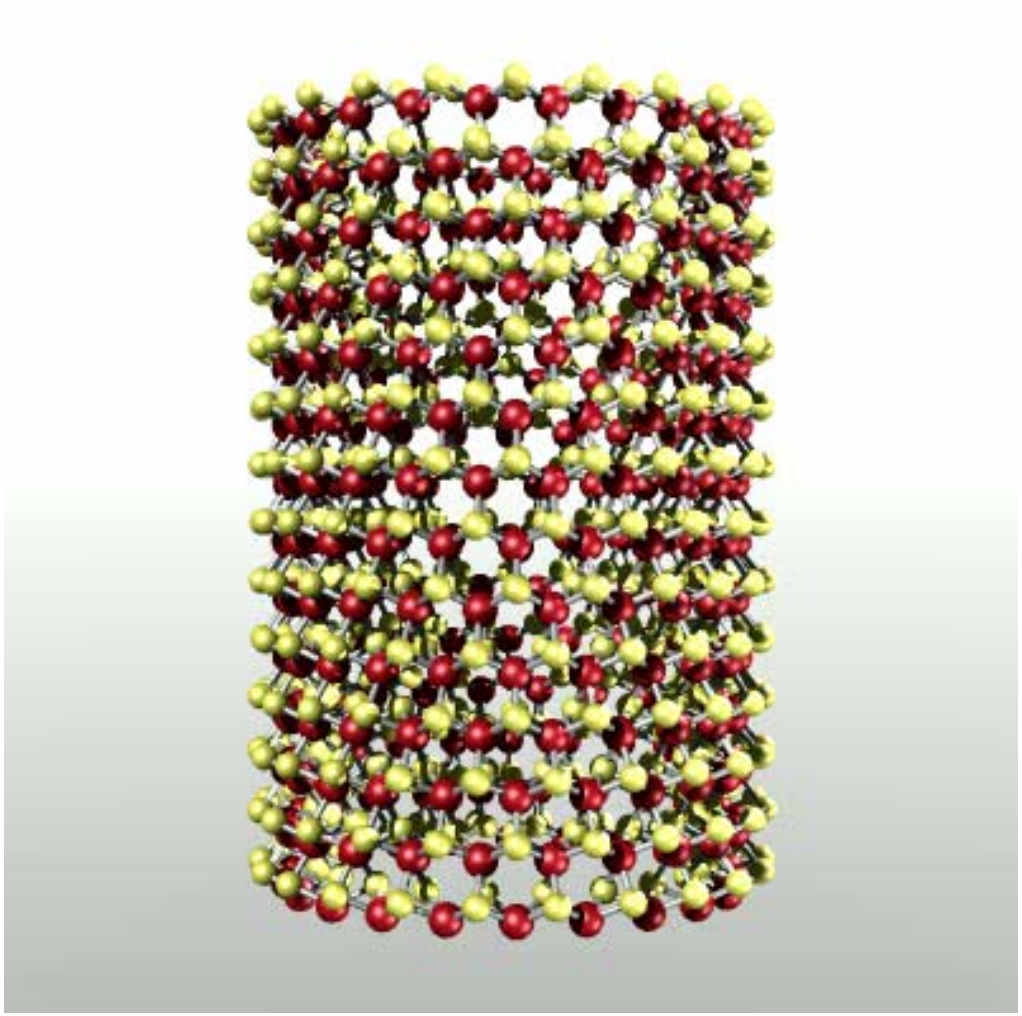
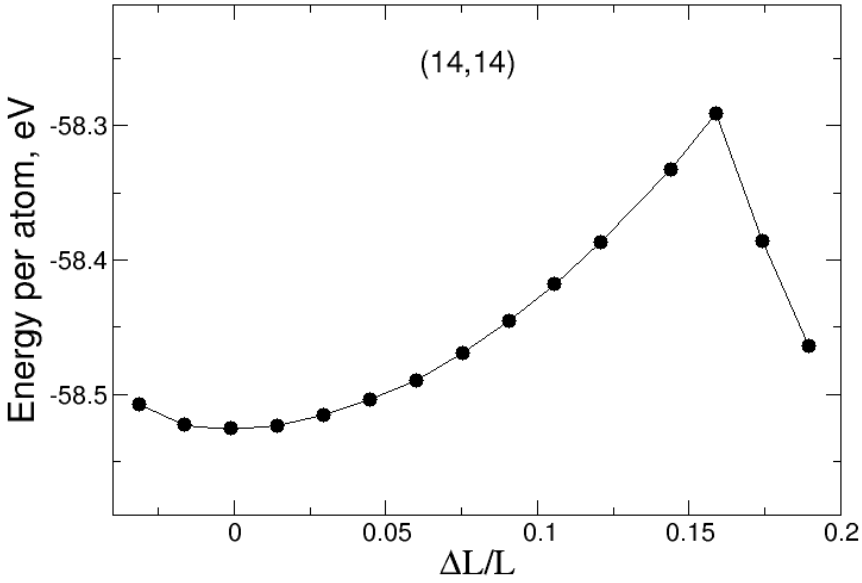
Mechanical properties of MoS_2 nanotubes - simulation



Breaking a MoS_2 nanotube with an AFM

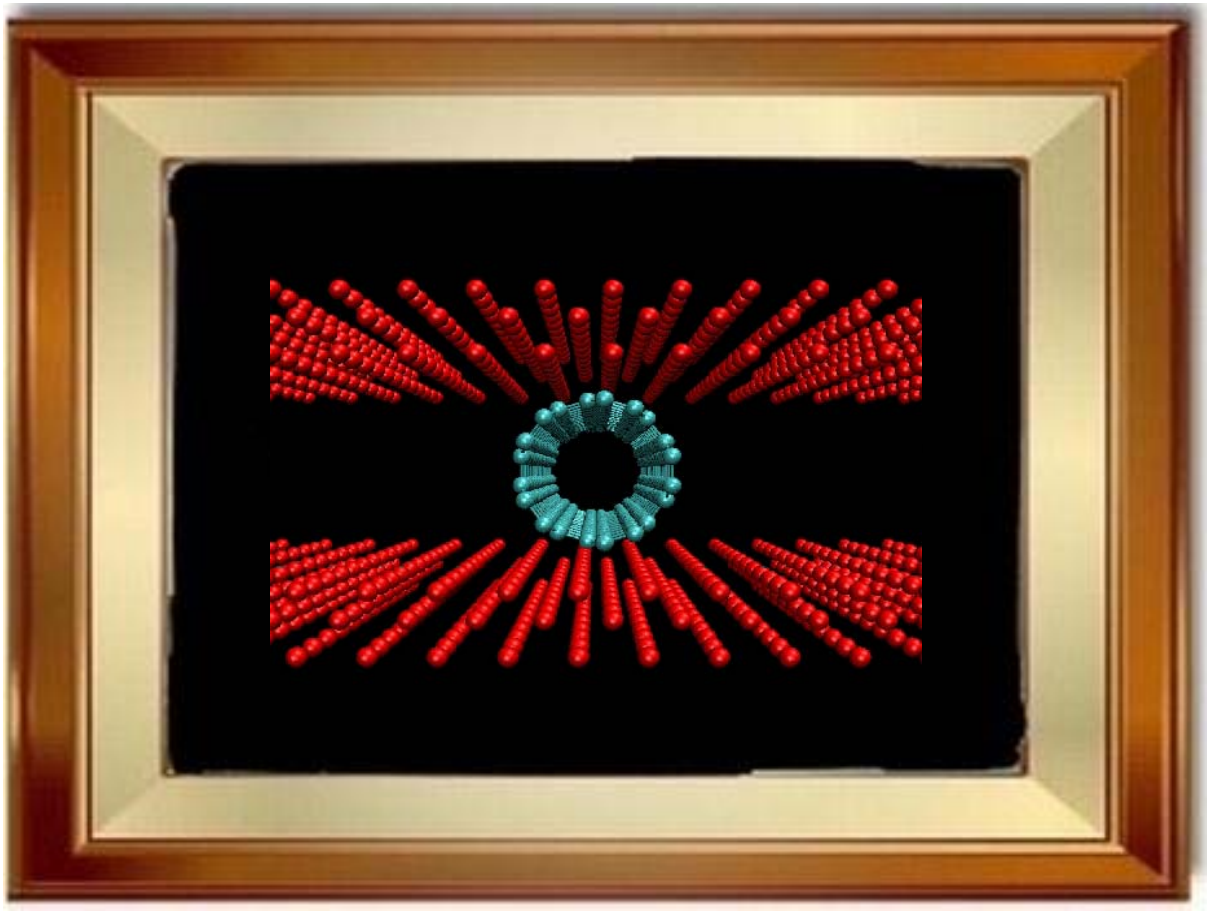


Almost harmonic behaviour until rupture!

Proc. Natl. Acad. Sci. USA 2006, 103, 523.

Email: thomas.heine@chemie.tu-dresden.de

Squeezing nanotubes



Molybdenum grips, MM, fixed positions, van-der-Waals forces to the NT

Nanotubes/Fullerenes: DFTB (QM)

Periodic boundary conditions

Milen St. Stefanov Dobrev, Andrey Enyashin, G. Seifert, T. Heine, to be published

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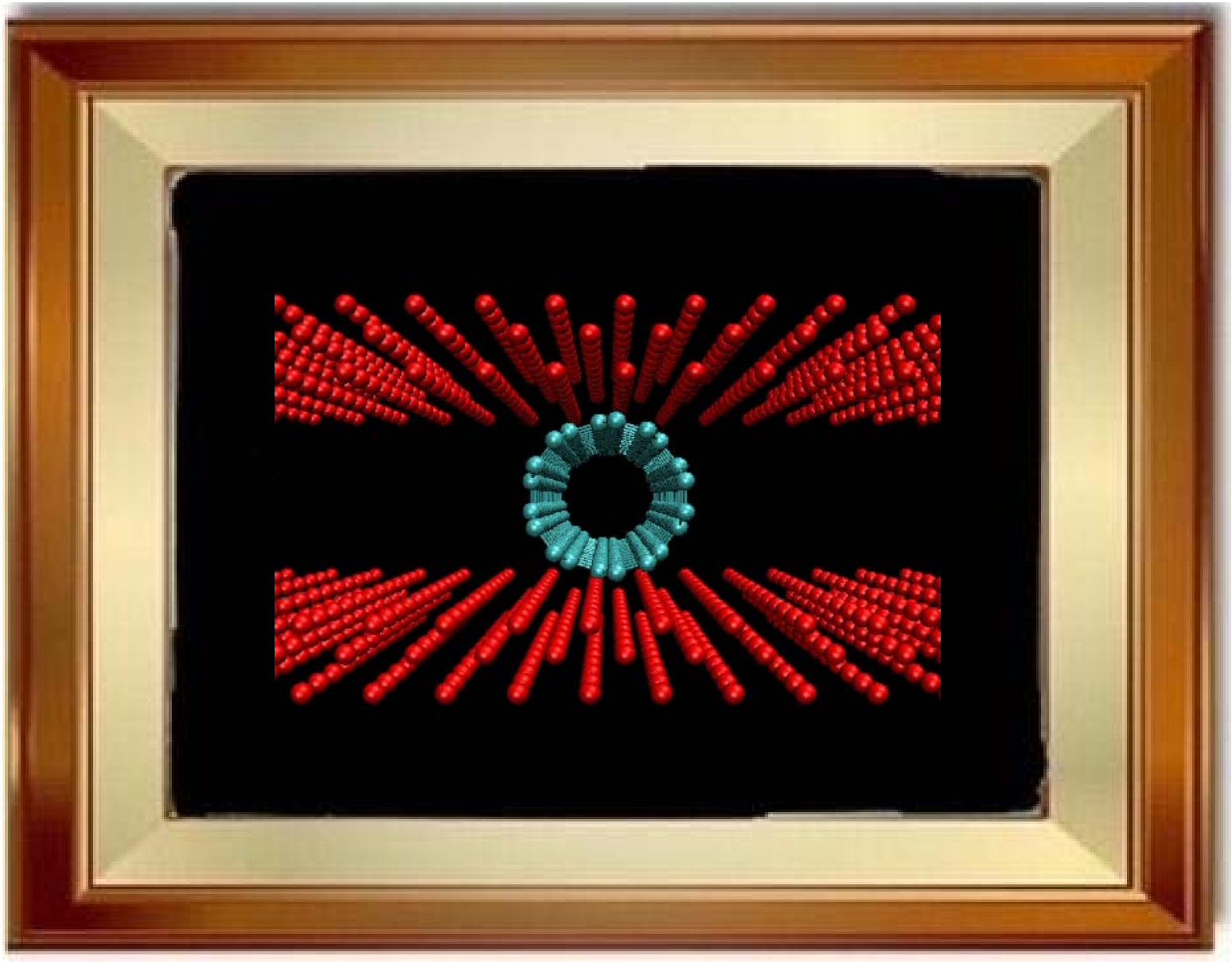
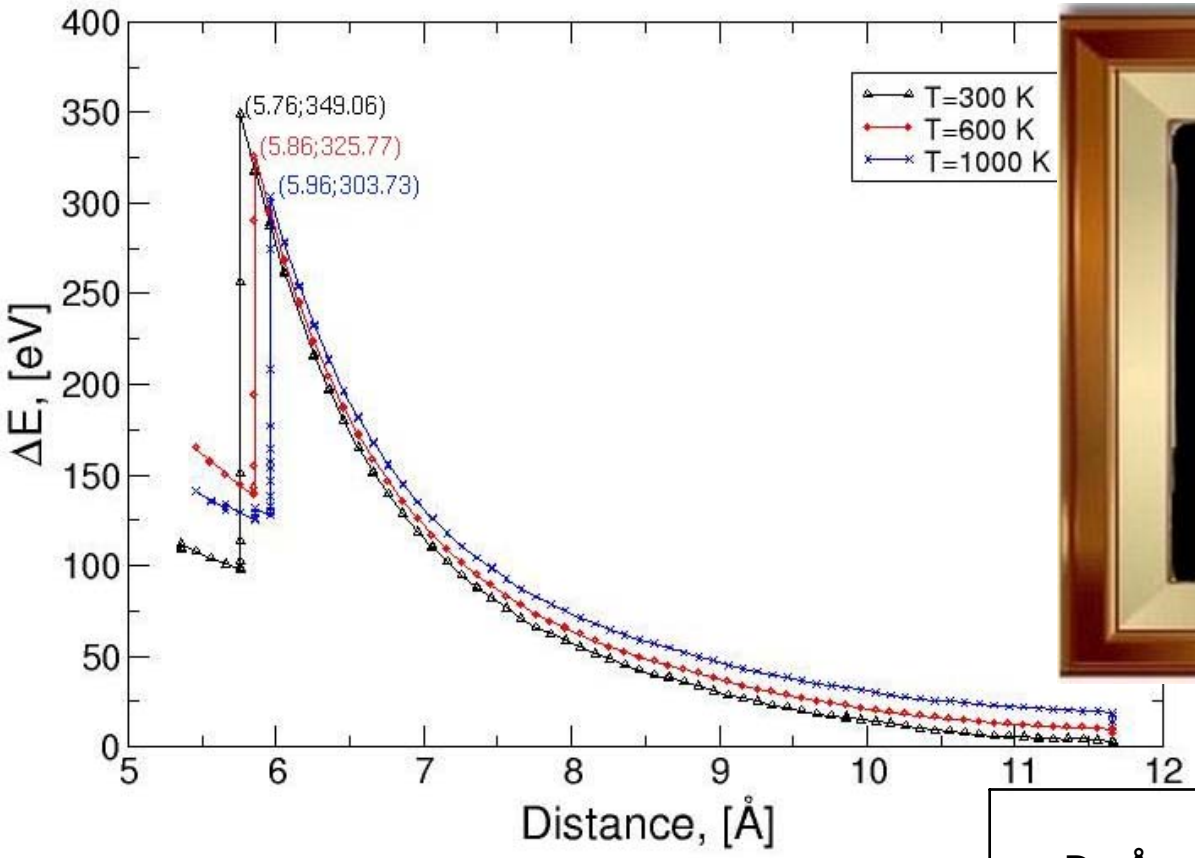
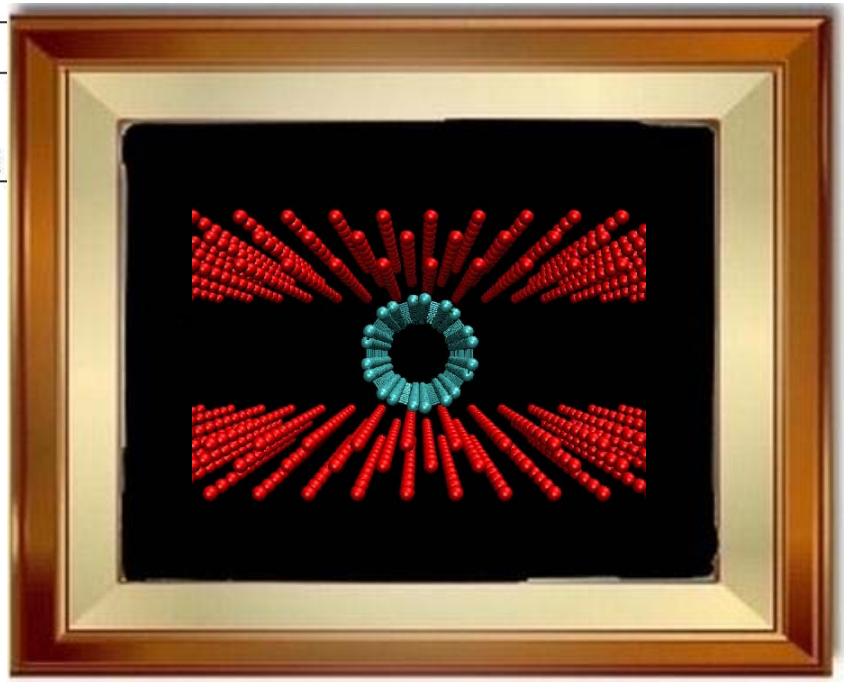
Squeezing Carbon Nanotubes



Elastic properties side-squeezed Nanotubes





(5,5) CNT

	D_c, Å	p_c, GPa	k, eV/Å^2 (x10^{-3})
300K	5.76	47.62	2.89
600K	5.86	46.38	3.23
1000K	5.96	38.61	3.47

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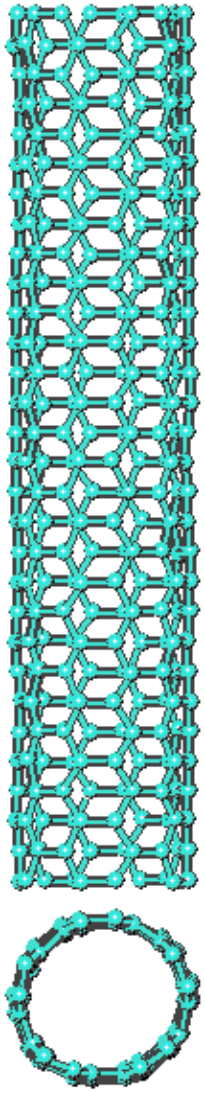
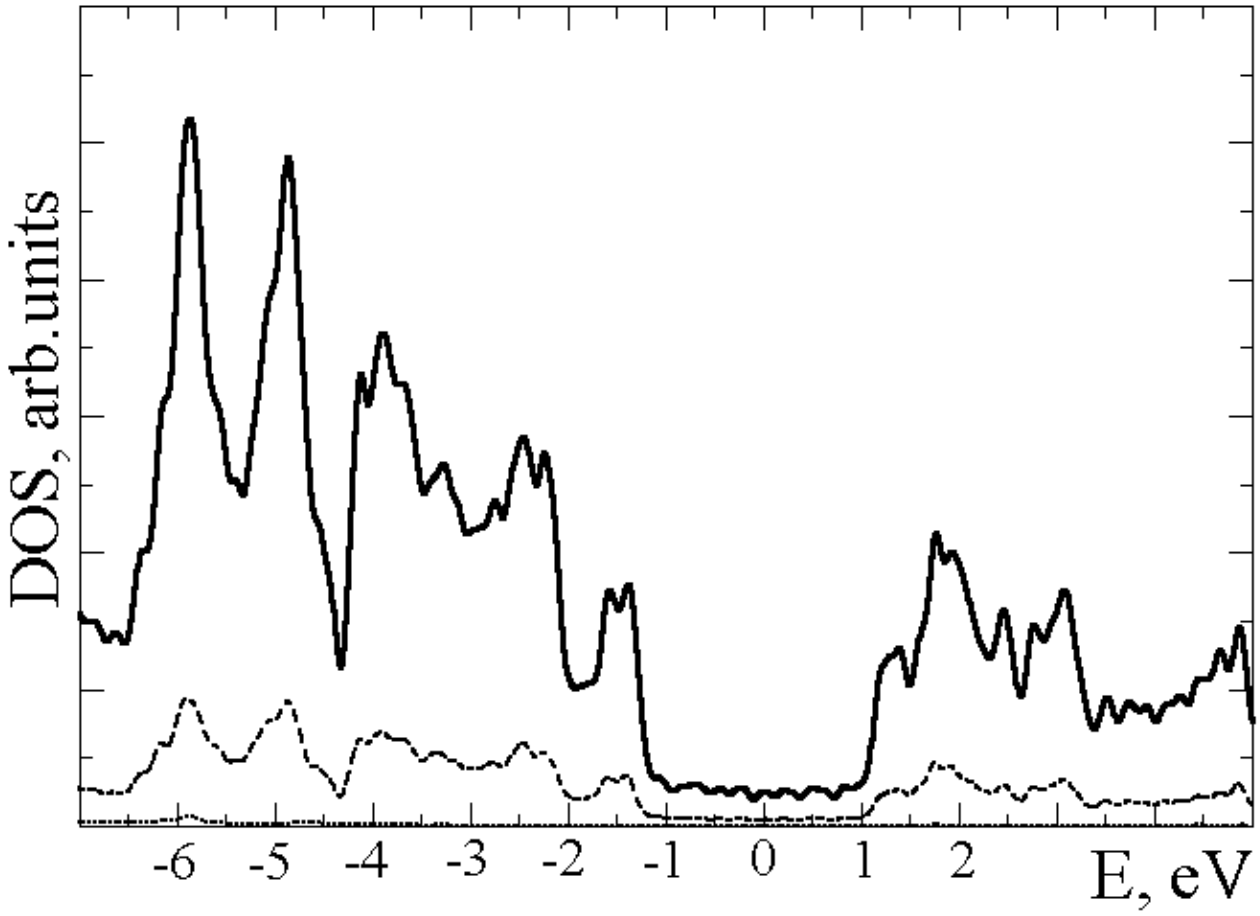
Influence on electronic properties of (5,5) CNT





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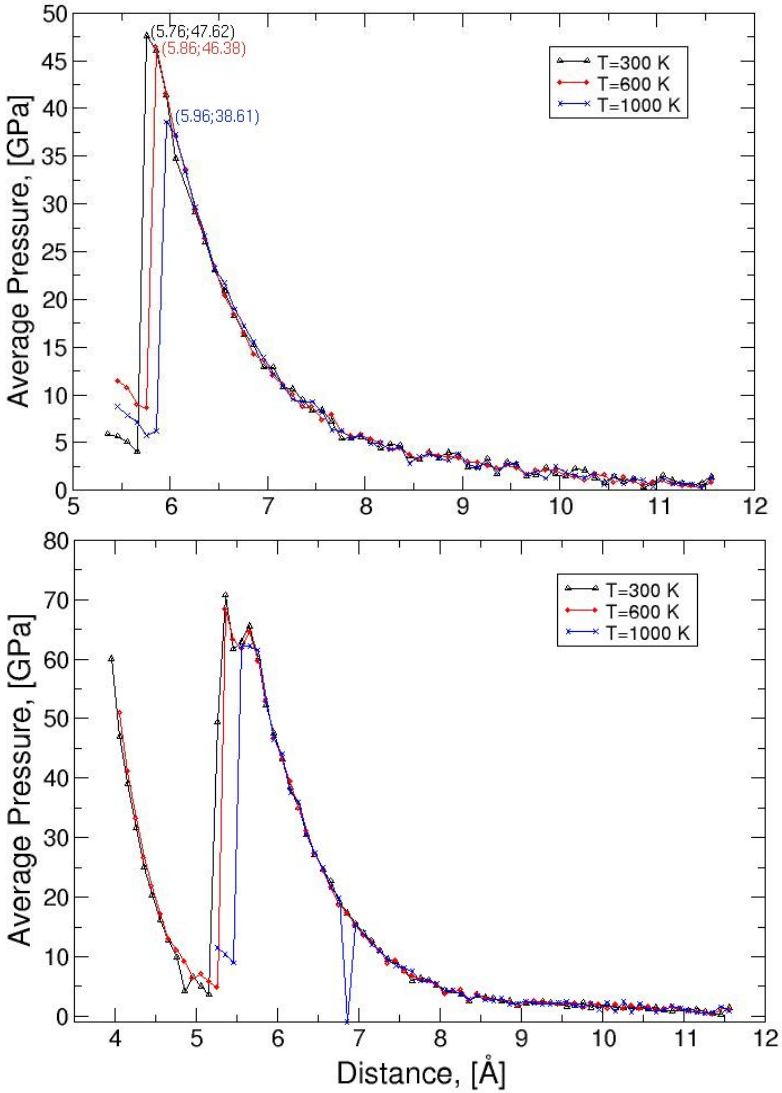
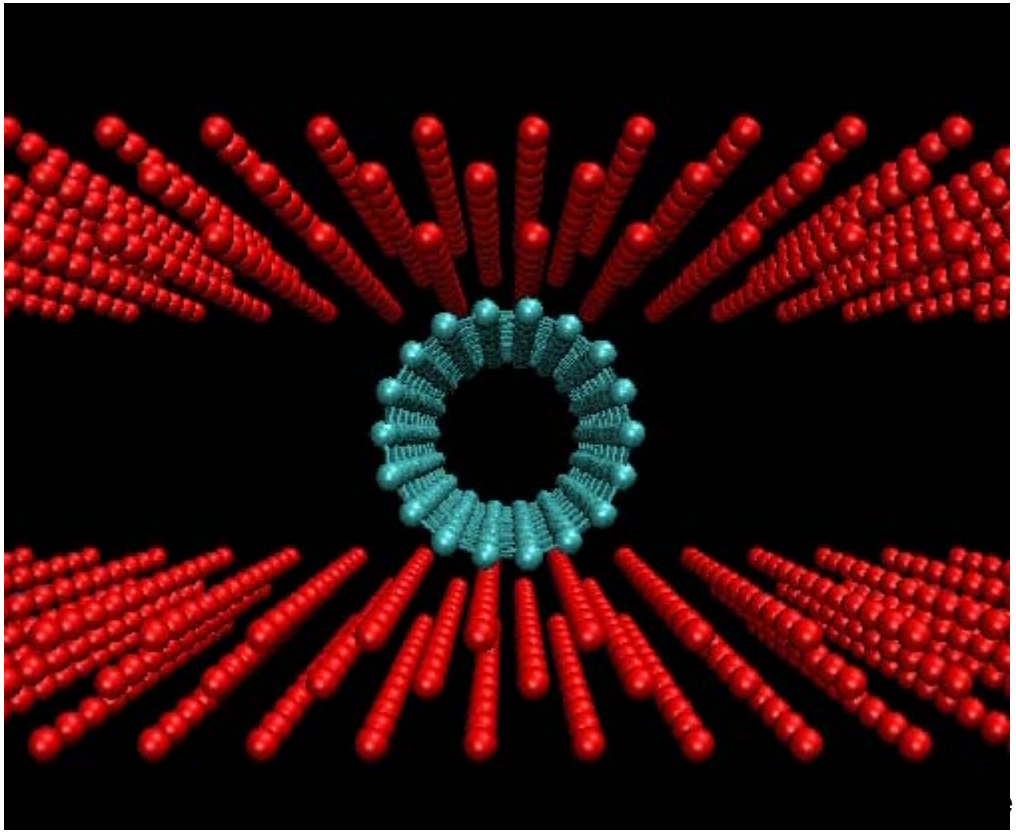
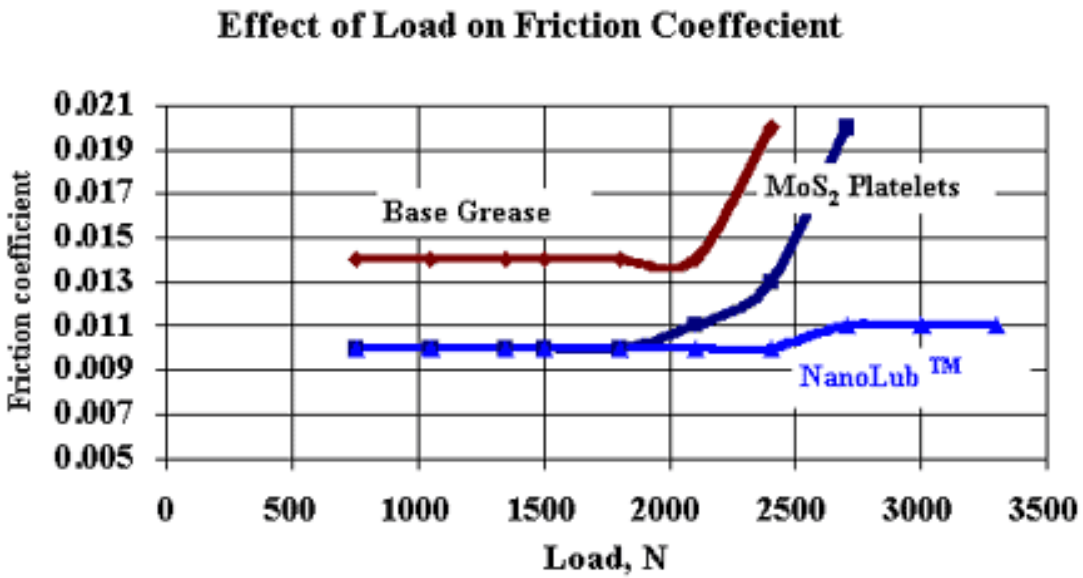
The (9,0) CNT is more stable than the (5,5) CNT

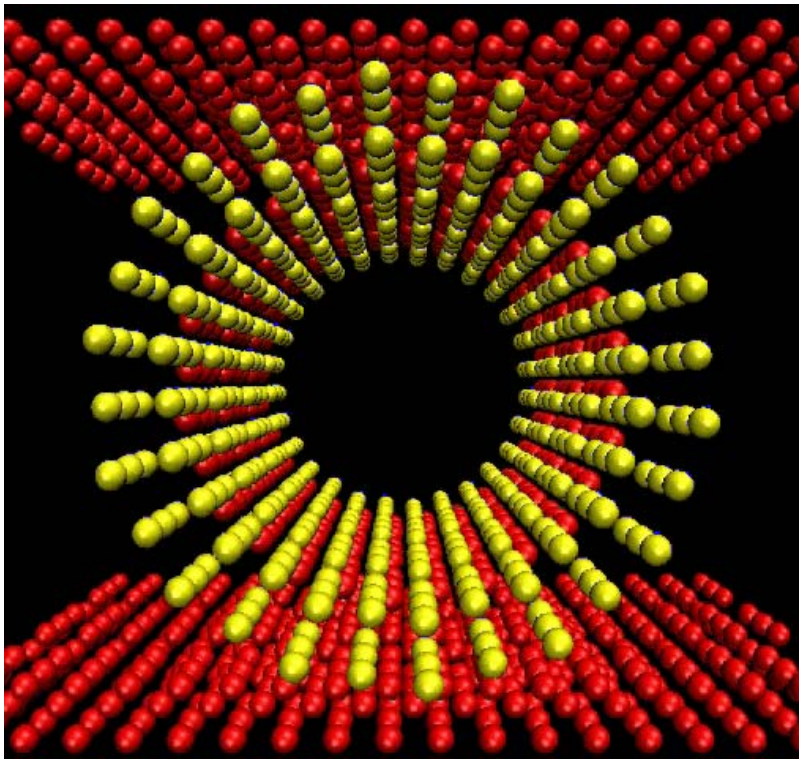


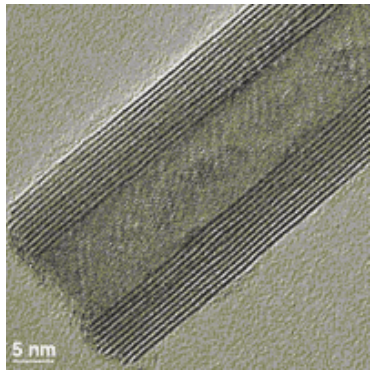
	D_c, Å 9,0 (5,5)	p_c, Gpa 9,0 (5,5)	k, eV/Å^2 (x10^{-3}) 9,0 (5,5)
300K	5.36 (5.76)	70.71 (47.62)	2.22 (2.89)
600K	5.36 (5.86)	68.28 (46.38)	2.05 (3.23)
1000K	5.56 (5.96)	62.15(38.61)	2.11 (3.47)

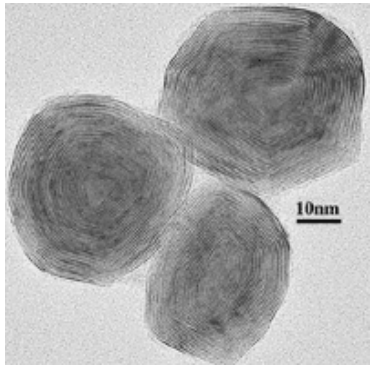


Applications of inorganic nanotubes – New insights









NanoMaterials

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Hydrogen storage by physisorption in aromatic carbon nanostructures

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Energy sources for mobile applications

One possible design of the car of the future

HydroGen3 liquid

- Fuel: 4.6 kg LH_2
- Range (EDC): 400 km

HydroGen3 compressed 700

- Fuel: 3.1 kg CH_2 at 700 bar (10,000 psi)
- Range (EDC): 270 km

Technology: H_2 tank → fuel cells → electric engines

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Problem: Storage of H_2

1 liter n-Octan : 36.2 MJ
1 liter Hydrogen (NPT) : 10.7 kJ

this is three order of magnitude lower than required for practical use !

European Driving Cycle EDC – Hydrogen Consumption
1.15 kg Hydrogen for 100 km (for that particular car)

1.15 kg Hydrogen

- **17 l H_2 (liquid -253 °C)**
- **29 l H_2 (gase 700 bar)**
- **Alternatives?**

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London dispersion

- No overlapping densities
- Interaction of two polarisable objects

$$E_{London} = -\frac{2}{3}\frac{I_1 I_2}{I_1 + I_2}\alpha_1\alpha_2\frac{1}{r^6}$$

London, F.; Z. Physik 1930, 63, 245.

Well-known application: Lennard-Jones potential:

$$E_{Lennard-Jones} = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$$

short-range repulsion long-range attraction

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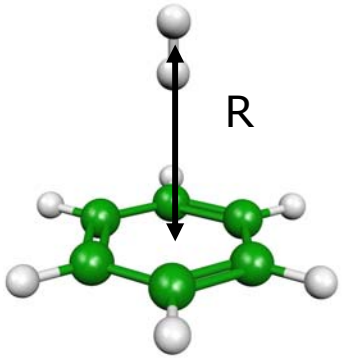
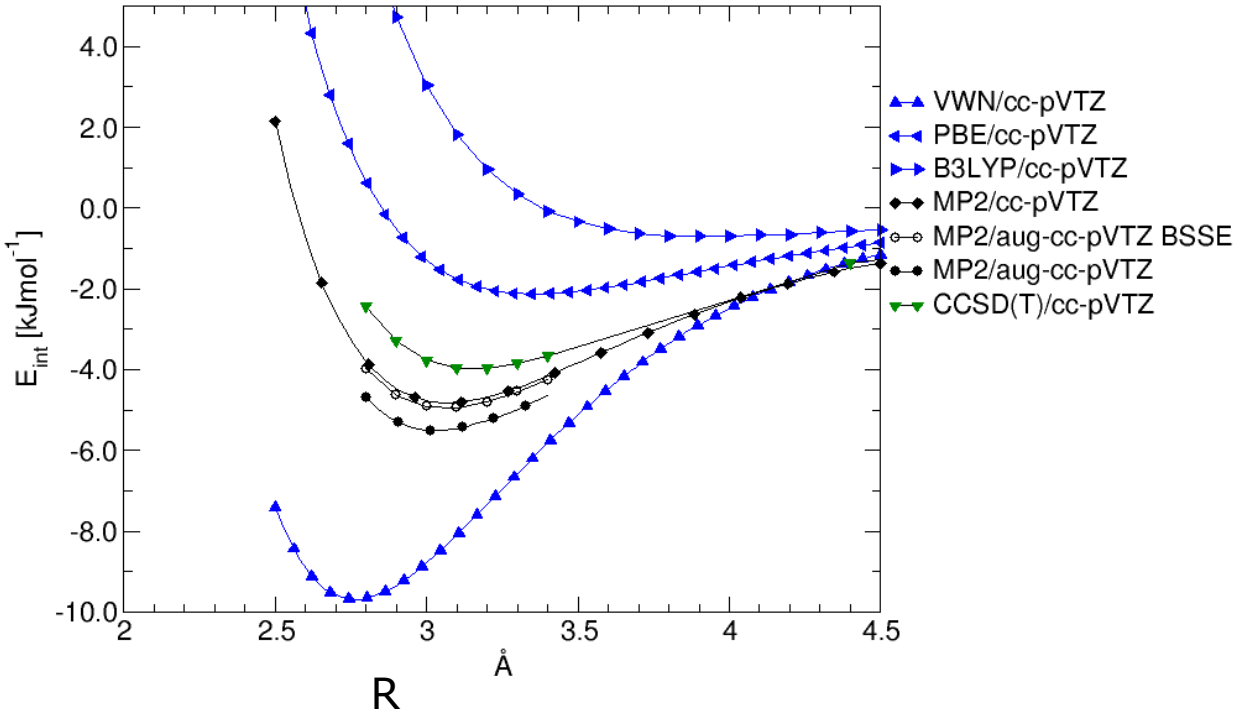
Weak interactions and DFT?

(Available) Density-Functional theory for London dispersion interaction





DFT is not appropriate for long-range dispersion

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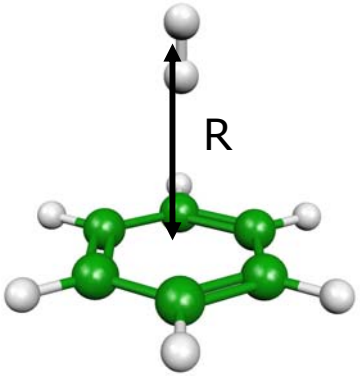
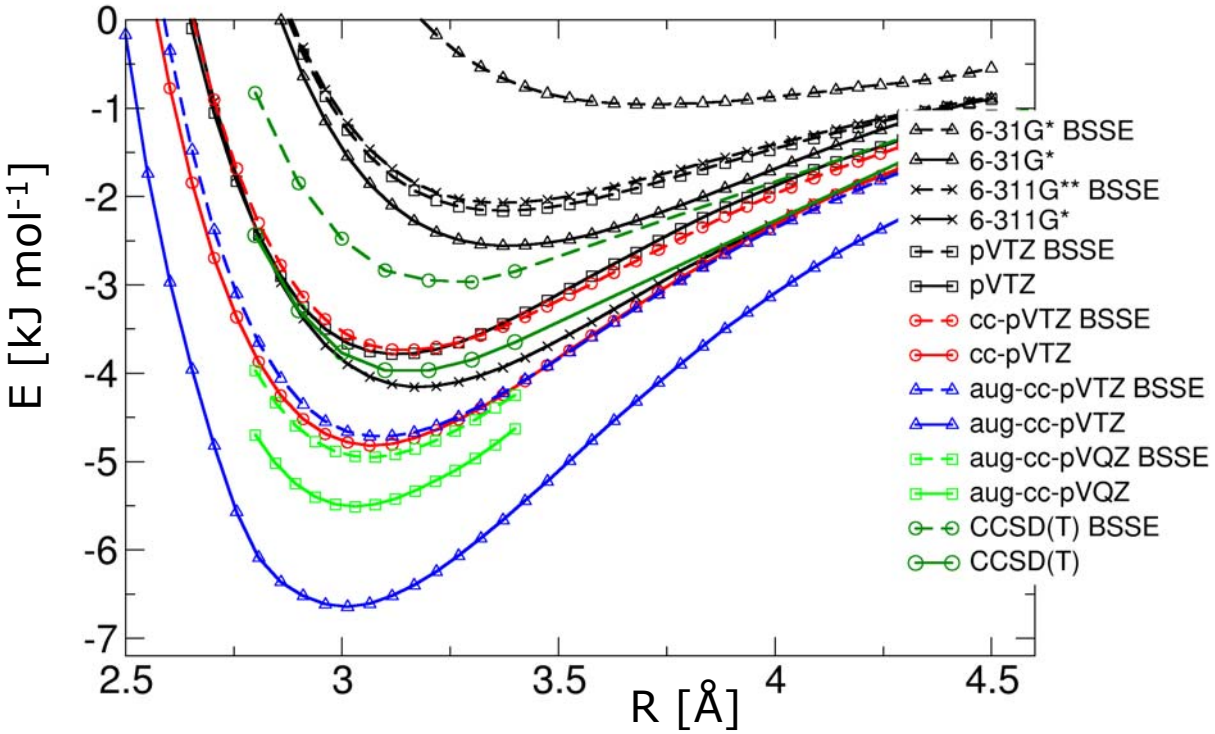
Weak interactions and ab initio theory?

Dispersion is a correlation phenomenon and extremely basis-set dependent. Ab initio theory (MP2, CCSD(T)) can account for it, but at a price we don't want to pay





Phys. Chem. Chem. Phys. 6 (2004) 980

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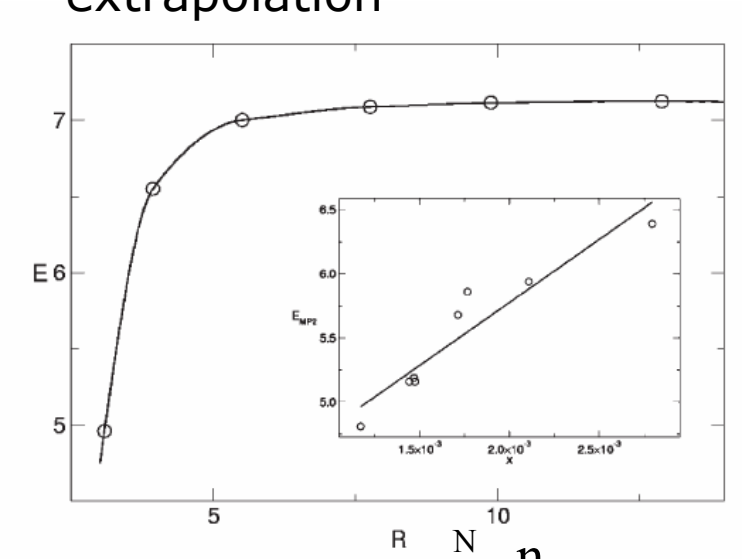
Alternatives

DFT gives wrong results
Decent ab inito is prohibitely expensive

Find a reasonable model for the application

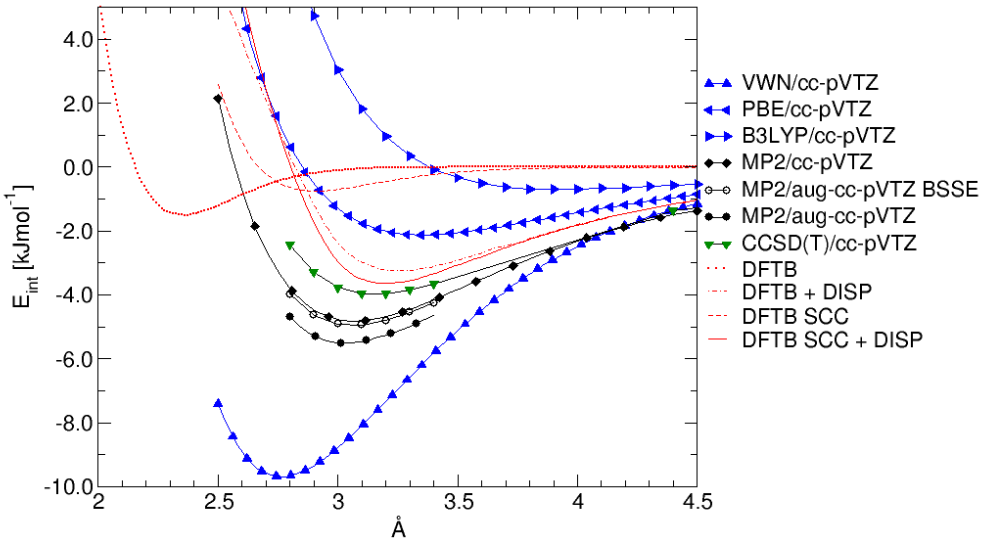
H_2-graphene interaction by extrapolation



$$E = E_{over} + C_6 \sum_{i=1}^{N} \frac{n_i}{R_i^6}$$

Use a pragmatic method

Add a C_6 term to a method which excludes dispersion as approximate DFT (DFTB)



JCTC 1, 2005, 841

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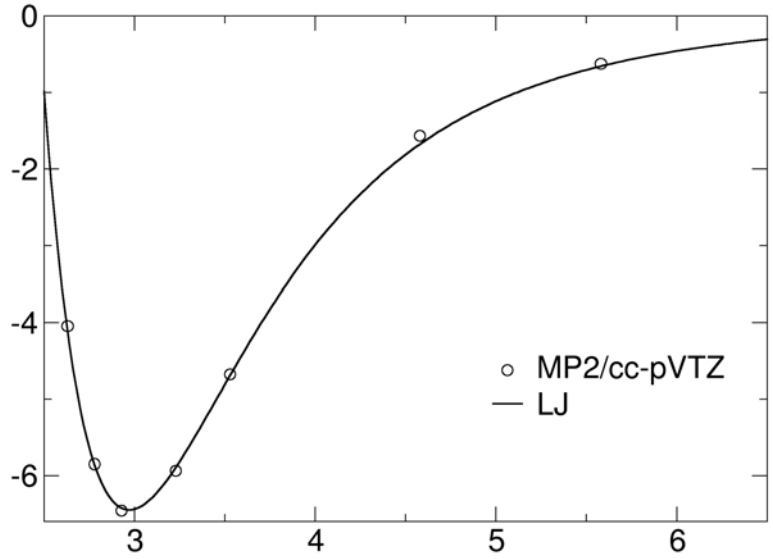
Create H_2-carbon interaction potential

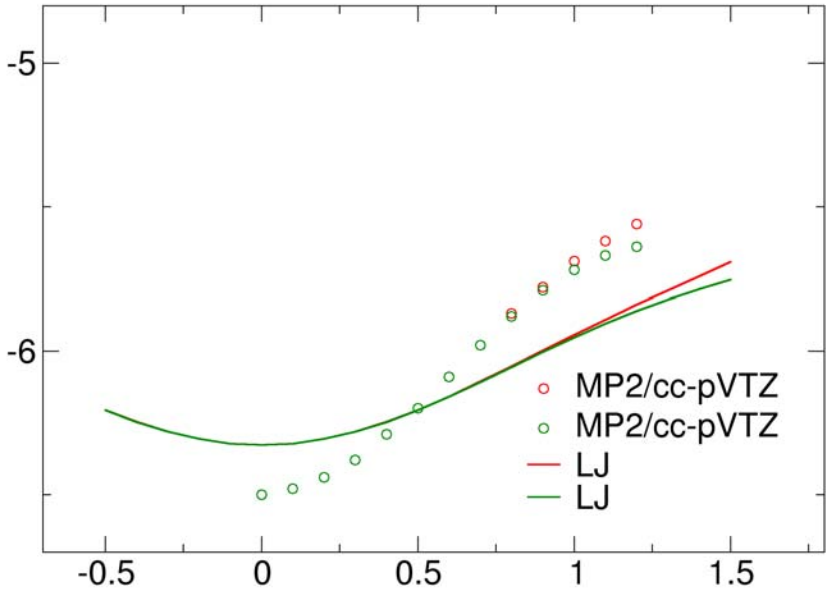
Fitting ab initio results to empirical potential

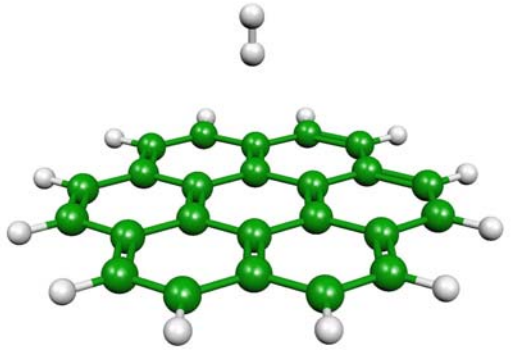
$$V(r) = \sum_i A e^{-\alpha r_i} + C_6 r_i^{-6}$$

$$r_i = \left| \vec{r} - \vec{R}_i \right|$$



Movement of H_2 normal to PAH →





← lateral movement

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Computation of free energy

- *Quantum-mechanical treatment for computation of free energy* as
  - H_2 is light-weighted → zero point vibrations are large
  - H_2-host potential is very soft → motion even at 0K
  - H_2-host potential is strongly anharmonic → popular approximations fail
- *Computational strategy:*
  - solve stationary Schrödinger equation of one shapeless particle with mass of H_2 in the external potential of the frozen host structure
  - Compute the relative free energy ΔF with respect to free H_2 (gas state) within the same approximation (counterpoise correction)
- *Note:*
  - Classical simulation possible (e.g. Monte Carlo), but many simulations necessary to obtain statistically relevant number

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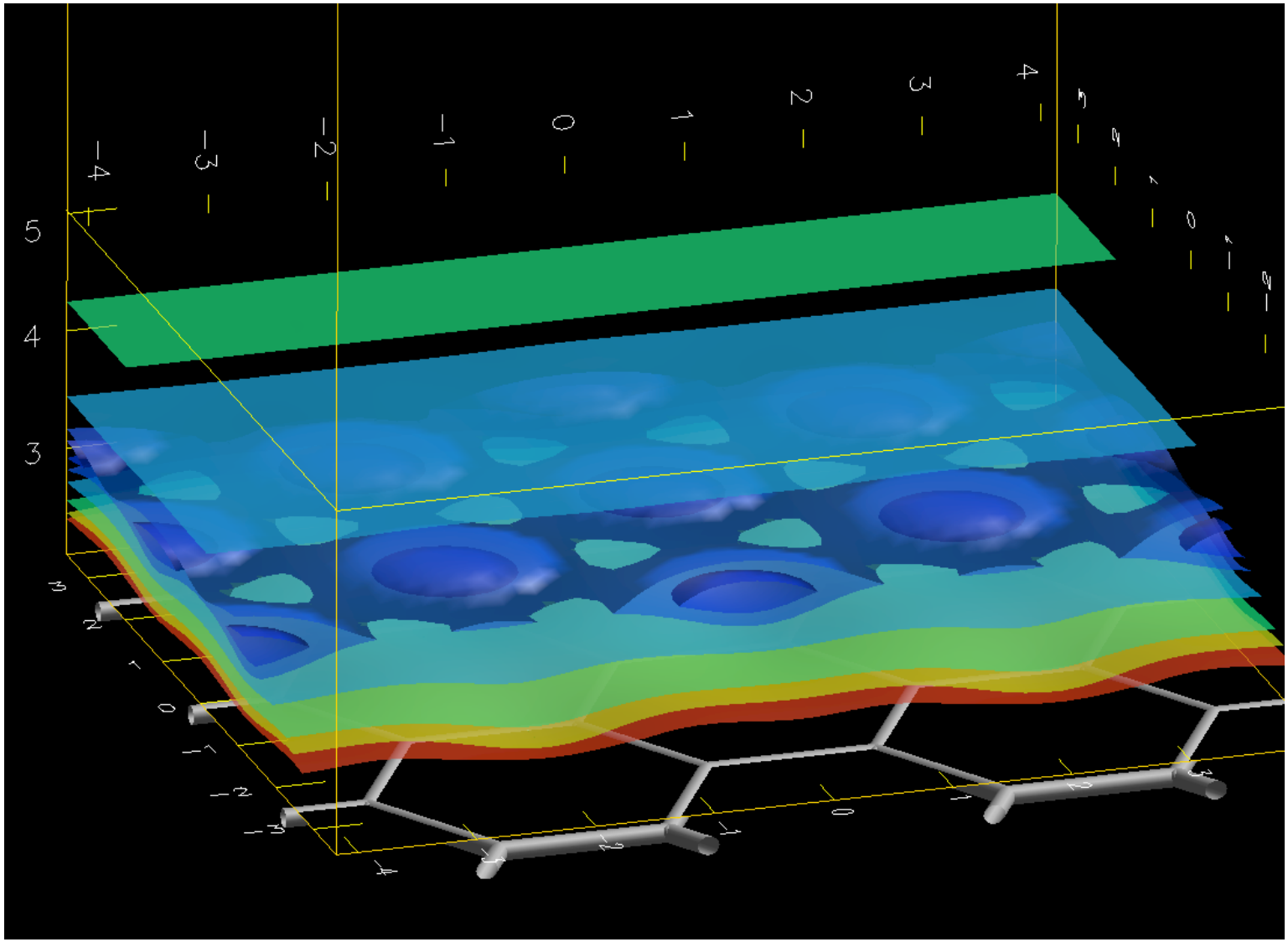
Potential of graphite in the box



V [kJ/mol] = −7.35 (deep blue), -7.13 (blue), -6.0 (teal), -3.0 (green), 0.0 (yellow), and 3.0 kJ/mol (red)

PNAS 2005, 102, 10439

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Computation of adsorption free energy ΔF

- compute eigenstates ε_i of the two systems (in host potential and reference free particle)
- Compute partition function

$$q = \sum_i \exp\left(\frac{-\varepsilon_i}{kT}\right)$$

- Compute relative free energy

$$\Delta F = -RT \ln\left(\frac{q}{q_r}\right)$$

- Compute equilibrium constant

$$K_{eq} = \exp\left(-\frac{\Delta F}{RT}\right)$$

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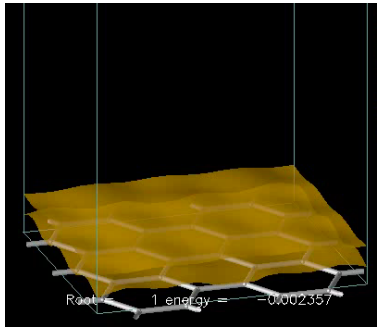
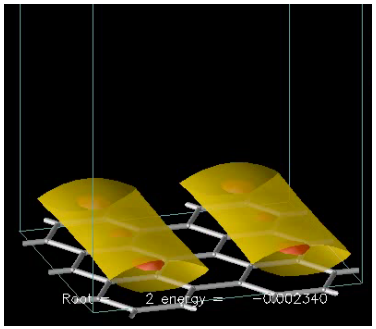
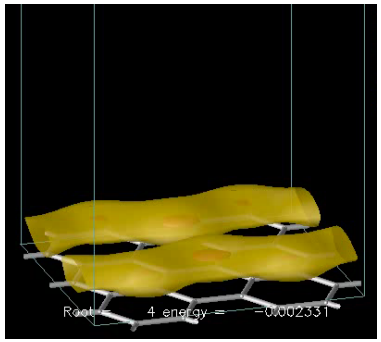
Probability densities of H_2 on graphene







1st, 2nd, and 4th eigenstates for the single-layer graphene structure.

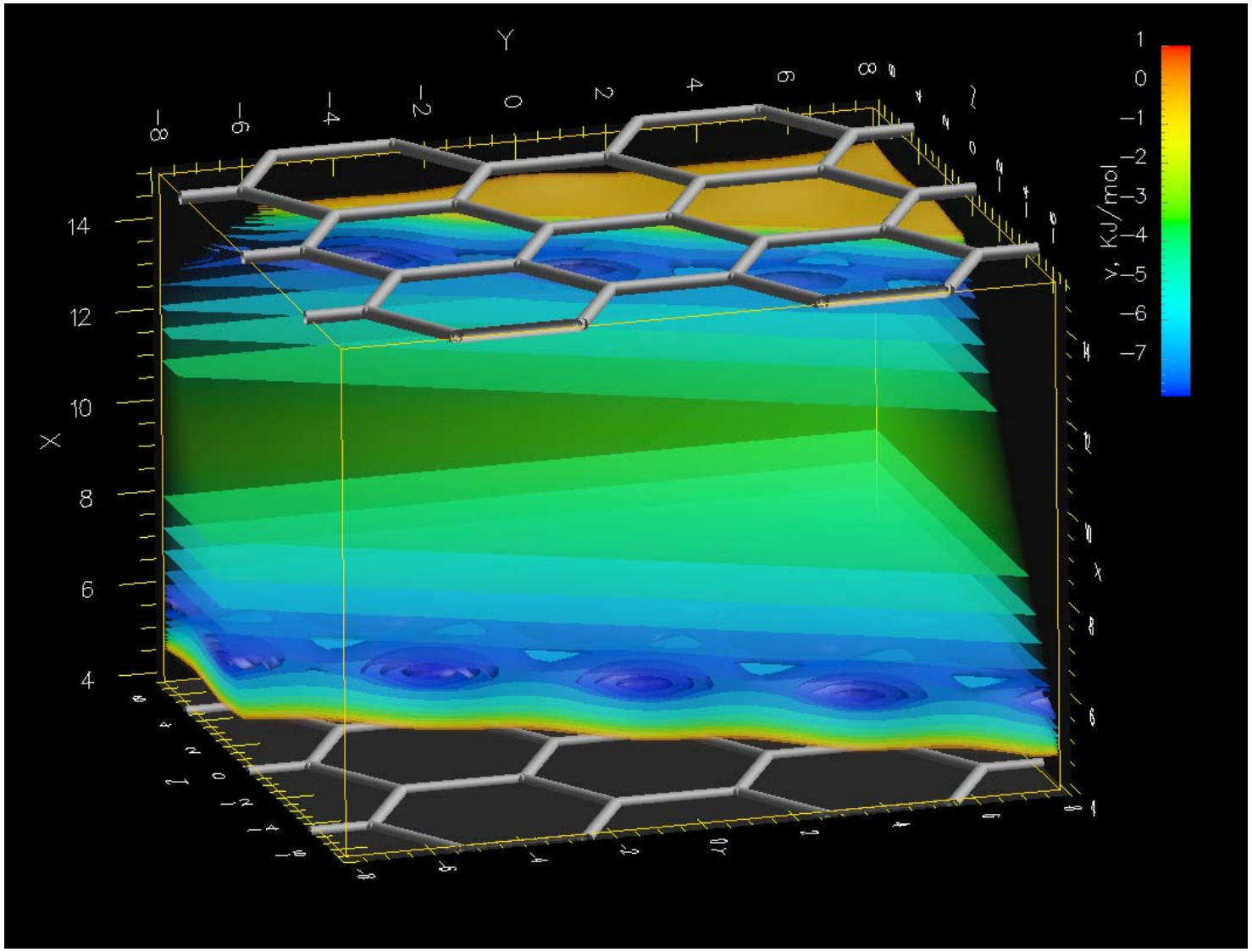
$\Delta F(0K) = -6.2$ kJ/mol
$\Delta F(300K) = -1.2$ kJ/mol
$K_{eq}(300K) = 1.6$

→ Graphite surfaces are lousy H_2 storage materials!

S. Patchkovskii, J. Tse, S. Yurchenko, L. Zhechkov, G. Seifert, T. Heine, PNAS 2005, 102, 10439

Email: thomas.heine@chemie.tu-dresden.de

Potential of graphite in the box



V [kJ/mol] = –7.35 (deep blue), -7.13 (blue), -6.0 (teal), -3.0 (green), 0.0 (yellow), and 3.0 kJ/mol (red)

PNAS 2005, 102, 10439

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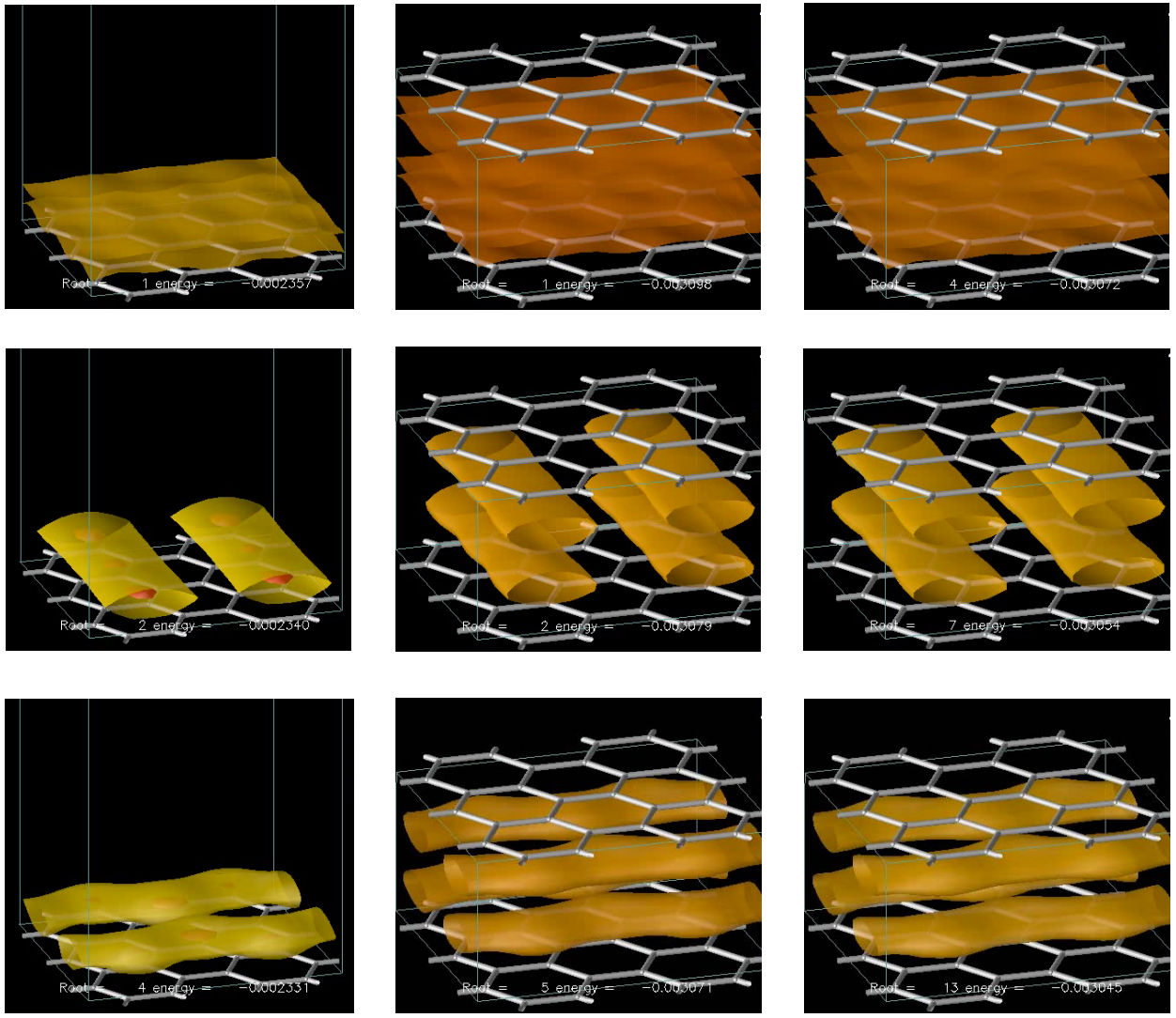
Probability densities of H_2



A B C

A: 1st, 2nd, and 4th eigenstates for the single-layer graphene structure. B, C: Corresponding in-phase (B: 1st, 2nd, and 5th) and out-of-phase (C: 4th, 7th, 13th) eigenstates for the double-layer structure (8Å interlayer separation).

PNAS 2005, 102, 10439

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H_2 in a graphite bilayer of distance c

c, Å	ΔF(0K), kJ/mol	ΔF(300K), kJ/mol	K(300K)
∞[a]	-6.2	-1.2	1.6
12	-6.4	-4.2	5.5
10	-6.7	-5.2	8.0
8	-8.1	-7.3	18.6
6	-13.0[a]	-10.0[a]	56.2[b]

[a]The infinite distance is computed in a box with c=80 Å, but with only one monolayer contributing to the potential.
[b]Due to inherent inaccuracies of our model these numbers are subject to larger error bars.

Result: graphene is a lousy H_2 storage material
But: Bilayer appears to be a good H_2 storage material

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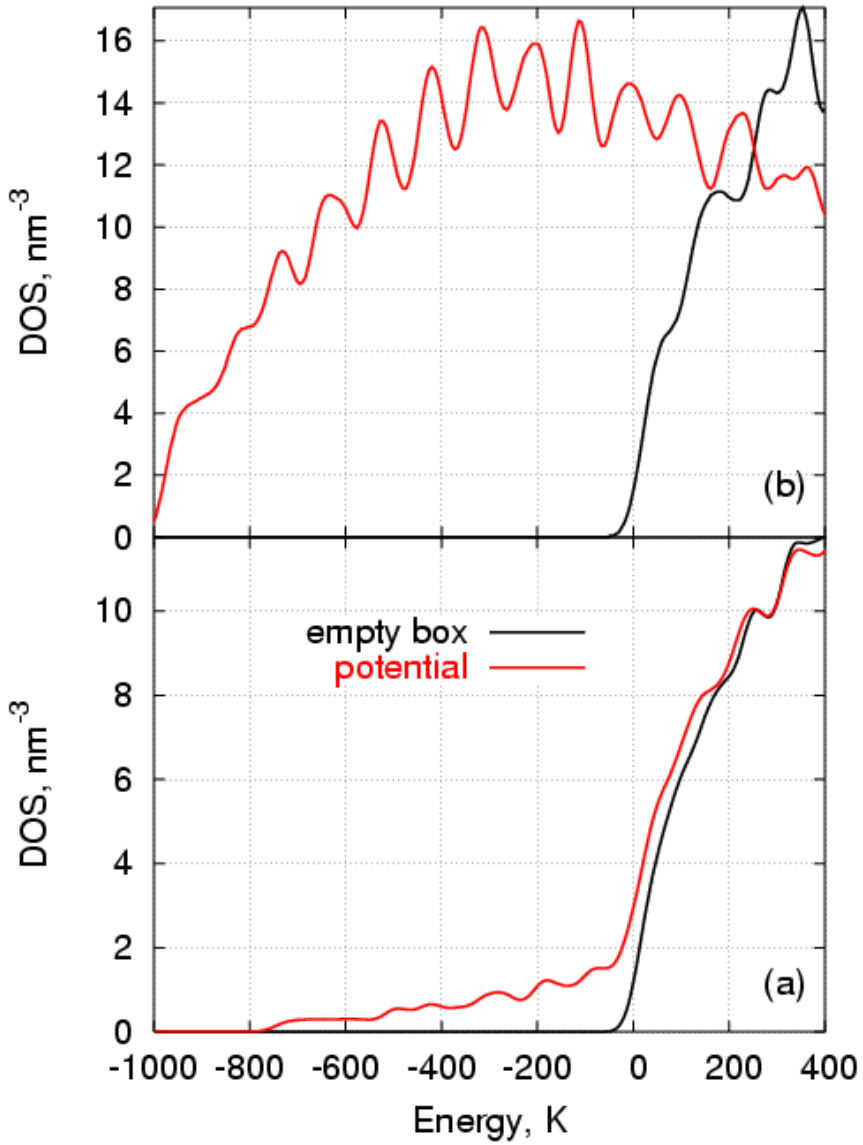
Density-of-states (DOS)



bilayer, c=8Å

Note: H_2 is a boson, so states can be occupied with many particles

monolayer, c=∞

PNAS 2005, 102, 10439

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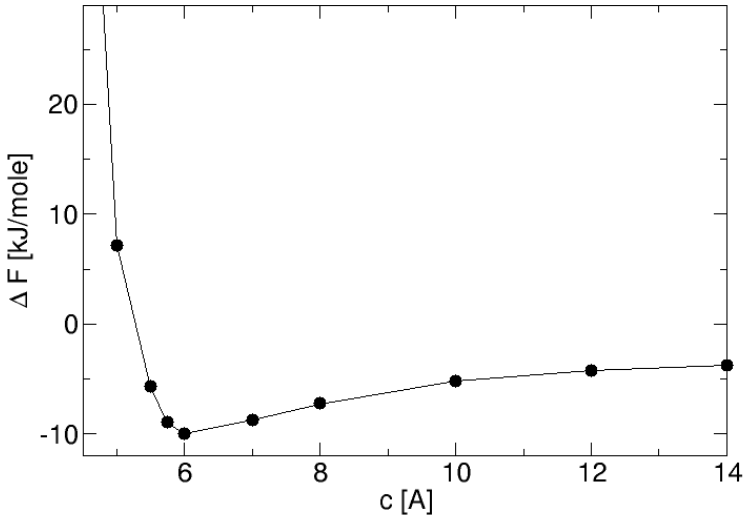
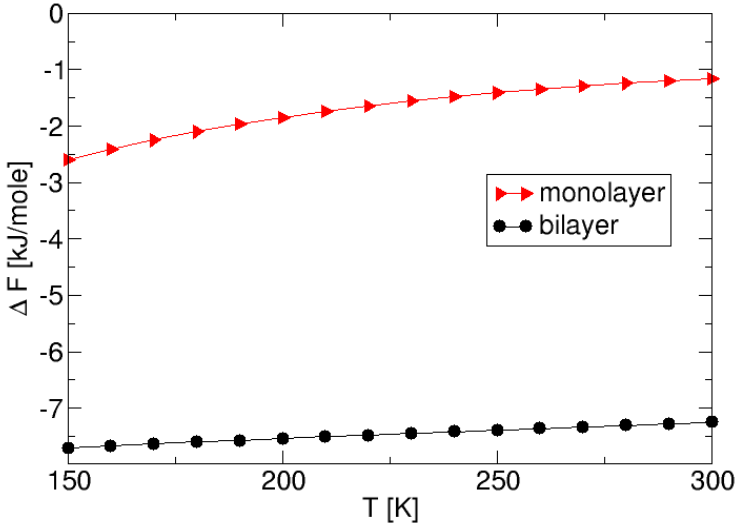
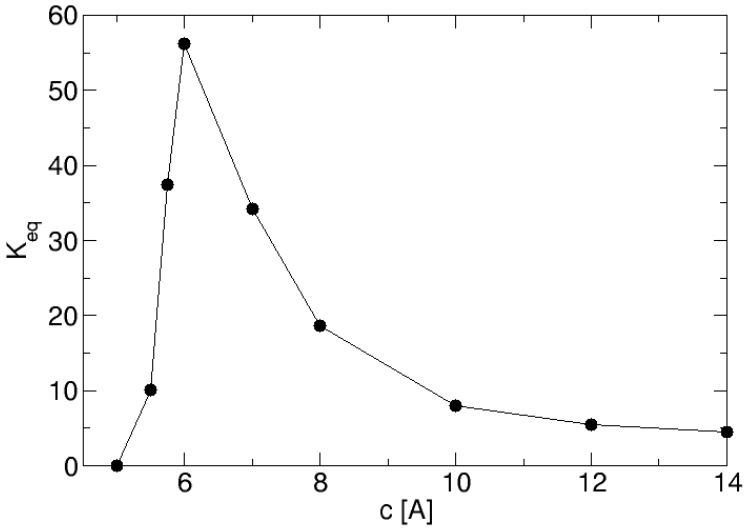
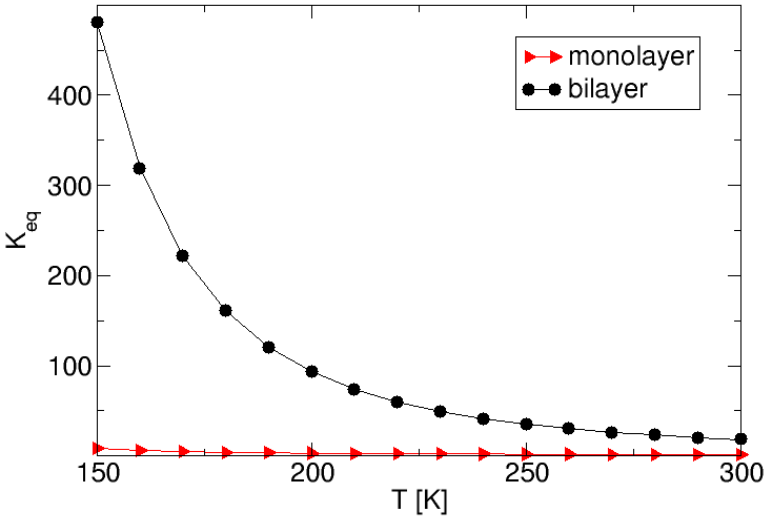
Influence on ΔF_{300} and K_{eq}









len.de

Experimental confirmation

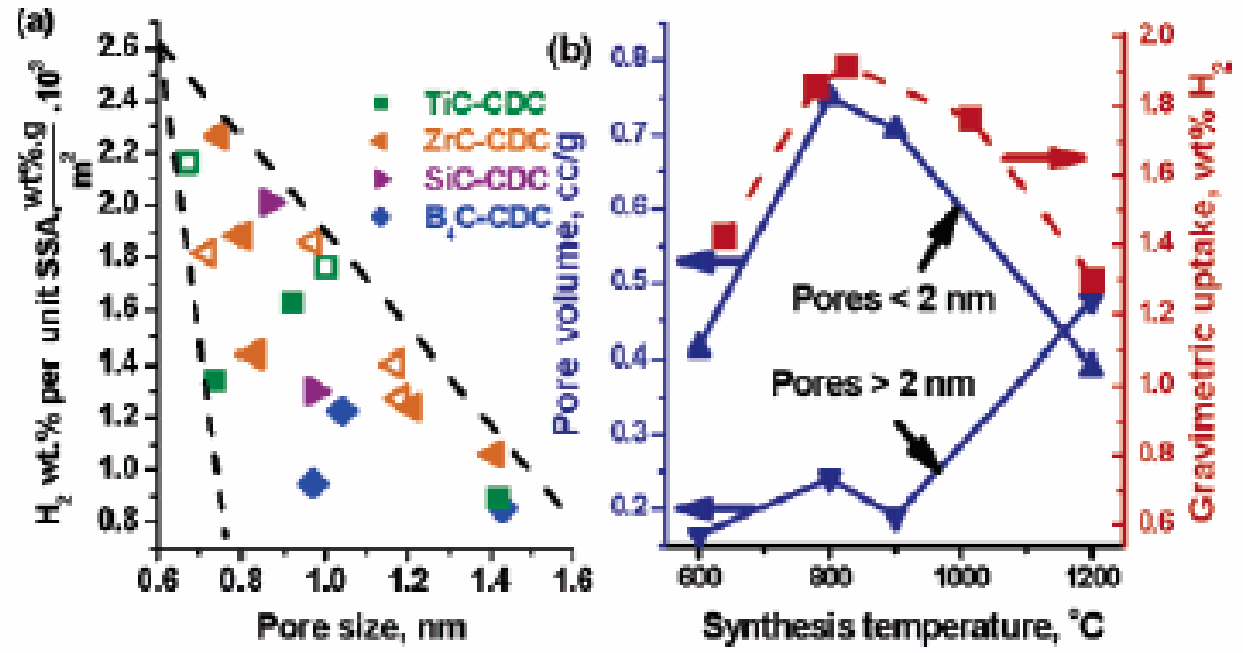


Figure 2. Effect of pore size on hydrogen sorption. (a) Hydrogen storage normalized to surface area plotted as a function of pore size for several CDCs. The general trend defined by the dashed line envelopes indicates that small pores are more efficient than large ones for a given SSA. Solid symbols stand for as-produced and empty for hydrogen-annealed CDC. (b) Pore volume for micropores (< 2 nm) and mesopores (> 2 nm) in comparison with the gravimetric hydrogen uptake as a function of chlorination temperature for B_4C-CDC.

Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J. E. Fischer, J. Am. Chem. Soc. 2005, 127, 16006.

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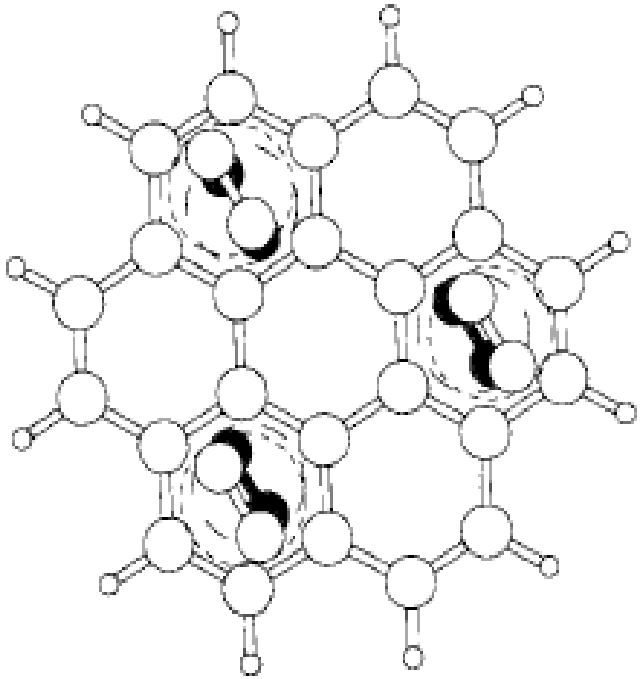
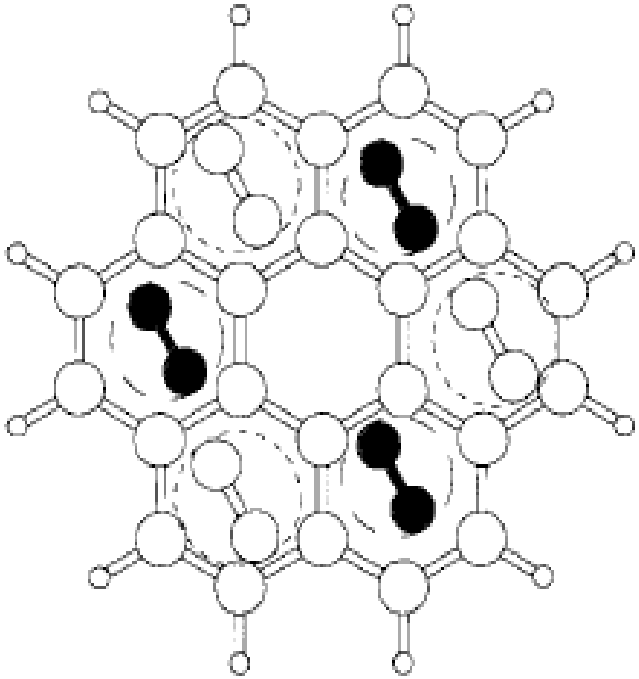
Second challenge for reproducible experimental results in the field of H_2 physisorption

Interaction of N_2 with PAHs is ~3 times stronger than that of H_2!



non-alternating occupation.



alternating occupation

L. Zhechkov, T. Heine, G. Seifert, Int. J. Quantum Chem. 106 (2006) 1375.

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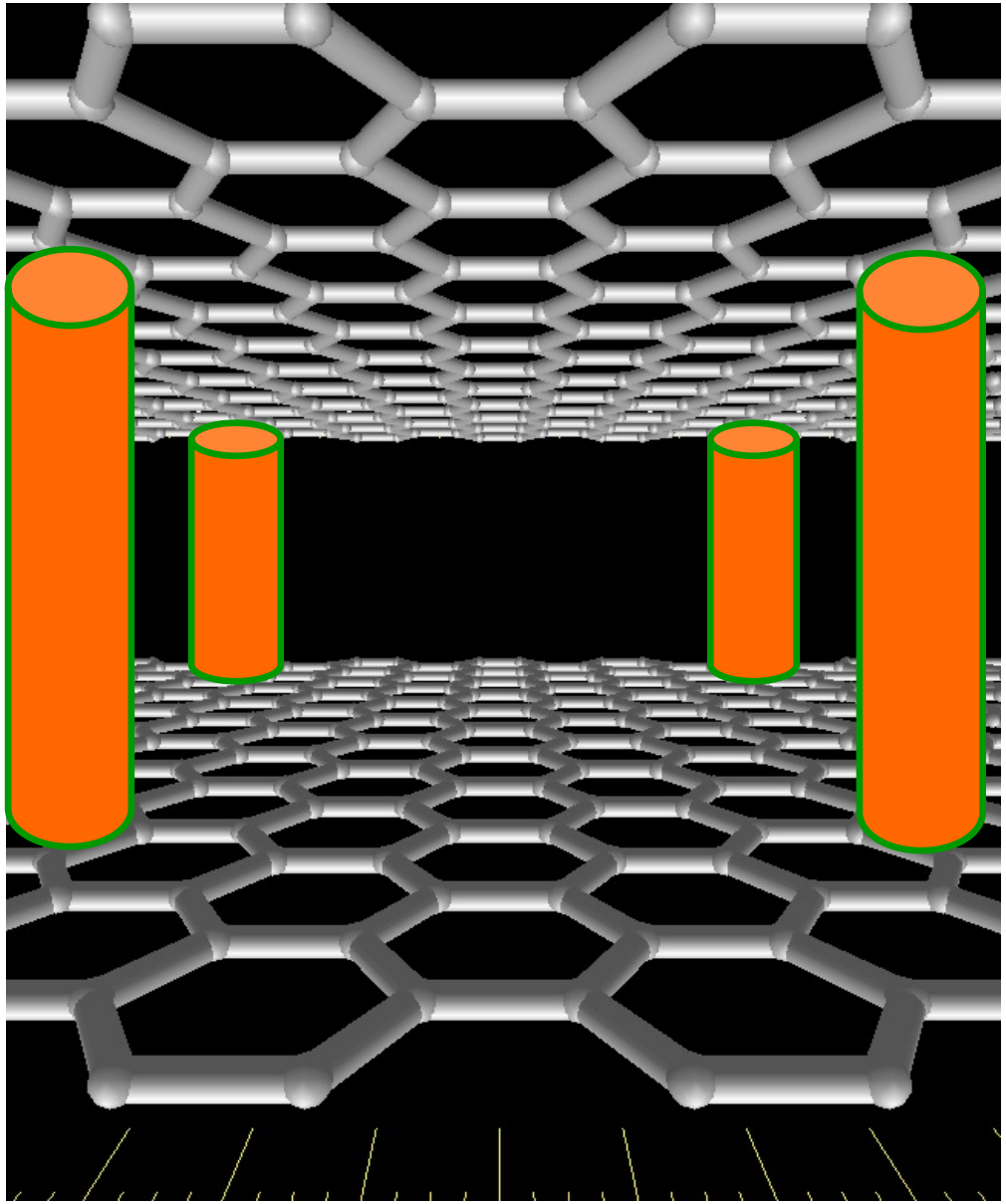
Message: Interlayer distance needs to be fixed!



There are several ways to fix the interlayer distance (functionalisation, internal polymerisation, intercalation with cations or spacers…).
Our favourite: Introduction of spacer molecules → „nano combs“
Additional beneficial effect: nano combs can act as nano sieve and protect the carbon nanostructures from gas impurities.

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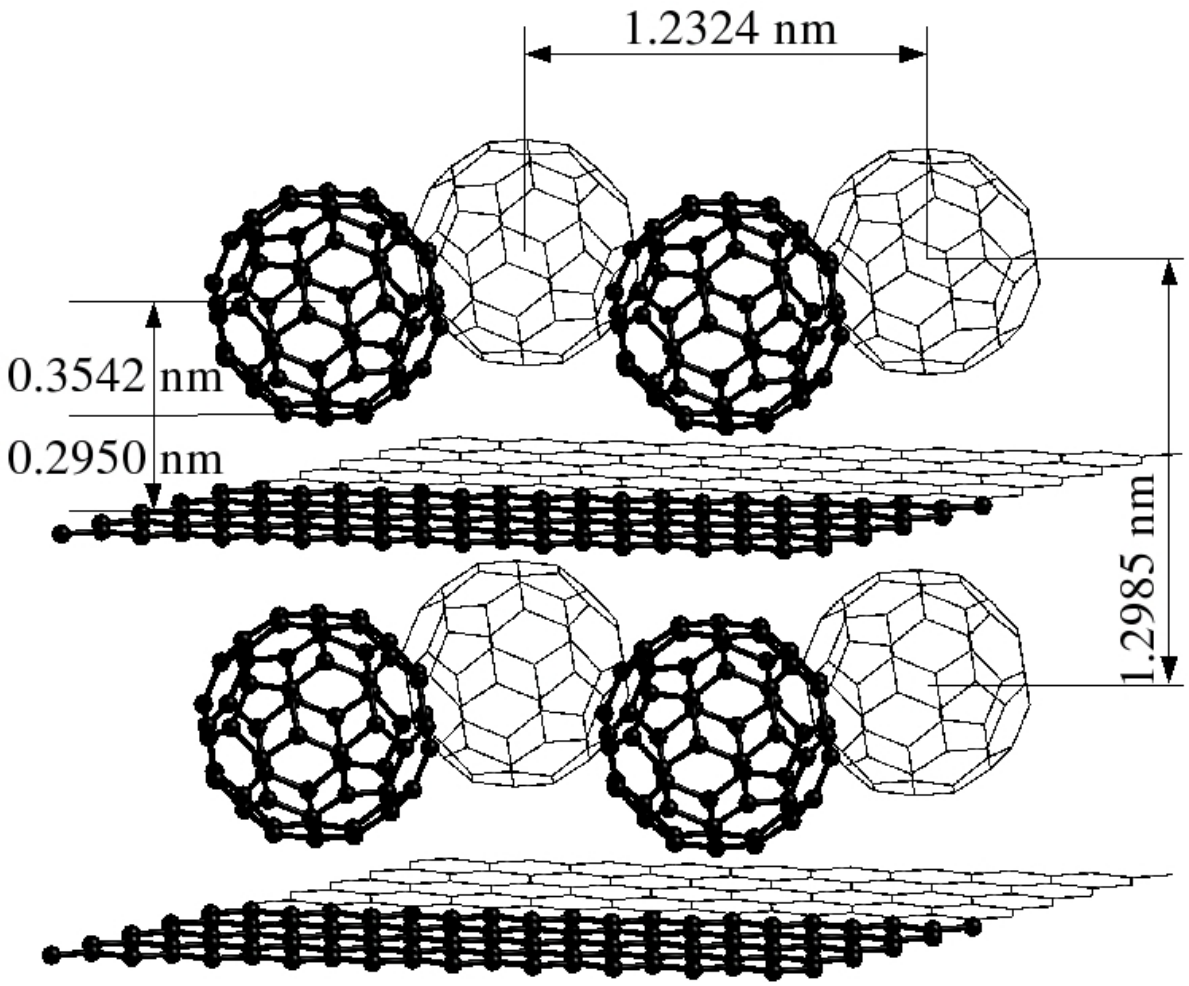
Recent experiment: fullerenes as spacers in graphite, C_{60}-intercalated graphite (CIG)



C_{60}-intercalated graphite (CIG) has been synthesised and characterised.

Gupta, V., Scharff, P., Risch, K., Romanus, H., Müller, R., Solid State Comm. 2004, 131, 153.

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Stability of CIG

Calculated (DC-DFTB) cohesion energies per C-atom (E_{atom}), HOMO-LUMO-gaps (Δ) and mass densities (ρ) for several carbon allotropes. Experimental values are given in parenthesis.

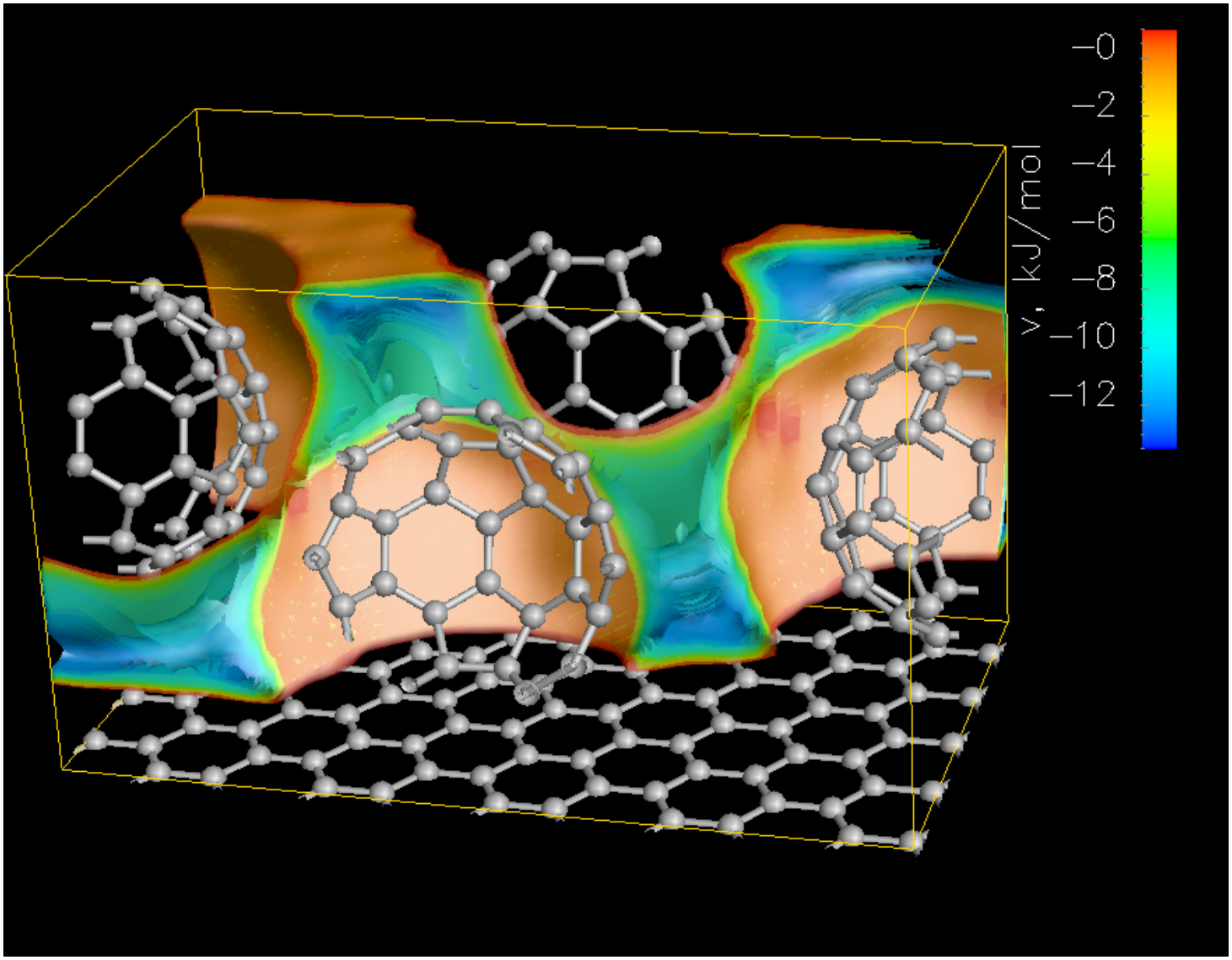
structure	E_{atom} (eV/atom)	Δ (eV)	ρ (g/cm^3)
graphite	-9.09	0 (0)[1]	2.27 (2.266)[1]
graphene layer	-8.90	0 (0)	--
diamanond	-8.87	6.88 (6.01)[1]	3.54 (3.514)[1]
C_{60} (gas phase)	-8.51	1.78 (1.7)	--
C_{60} (solid state)	-8.54	1.67 (1.70)[2]	1.73 (1.72)[2]
CIG	-8.71	0	1.28

[1]Greenwood, N. N.; Earnshaw, A., *Chemistry of the elements. Elsevier: Amsterdam, 1997.*
[2]Dresselhaus, M. S.; Dresselhaus, G., Fullerenes And Fullerene-Derived Solids As Electronic Materials. *Annual Review Of Materials Science* ***1995,*** 25, 487-523.

A. Kuc, L. Zhechkov, S. Patchkovskii, G. Seifert, T. Heine, Nano Letters, 7 (2007) 1.

Email: thomas.heine@chemie.tu-dresden.de

H_2-CIG interaction potential



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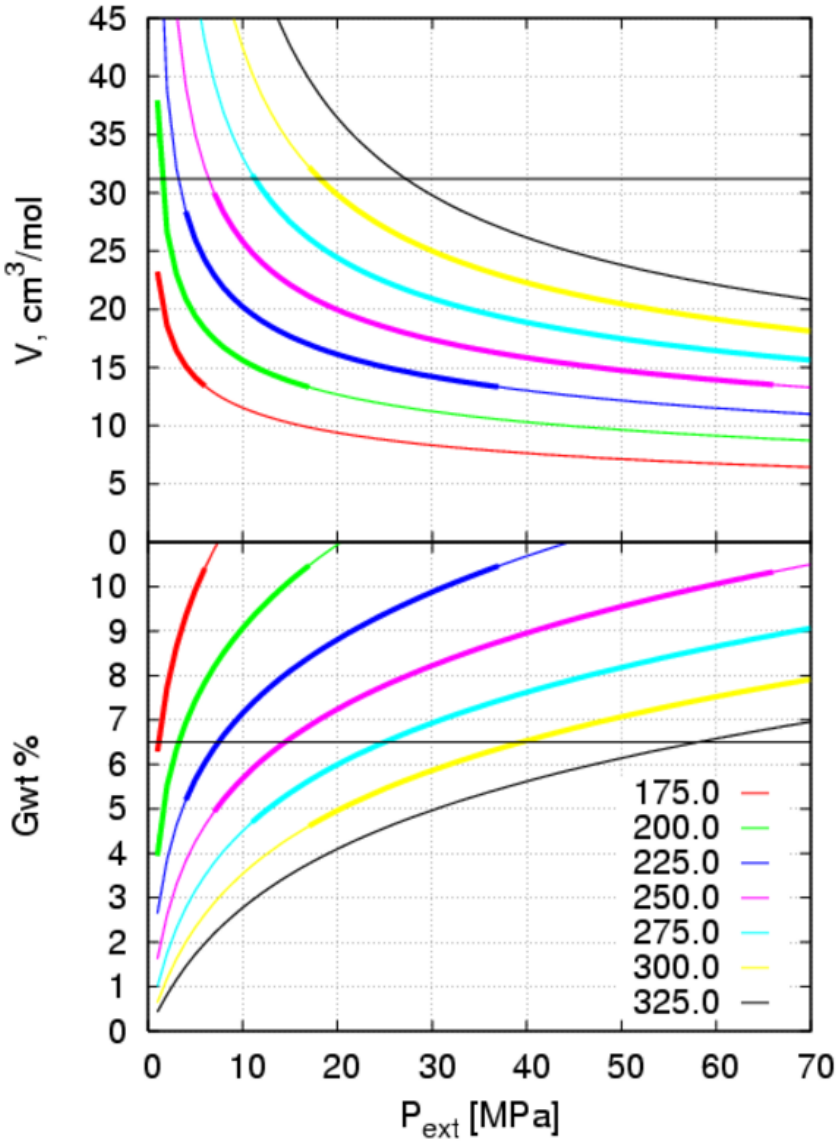
H_2 storage capacity of CIG



Volumetric (top) and gravimetric H_2 storage capacity of CIG, calculated using the real gas equation as function of the external pressure. Isotherms for various temperatures (colour coded) are plotted. Our approximations hold for the bold parts of the isotherms.

A. Kuc, L. Zhechkov, S. Patchkovskii, G. Seifert, T. Heine, Nano Letters, 7 (2007) 1.

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CIG as molecular sieve

- Diffusion constants, calculated through Einstein's relation, from a MD simulation of a CIG supercell containing ~2000 atoms over 1 ns.
  - H_2 : 8.5 10^{-3} cm^2/s
  - N_2 : 3.8 10^{-4} cm^2/s
  - C_{60}: 1.7 10^{-4} cm^2/s
- Conclusion: The fullerene pockets are trapping N_2. Therefore, CIG can separate H_2 from N_2 („Nano-HPCL")

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Magnetic properties of aromatic systems

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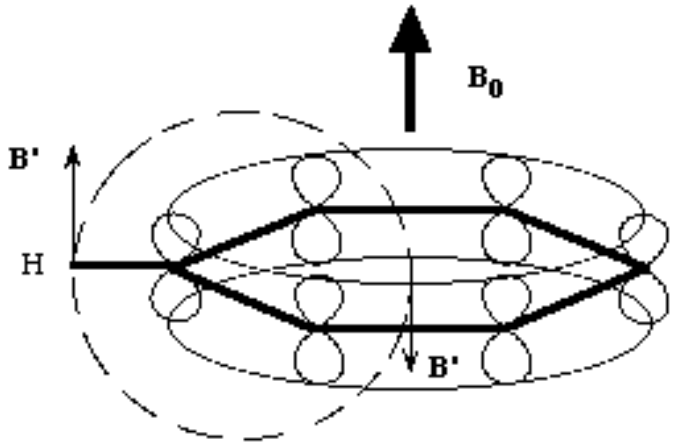
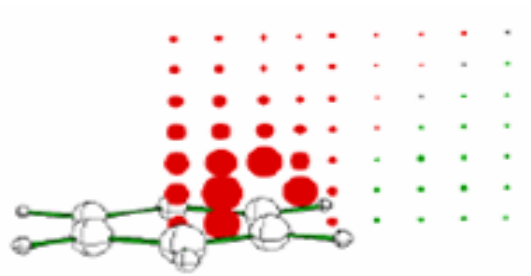
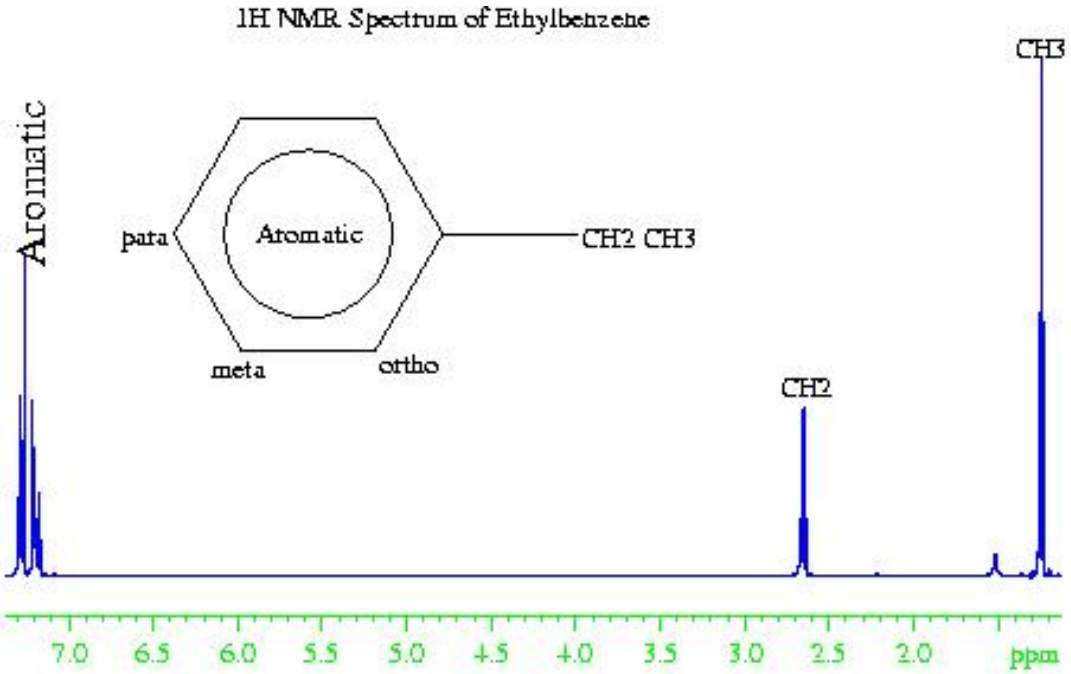
The Pople model

- External magnetic field $\mathbf{B_0}$ induces ring current in π system
- π current induces magnetic counter field **B'**
- **B'** increases $\mathbf{B_0}$ at positions of protons (deshielding)
- **B'** shields ring centre







Nucleus-independent chemical shifts (NICS)
Schleyer et al., J. Am. Chem. Soc. 1996, 118, 6317

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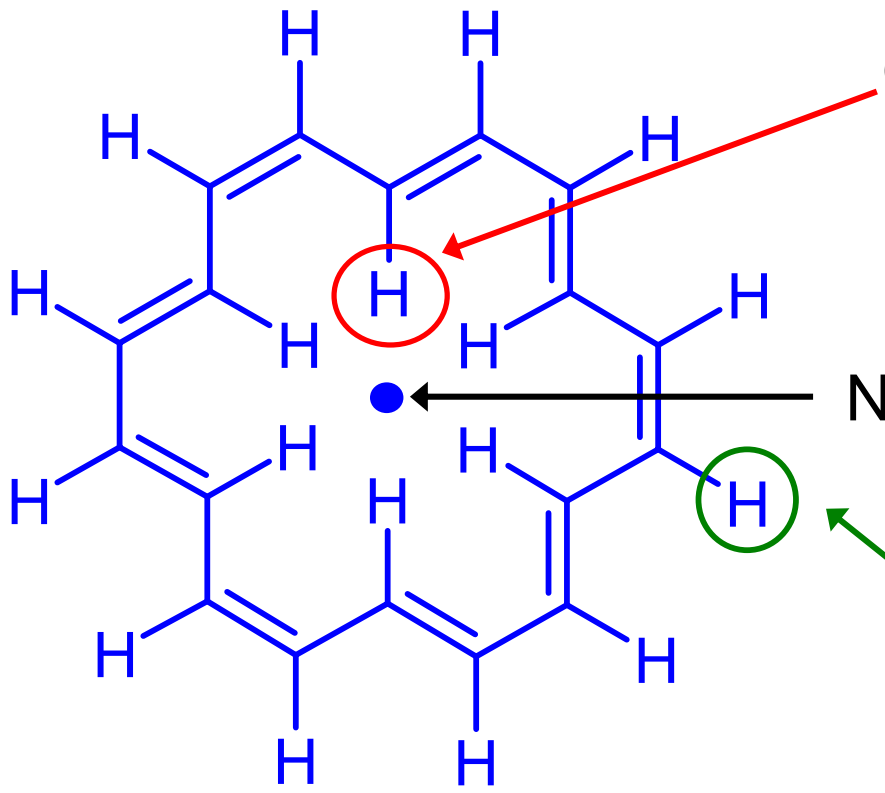
Experimental evidence: [18] annulene



The six hydrogens on the inside of the ring resonate at δ =-3.0 ppm

NICS

The twelve hydrogens on the outside of the ring resonate at δ = 9.0 ppm

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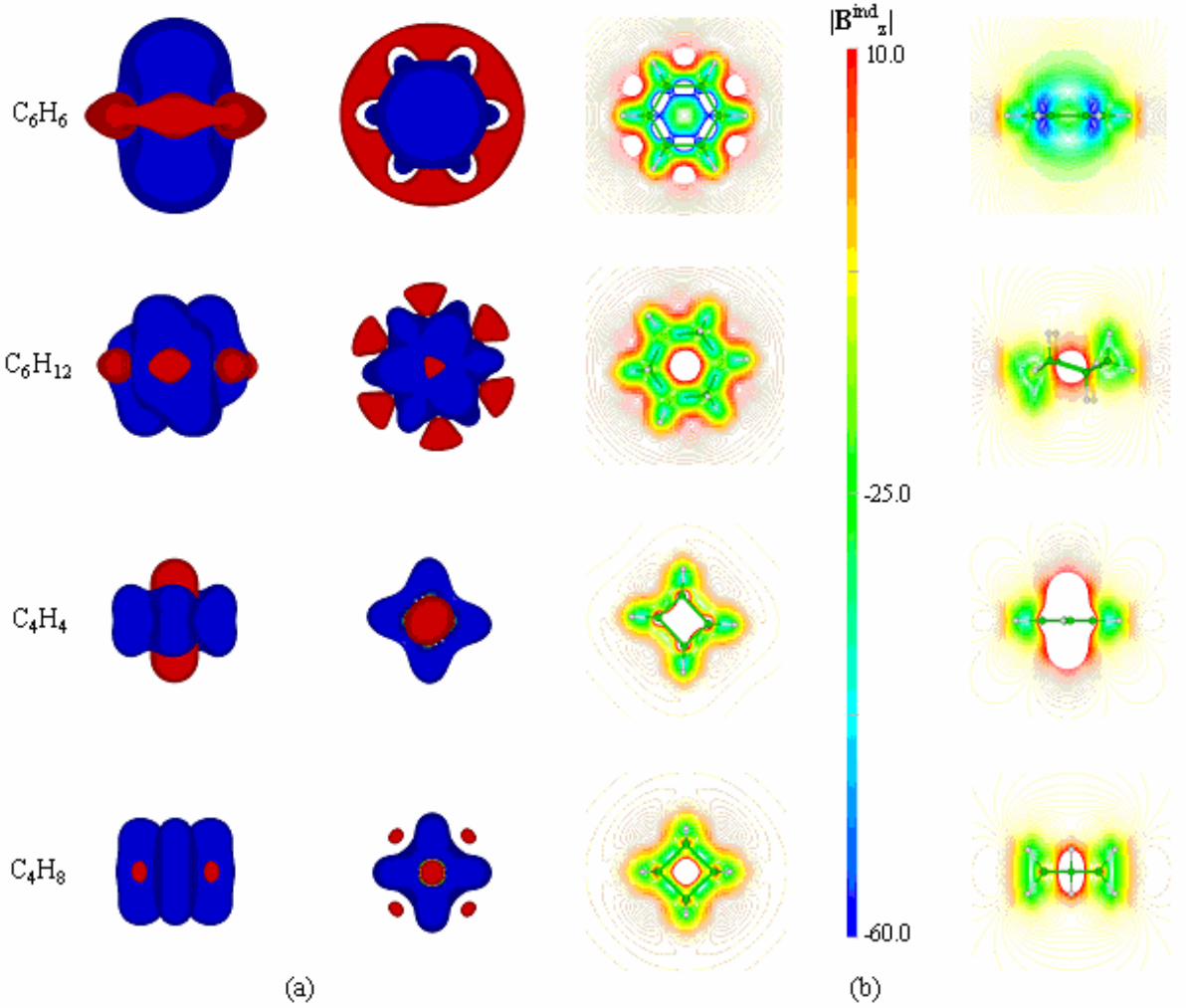
What about antiaromatic and non-aromatic molecules?

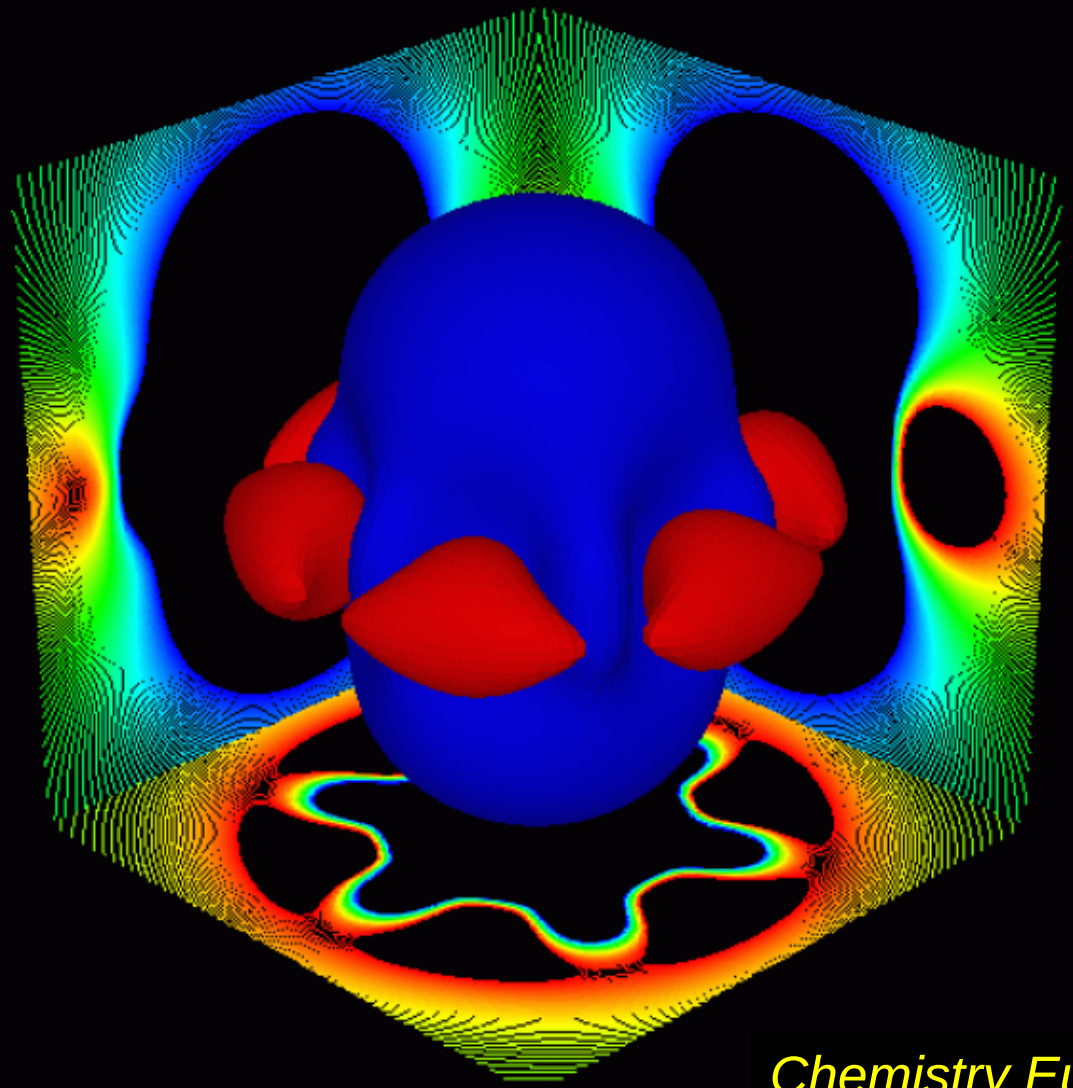


a) Isosurfaces of the z component of the induced magnetic field (IMF, $\mathbf{B}^{ind}_z$). $|\mathbf{B}^{ind}_z|$ = 4 mT and $\mathbf{B}_{ext}$=1 T perpendicular to the molecular plane, given in top and front view of the molecule. Blue and red indicate shielding ($|\mathbf{B}^{ind}_z| < 0$) and deshielding areas, respectively.
b) Contour lines of $\mathbf{B}^{ind}_z$ in the molecular plane and perpendicular to the molecular plane through the origin. The scale is given in ppm (or mT for an external field of 1 T).

Chemistry – Eur. J. 2004, 10, 4367

Email: thomas.heine@chemie.tu-dresden.de

Induced magnetic field (IMF) of benzene



Blue: 5 ppm (5μT) iso-line
Red: -5 ppm (-5μT) iso-line

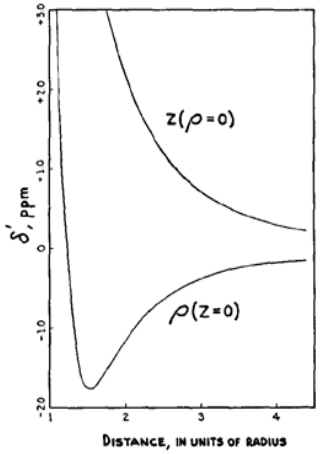
$$\left(\vec{B}_{ind}\right)_{\alpha} = -\sum_{\beta=1}^{3} \sigma_{\alpha\beta} \left(\vec{B}_{ext}\right)_{\beta}$$

Chemistry Eur. J. 2004, 10, 4367

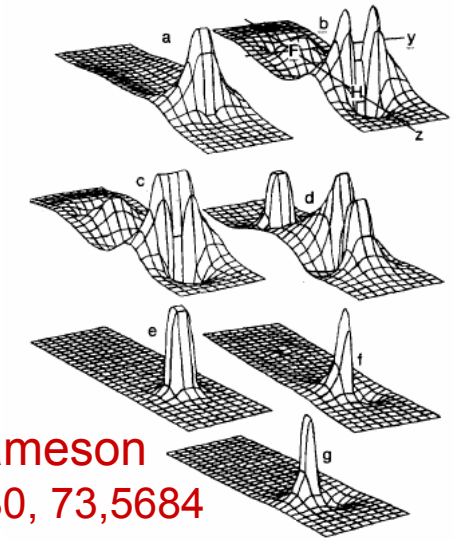
Chemical shieldings at non-nuclear positions

They give the shielding of an external magnetic field by the molecule

$$\left(\vec{B}_{ind}\left(\vec{r}\right)\right)_{\alpha} = -\sum_{\beta=1}^{3}\sigma_{\alpha\beta}\left(\vec{r}\right)\left(\vec{B}_{ext}\right)_{\beta}$$

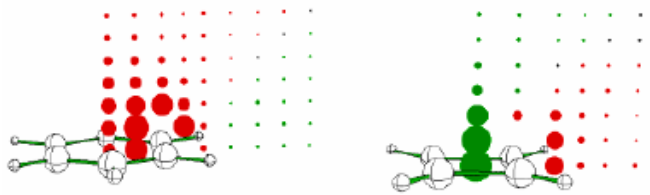


Isoshielding lines
Johnson & Bovey
J. Chem. Phys. 1958, 29, 1012

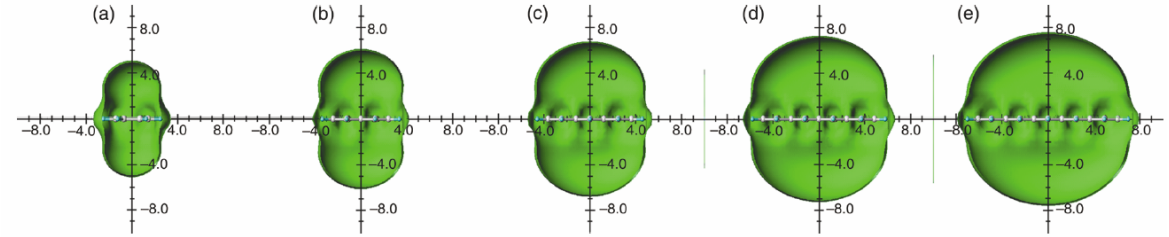


Shielding density
Buckingham & Jameson
J. Chem. Phys. 1980, 73,5684

Neutron chemical shift
Wolinski,
J. Chem. Phys. 1997, 106, 6061



Isochemical Shielding Sufface (ICSS)
Klod & Kleinpeter,
J. Chem. Soc. Perkin Trans. 2, 2001, 1893



Nucleus-independent chemical shifts (NICS) Schleyer et al.,
J. Am. Chem. Soc. 1996, 118, 6317

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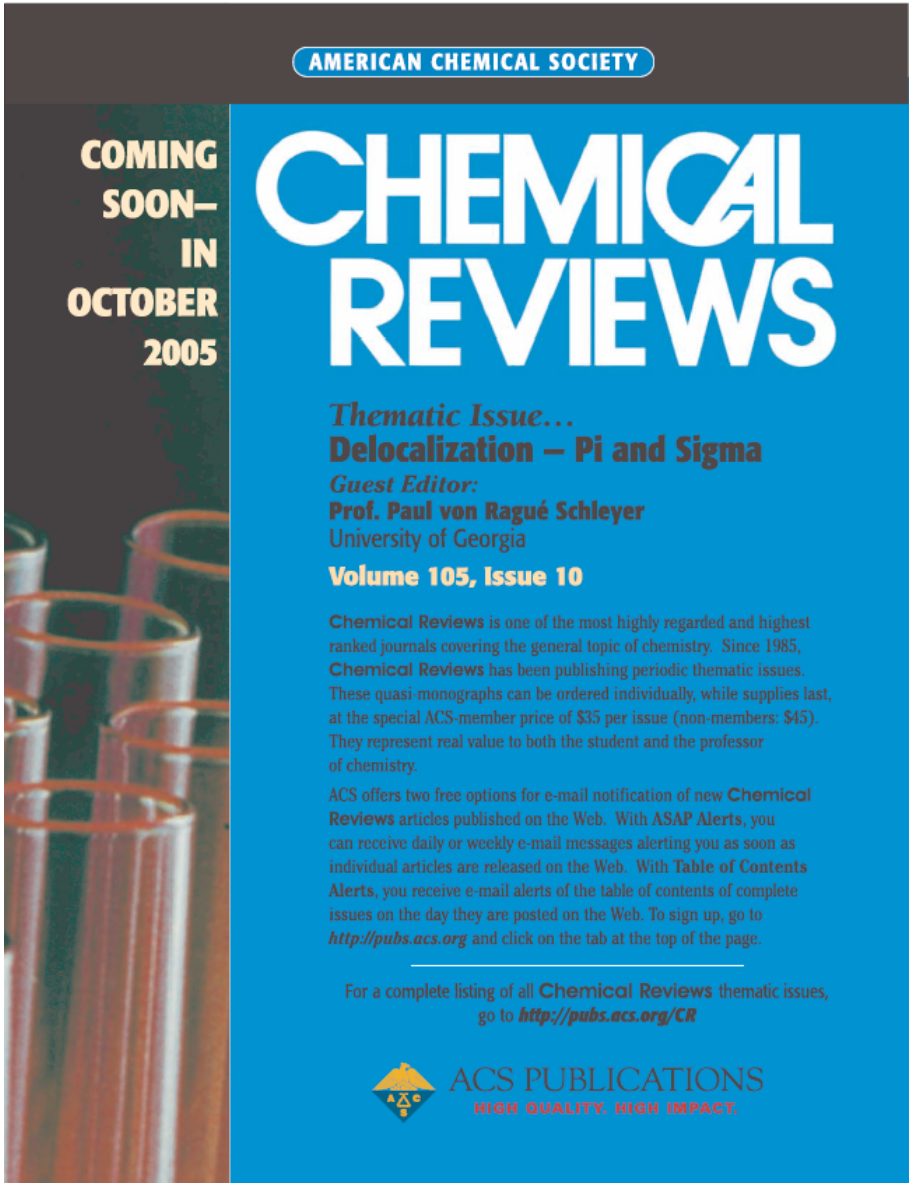
Commercial break



The magnetic shielding function of molecules and pi electron delocalization
T. Heine, C. Corminboeuf, G. Seifert
Chem. Rev. ***105*** *(2005) 3889-3910.*

Description of Electron Delocalization via the Analysis of Molecular Fields
G. Merino, A. Vela, and T. Heine
Chem. Rev. ***105*** *(2005) 3812-3841.*

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Magnetic shielding in DFT

Traditional concept

- (Ramsey, Phys. Rev. 1950, 78, 699)

$$\sigma_{\alpha\beta} = \frac{\partial^2 E}{\partial\left(\vec{B}_{ext}\right)_\alpha \partial\left(\vec{\mu}\right)_\beta}$$

- Holds at position of a nucleus with moment $\vec{\mu}$
- Implemented in most electronic structure codes (CPHF and beyond, DFT)

Alternative concept

- (Eschrig et al., Solid State Comm. 1985, 56, 777; Bieger et al., Chem. Phys. Lett. 1985, 115, 275):
- Biot-Savart's law:

$$\vec{B}_{ind}\left(\vec{r}\right) = \frac{1}{c}\int \frac{\vec{j}\left(\vec{r}\,'\right)\times\vec{r}}{\left(r'\right)^3} d^3r'$$

- Shielding from induced field:

$$\left(\vec{B}_{ind}\right)_\alpha = -\sum_{\beta=1}^{3}\sigma_{\alpha\beta}\left(\vec{B}_{ext}\right)_\beta$$

- Holds in full space
- Requires current density $\vec{j}\left(\vec{r}\right)$

Chem. Rev. 105 (2005) 3889-3910.

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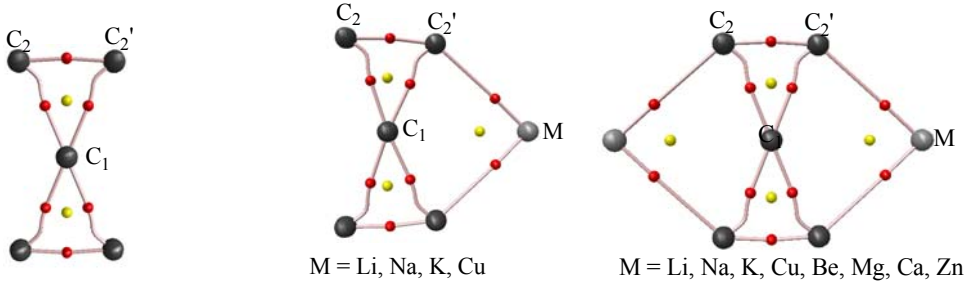
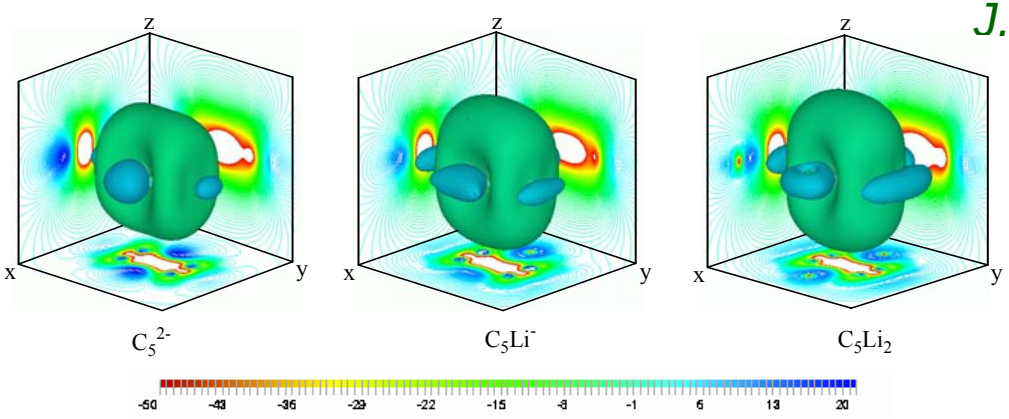
Molecular stability and electron delocalization

- Non-bound electrons can interact and be stabilized. Most well-known example: “aromaticity” (Hückel-rules).
- Magnetic properties (shieldings, induced magnetic fields, ring currents) characterize diatropic (=shielding=stabilizing) and paratropic (=deshielding=destabilizing) electronic systems
- New examples: planar tetracoordinate carbon (ptC) based on C_5^{2-}



Topological analysis of $\rho(\vec{r})$

J. Am. Chem. Soc. 2004, 126, 1610.



Induced magnetic field

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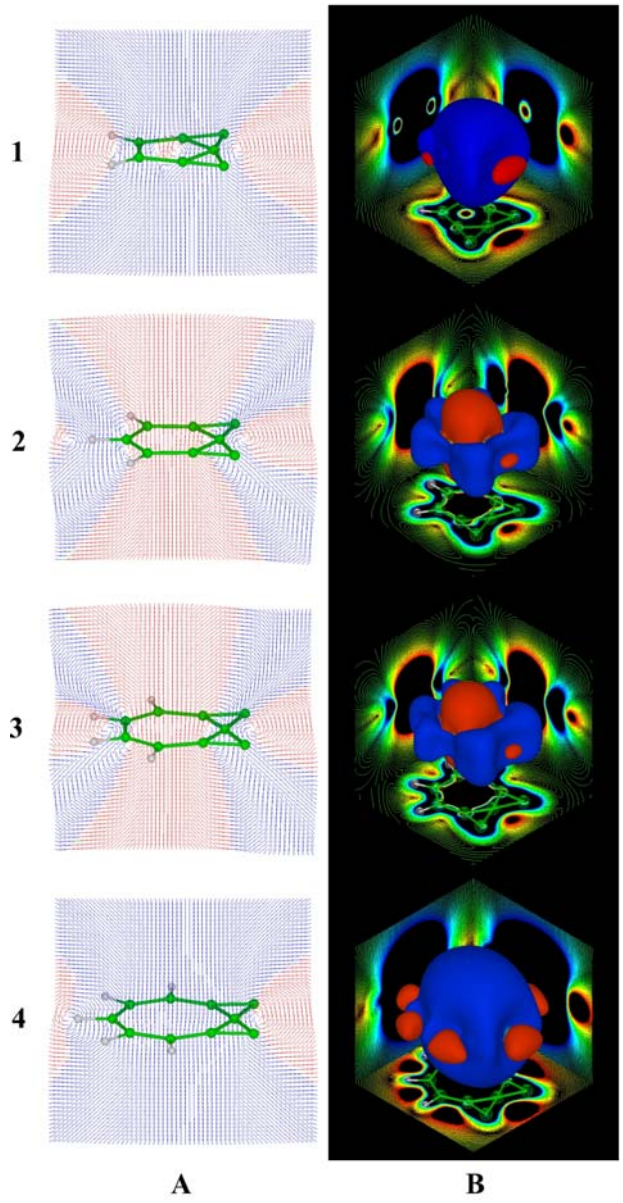
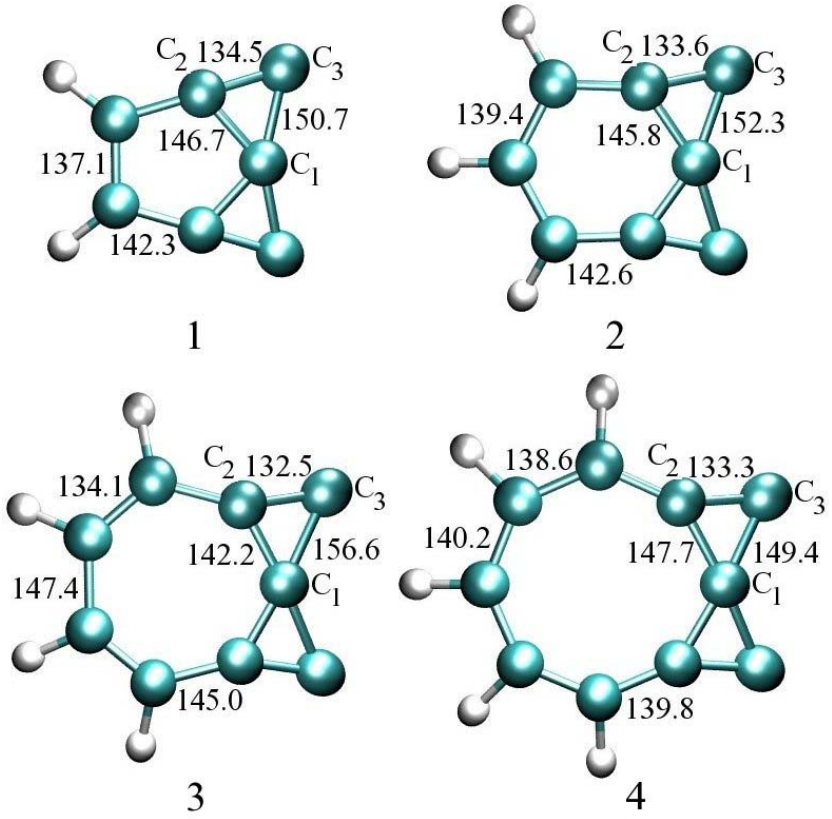
Organic cycles containing a ptC



Cyclic hydrocarbons containing a ptC
Mechanical vs. electronic stabilization (for "aromatic" isomers: life time of 5-10 ps at 300 K)



Org. Lett. 2005, 7, 1509.

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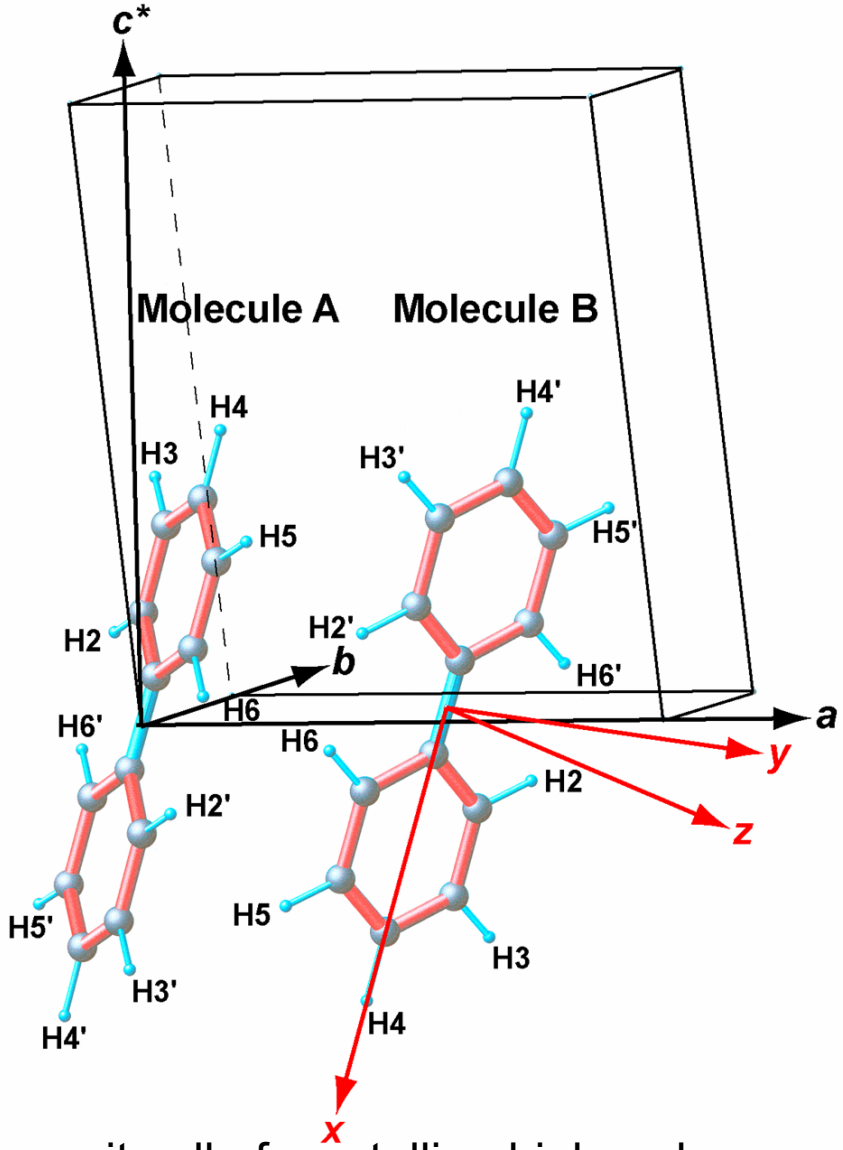
The shielding tensor of biphenyl



unit cell of crystalline biphenyl

Biphenyl: van-der-Waals crystal

^{1}H NMR (multi-pulse NMR) measurement at low T (250K) to avoid flipping of phenyl rings

Direct assignment of ^{1}H NMR shift tensors to protons impossible

^{1}H NMR computations of single biphenyl molecule fail to describe ^{1}H NMR solid state chemical shift (tensor) (cf. Wolinski et al., J. Am. Chem. Soc. 1990, 112, 8251)

J. Magn. Res. 2005, 175, 52

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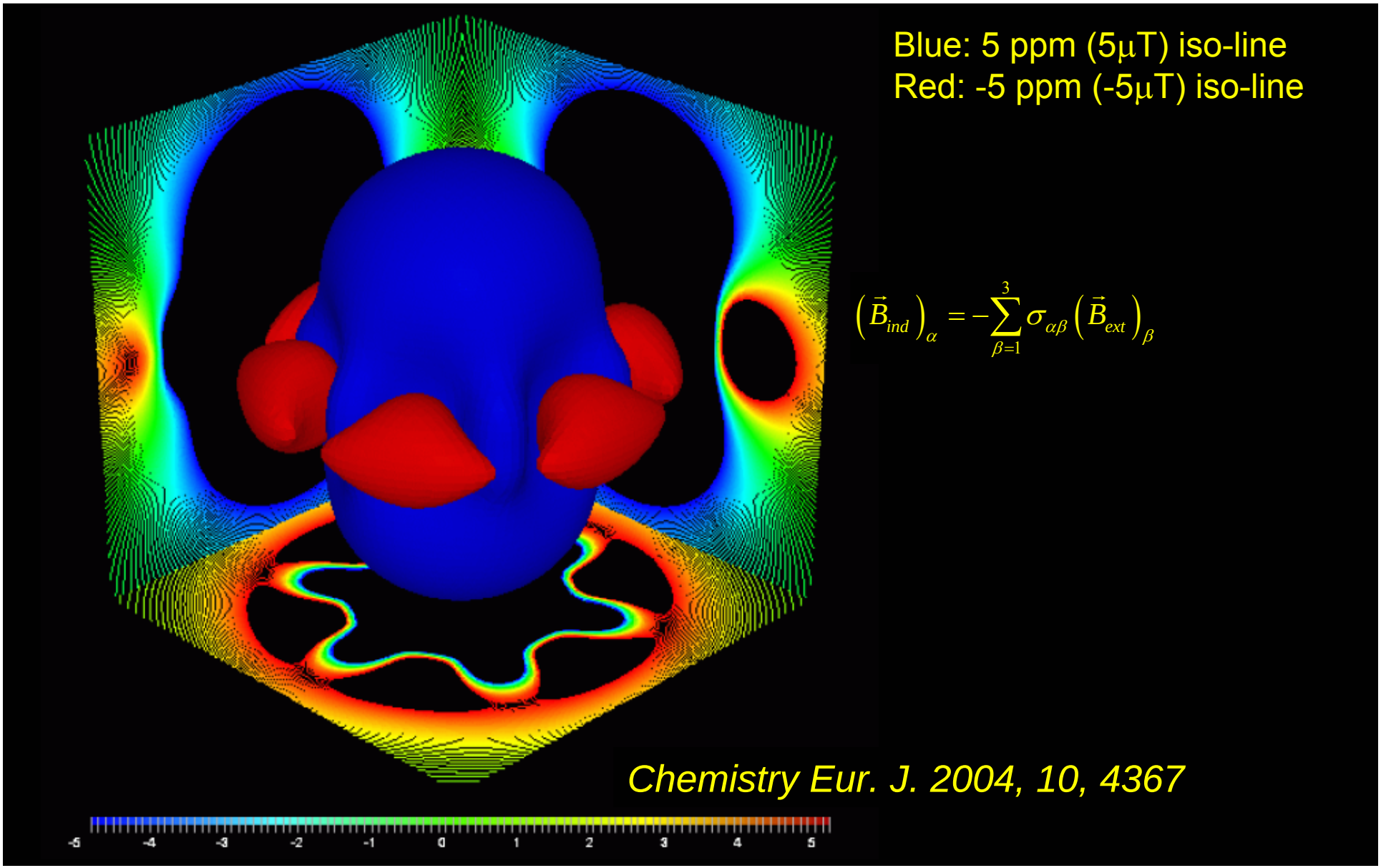
Induced magnetic field (IMF) of benzene



Computation of ^{1}H NMR chemical shift

$$\left(\vec{B}_{ind}\right)_\alpha = -\sum_{\beta=1}^{3} \sigma_{\alpha\beta} \left(\vec{B}_{ext}\right)_\beta$$

$$\vec{B}_{ind} = \underbrace{\vec{B}^0_{ind}}_{\text{short range}} + \underbrace{\sum_i \vec{B}^i_{ind}}_{\text{long range}} \quad \Rightarrow \quad \sigma_{\alpha\beta} = \underbrace{\sigma^0_{\alpha\beta}}_{\sim 30\ ppm} + \sum_i \underbrace{\sigma^i_{\alpha\beta}}_{<5\ ppm} + \underbrace{O\left(\frac{\left|\vec{B}^{i\neq 0}_{ind}\right|}{\left|\vec{B}_{ext}\right|}\right)}_{\sim 5\cdot 10^{-6}\ ppm}$$

- Approach works for non-polar molecules
  - Explicit tests
  - Similar work for C_2H_2

    (Pecul et al., Solid State NMR 1997, 8, 139)
- Does not work for
  - polar molecules (Martin et al., Org. Lett. 2001, 3, 3823)
  - intermolecular interactions (Caramori et al., J. Org. Chem. 2005, 70, 3242.)

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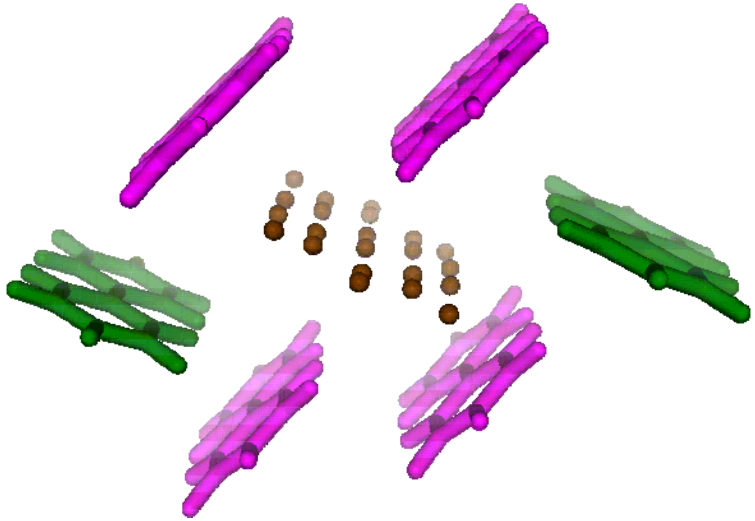
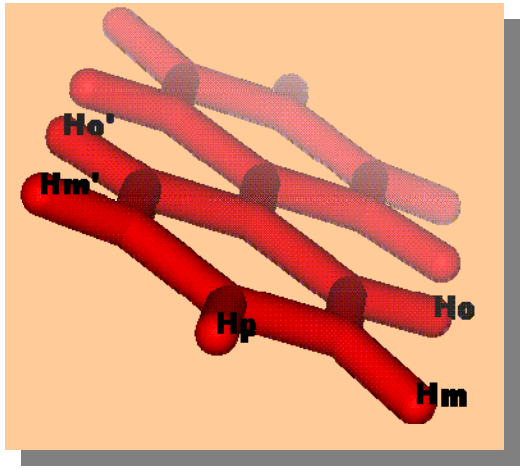
Computational methodology



Proton Labels



IGLO PBE/IGLOIII/GEN-A2*

	single biphenyl	3 biphenyl	Single+ NICS of 18	Single+ NICS of 57	Expt.
H_p	0.00	0.00	0.00	0.00	0.00
H_m	0.27	0.03	0.57	0.43	0.41
$H_{m'}$	0.28	1.19	1.42	1.36	1.39
H_o	0.89	0.97	1.45	1.37	1.27
$H_{o'}$	0.88	0.06	0.60	0.58	0.49

} These protons exchange when the } two rings flip

values are in ppm

Isotropic shieldings referenced to σ_{iso}(para)

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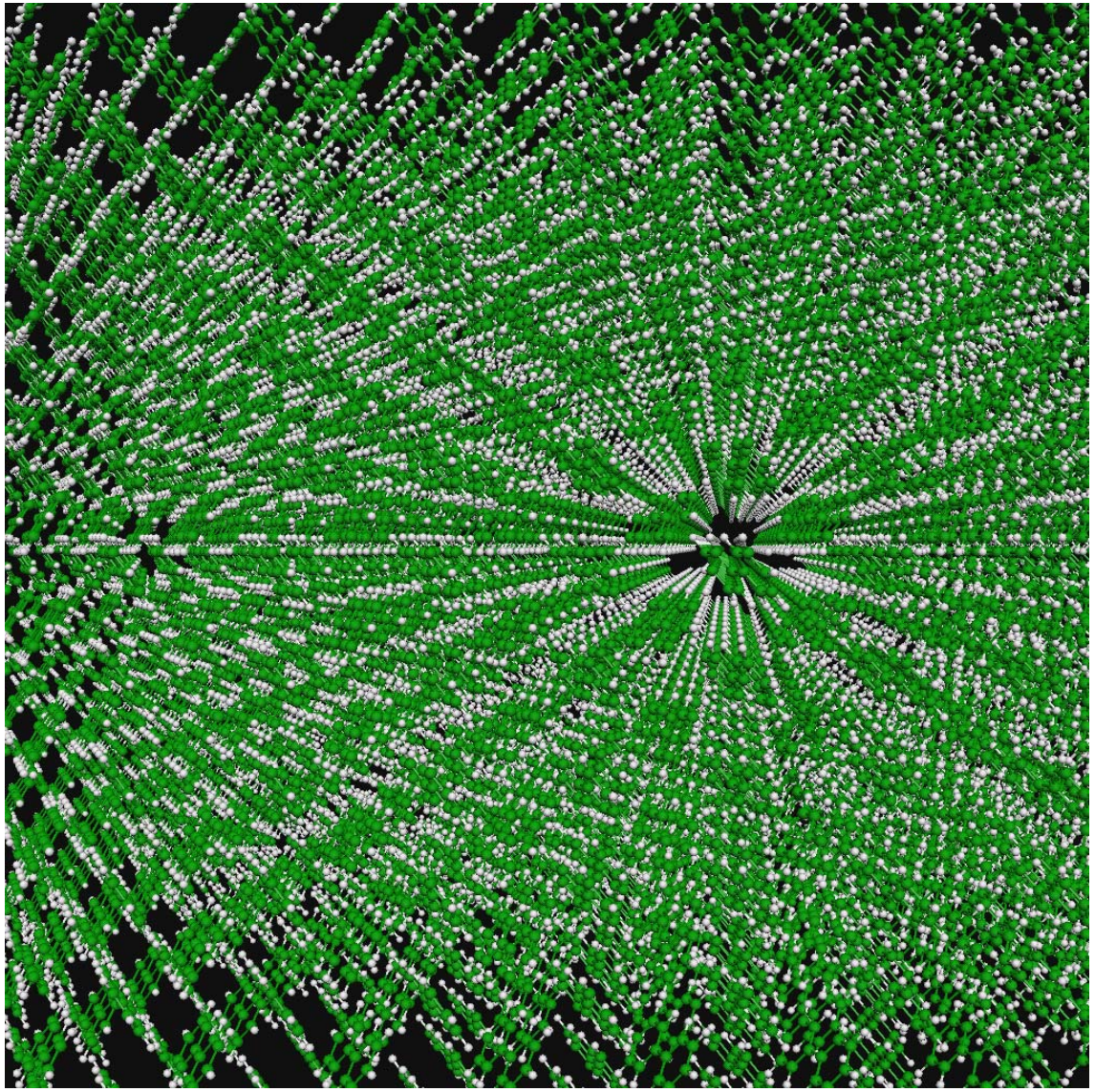
Cluster model of biphenyl



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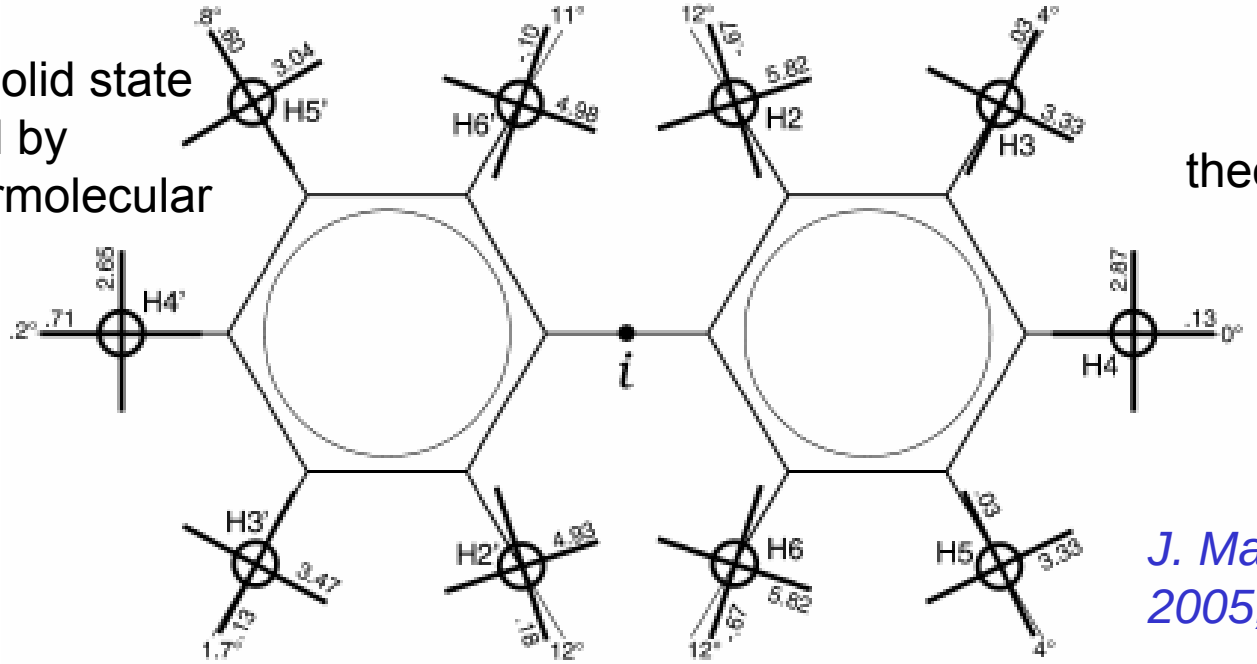
^{1}H NMR shielding tensor for isolated biphenyl

Experiment – solid state NMR corrected by calculated intermolecular contributions



theory

J. Magn. Res. *2005, 175, 52*

Proton	*method*	*isotropic*	*Principal axis components*			*Icosahedral representaion*						*difference*
			11	22	33							
para	i.m.	0.00	-3.36	0.71	2.65	1.26	1.24	1.03	0.95	-2.33	-2.14	**0.27**
	q.ch.	0.00	-3.00	0.13	2.87	0.90	0.88	1.25	1.25	-2.14	-2.14	
meta	i.m.	-0.22	-3.40	0.14	3.26	0.90	3.25	-0.40	-0.24	-1.70	-1.81	**0.13**
	q.ch.	-0.28	-3.37	0.03	3.33	1.01	3.29	-0.47	-0.47	-1.68	-1.68	
ortho	i.m.	-0.90	-5.00	0.04	4.96	4.70	2.04	-0.98	-1.01	-2.19	-2.57	**0.45**
	q.ch.	-0.88	-5.16	-0.67	5.82	5.33	2.29	-1.56	-1.56	-2.25	-2.25	

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One fatal conclusion

"The good news of this work is that there is no more a need to perform such (multiple pulse NMR on benzene) *an experiment. Actually, proton shielding tensors are hardly anymore a reason to perform line-narrowing multiple pulse experiments. There are adequate, even superior, alternatives: first, single crystal deuteron NMR in very high applied fields [16] and, second,* ***calculation by the quantum chemical method explored and tested against experiment here,*** *perhaps supplemented by the old susceptibility method. After elimination of systematic errors,* ***these theoretical methods allow with reasonable effort to access proton shielding tensors on a sub-ppm accuracy level not only in the isolated molecule but also in the natural crystal environment.*** *In a forthcoming publication we shall give a fuller account of these methods and shall apply them to benzene (T. Heine, C. Corminboeuf, G. Grossmann, U. Haeberlen)."*

U. Haeberlen in *J. Magn. Res. 2005, 175, 52*

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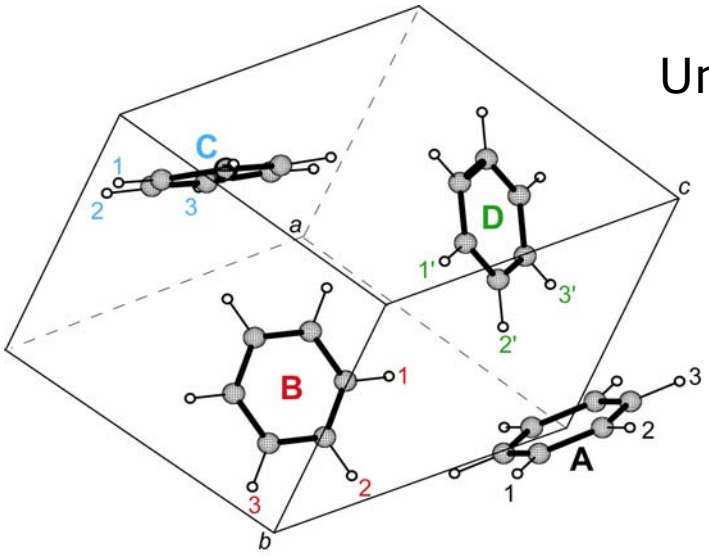
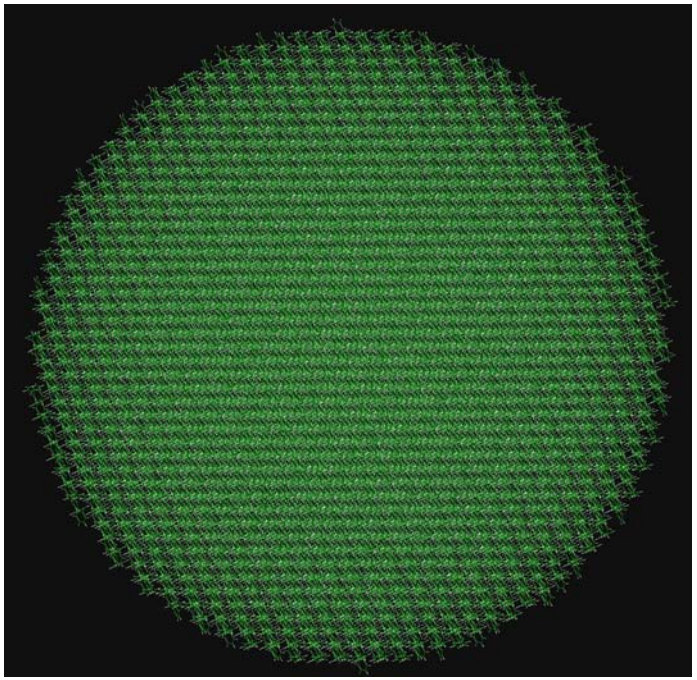
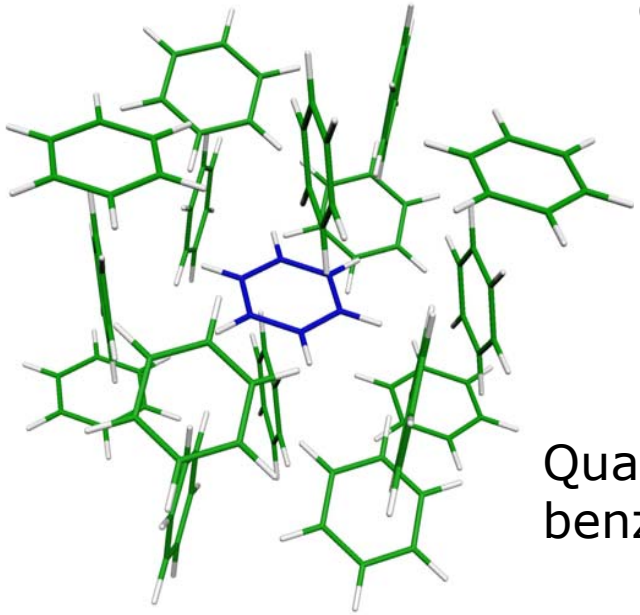
^{1}H NMR chemical shift of benzene



Unit cell contains 4 molecules

Long-range interactions of a cluster of 72 Å considered (13445 molecules)





Angew. Chem., 2006, 118, 2006, 7450.

Quantum-chemical calculation of a cluster of 17 benzene molecules (204 atoms)

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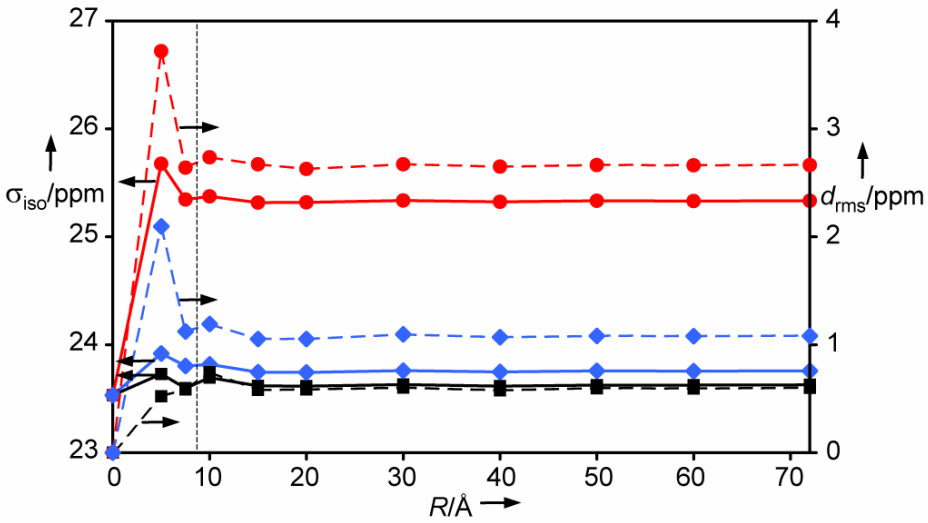
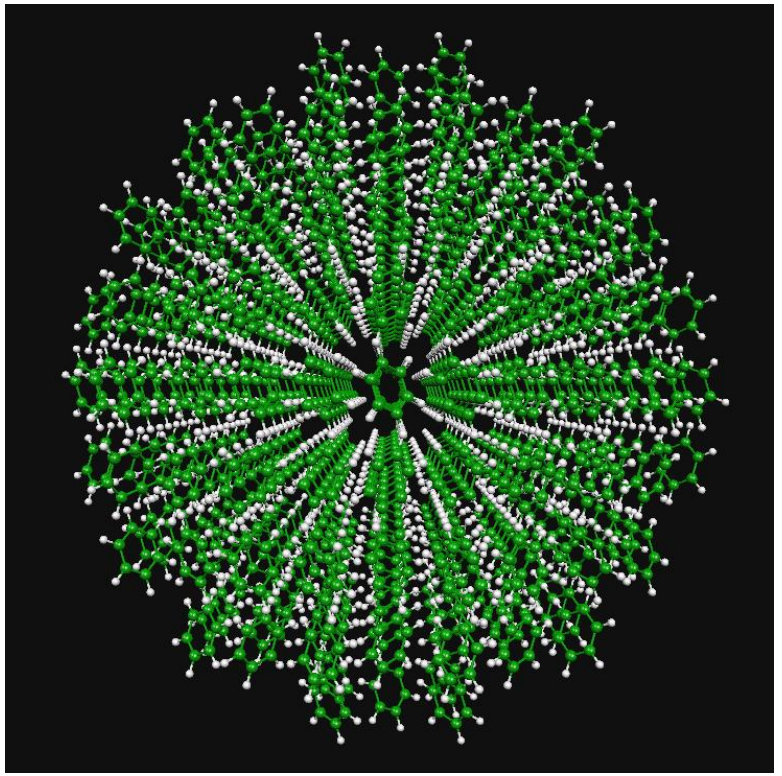
^{1}H NMR chemical shift of benzene



$$d_{rms} = \sqrt{\sum_{i=1}^{6}(\sigma_{i,R} - \sigma_{i,R=0})/6}$$

Three distinct protons
Shieldings differ considerably
20 Å sphere is needed:
293 molecules



Angew. Chem., 2006, 118, 2006, 7450.

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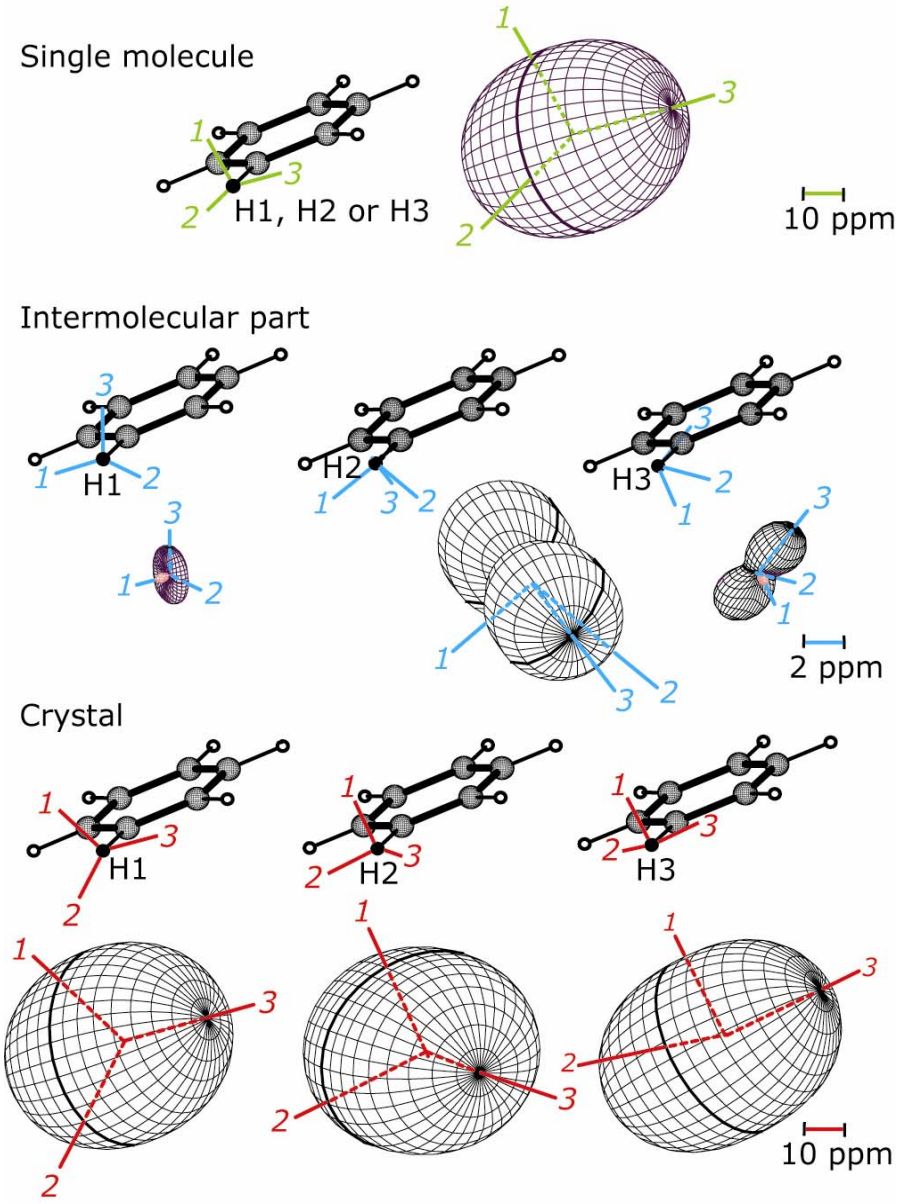
^{1}H NMR chemical shift of benzene



	H1 / ppm	H2 / ppm	H3 / ppm
σ_{iso}	23.63	25.33	23.76
σ_{11}	21.03	20.67	19.97
σ_{22}	22.77	24.34	22.96
σ_{33}	27.08	30.99	28.35

Tensorial representation as suggested by Radeglia.

T. Heine, C. Corminboeuf, G. Großmann, U. Haeberlen, Angew. Chem., 2006, 118, 2006, 7450.

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- Ulrich Häberlen
- Knut Vietze
- Serguei Patchkovskii
- Sergei Yurchenko
- Rafael Islas
- Agnieszka Kuc
- deMon and deMon-NMR developers
- VU developers
- Paul v. Ragué Schleyer

Deutsche Forschungsgemeinschaft DFG

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