Nucleation of Zeolites: The Big Nano-jigsaw

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Chemistry Department

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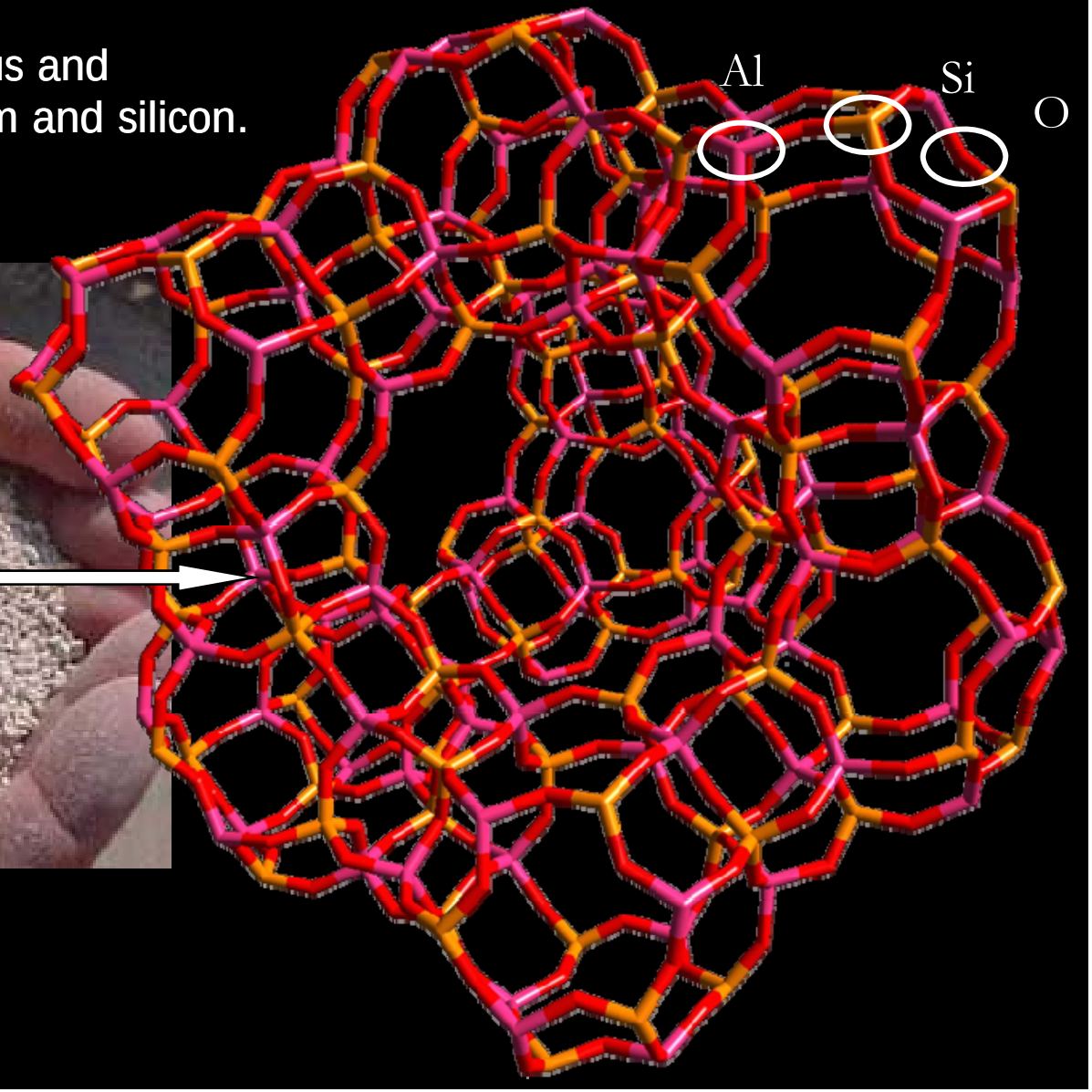
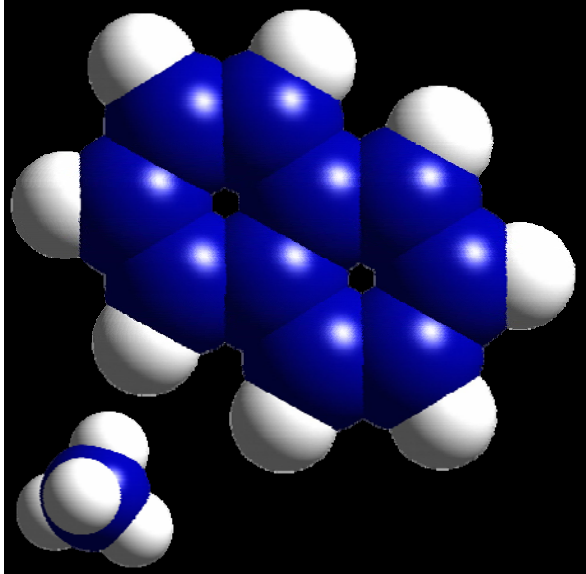
What are zeolites?

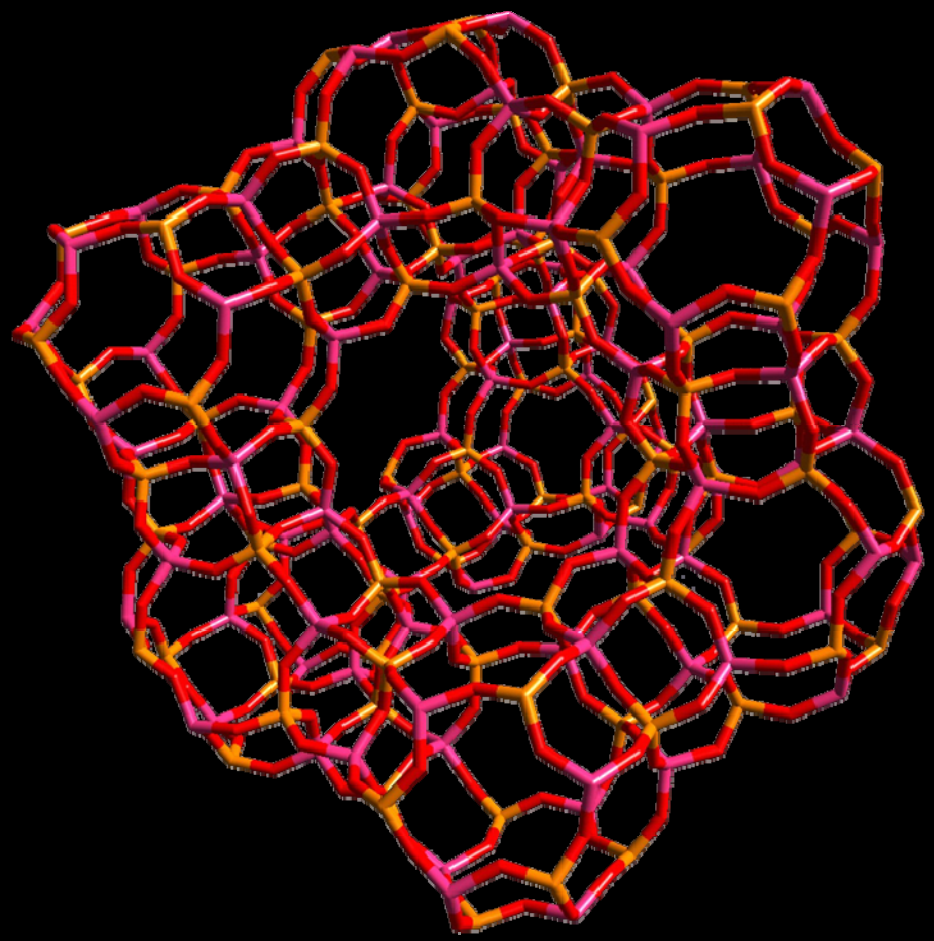
Zeolites are minerals, microporous and crystalline, made of aluminium and silicon.

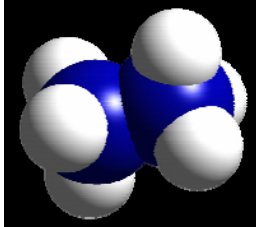


Properties

- ✓ **Sieving**

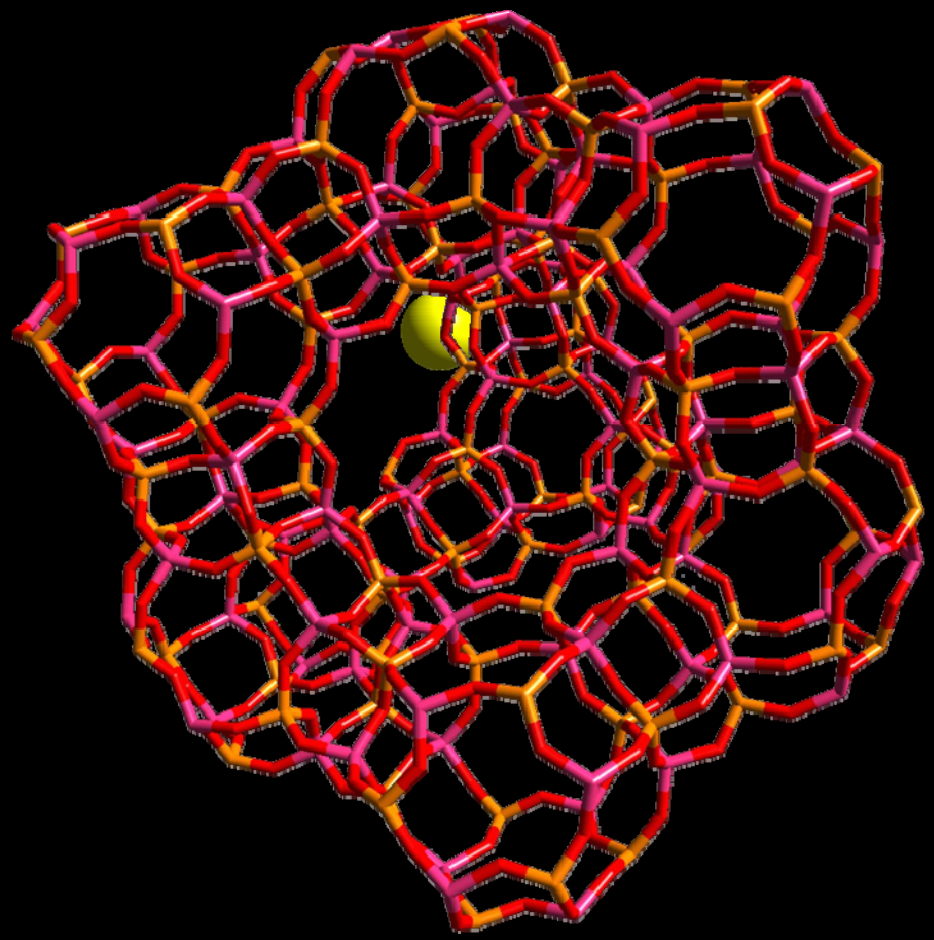


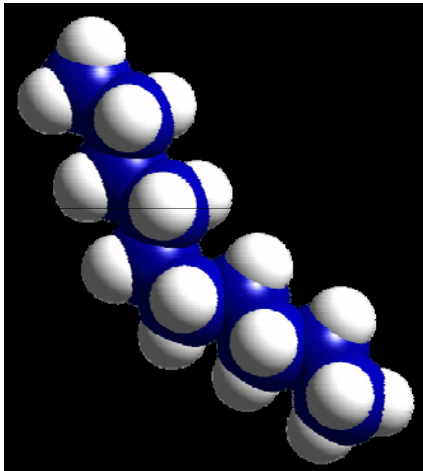




Properties

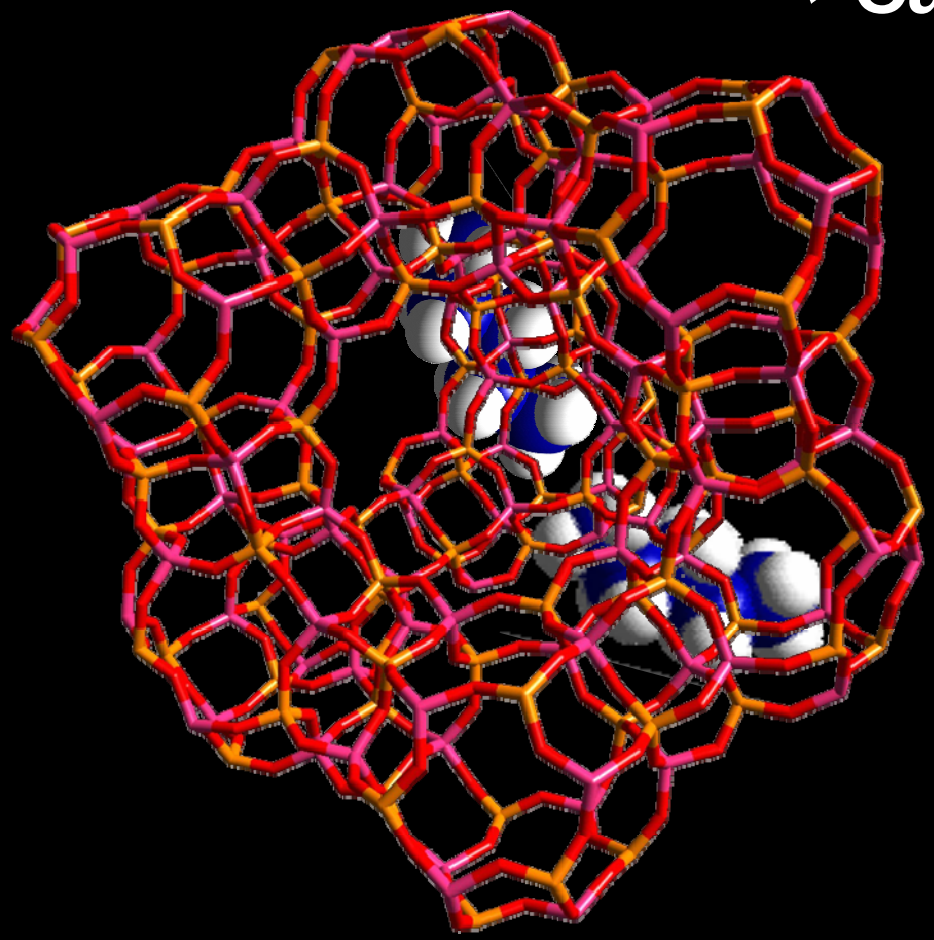
- ✓ **Sieving**
- ✓ **Cation exchange**





Properties

- ✓ **Sieving**
- ✓ **Cation exchange**
- ✓ **Catalysis**



BBC NEWS

Fuel p

NEWS

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Oil price dips below $90 a ba

Oil prices have fallen to an eight-month low of le
barrel.

Analysts say the decline reflects concern that the financial crisis in the US and Europe will lead to a global slowdown and a drop in demand for oil.

US crude settled down $6.07 at $87.81 a barrel after hitting an eight-month low of $87.56. London Brent crude fell $6.57 to $83.68.

Shares on Gulf stock markets also fell sharply. Banks and building contractors were among those shares hardest hit.

The Saudi Arabian stock market, the largest in the Arab world, dropped more than 9%.

Other markets saw falls of between 4% and 6% - Dubai was 4.5% down, Abu Dhabi and Qatar 4%, while Kuwait shed 3.5% and Oman dipped 6%.

When the last oil well runs dry

By Alex Kirby
BBC News Online environment correspondent

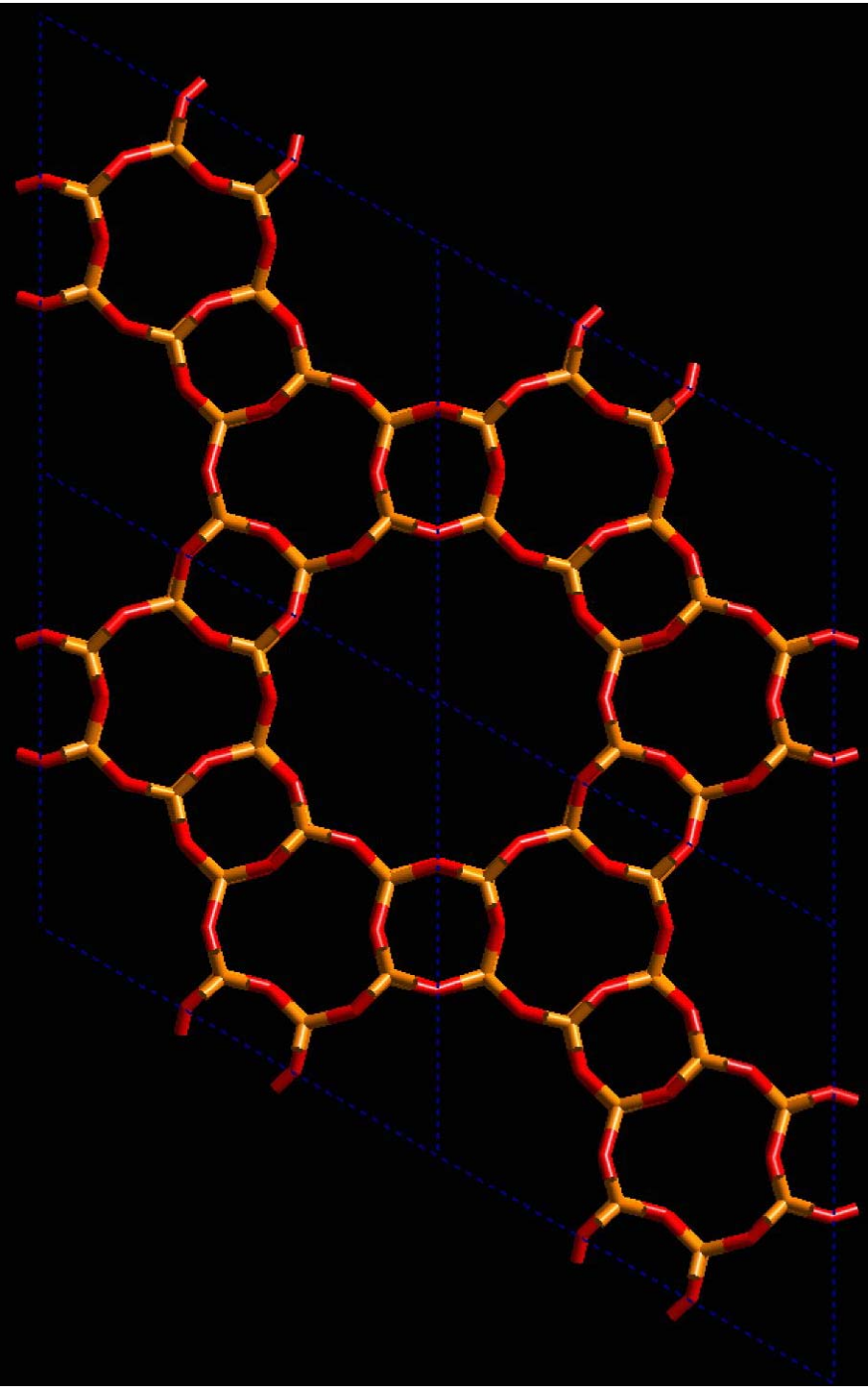
Just as certain as death and taxes is the knowledge that we shall one day be forced to learn to live without oil.

Exactly when that day will dawn nobody knows, but people in middle age today can probably expect to be here for it.

Sunset industry? Oil production could soon peak

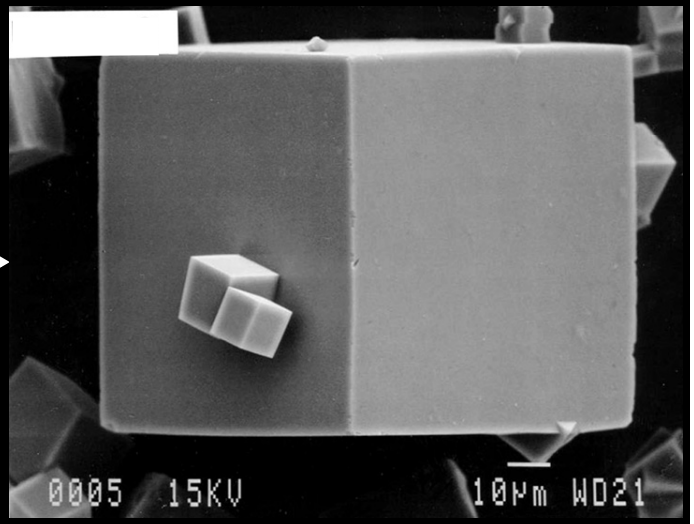
Objective

Analyse the mechanism of self-assembly in the zeolite synthesis.

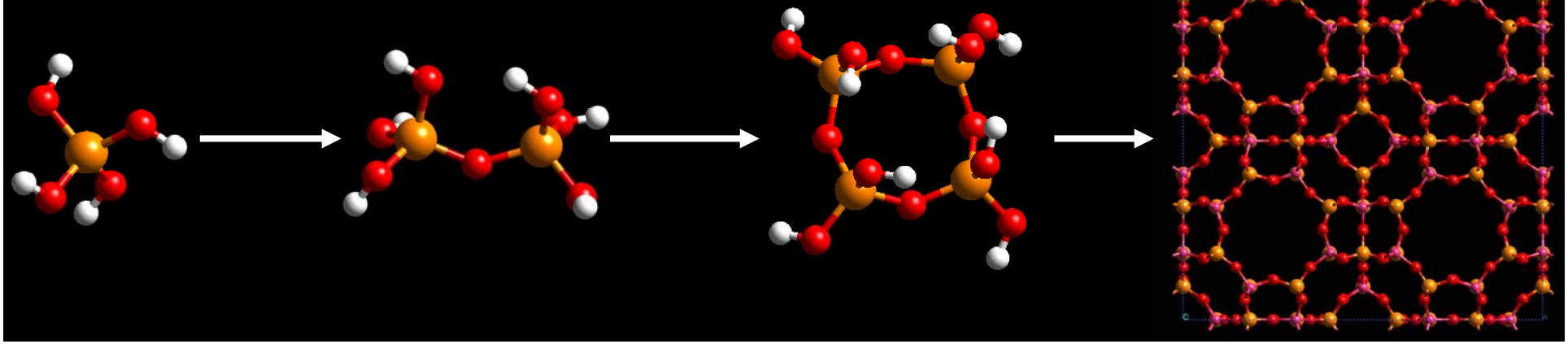


Zeolite synthesis

Raw material

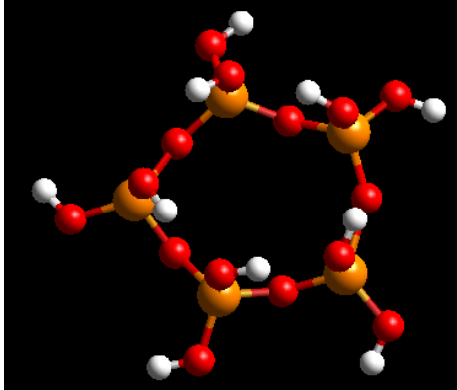


Minutes – days, 80°C-200°C, Very alkaline



The method

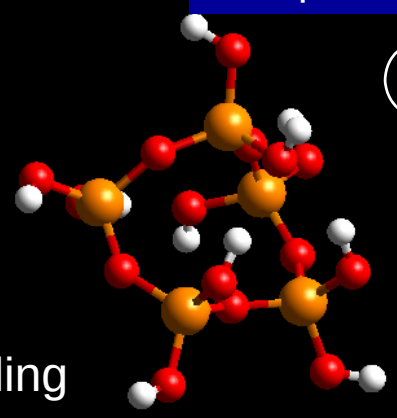
Computational Quantum Chemistry



1

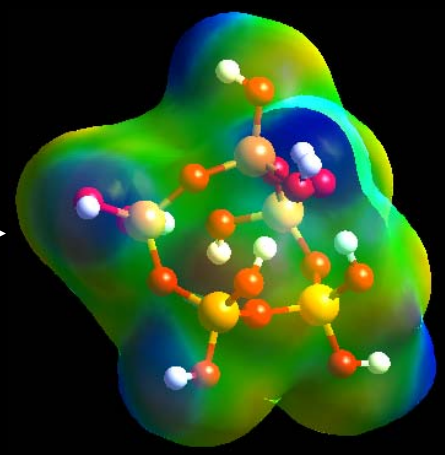
Simulated annealing
Local DFT PWC/Min
Molecular Dynamics
T_{max}=700 K
T = 1016.4 fs

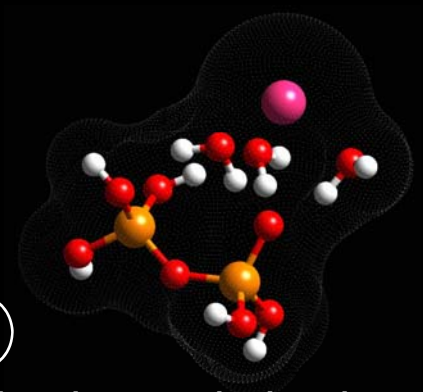
Gas phase



2 Optimization
Nonlocal DFT, BLYP/DNP
Full optimization without symmetry
Convergence criteria: Energy, 1 mHartree
Gradient, 100 mHartree/Bohr
Displacement, 100 mBohr

Solvation





3

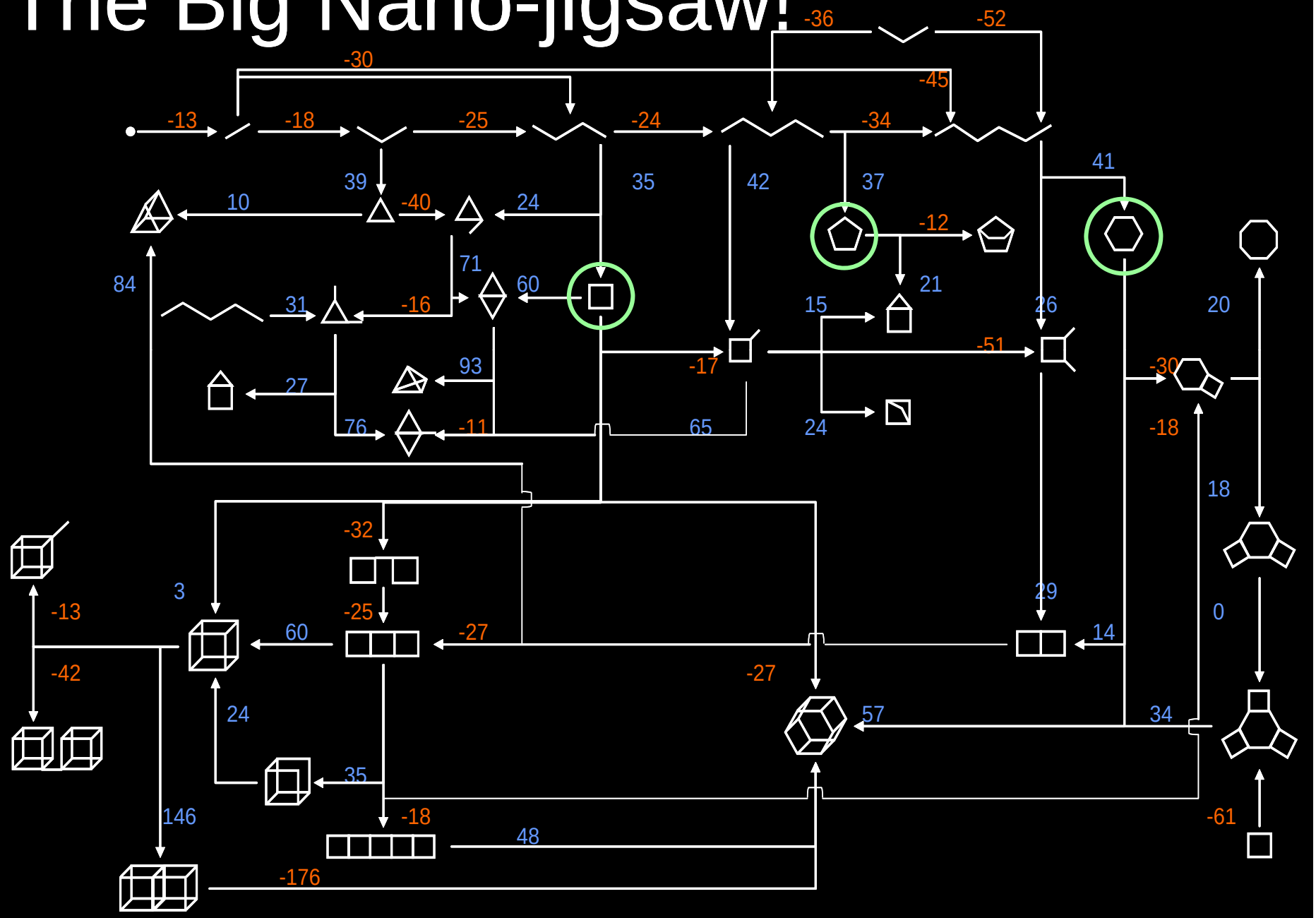
Solvation optimization
(COSMO)
Nonlocal DFT, BLYP/DNP

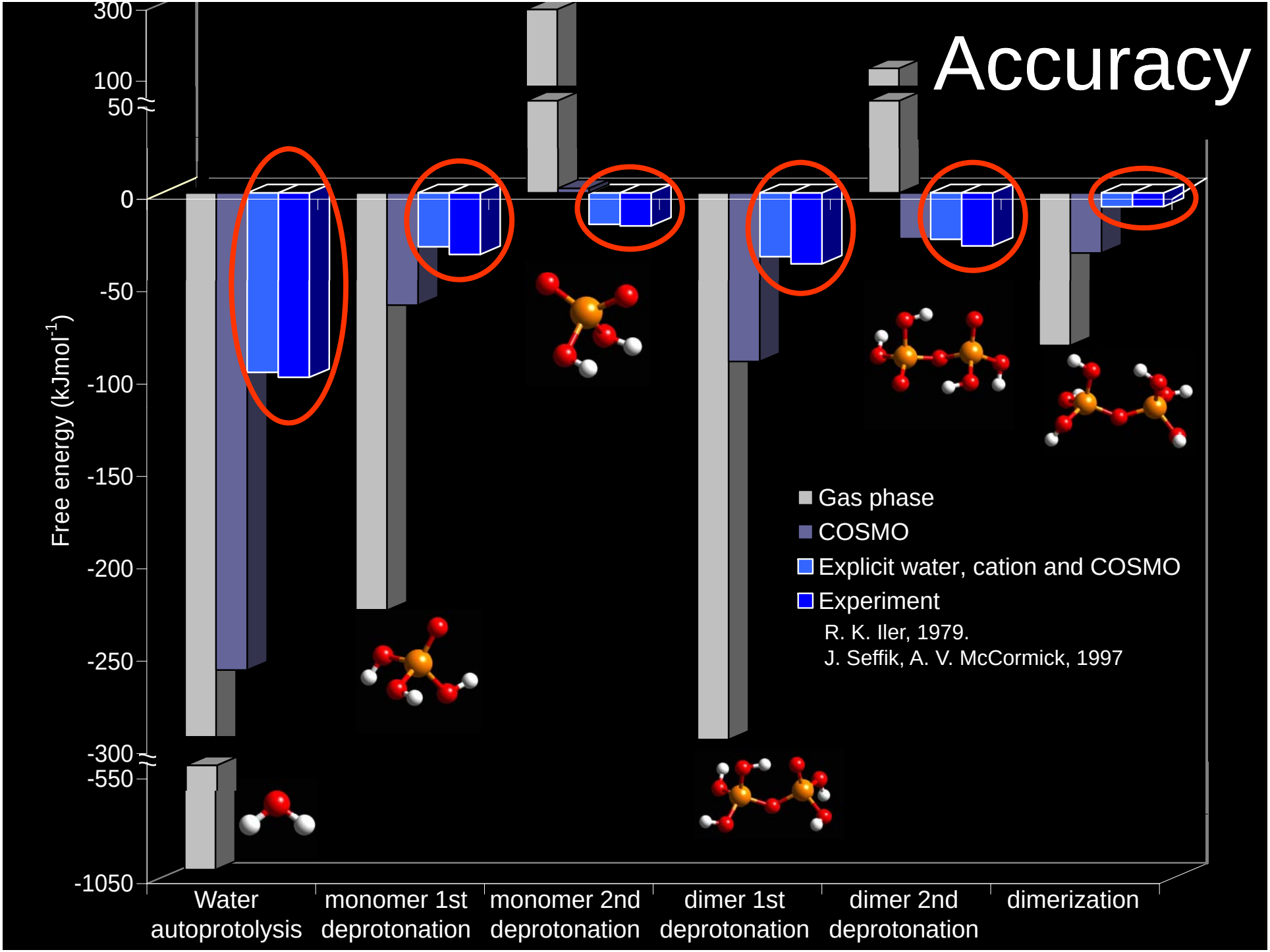
4 **Statistical Mechanics Calculation of Thermodynamic properties**
$G = (E+ZPE+E_{t,v,r}) - TS$

Results

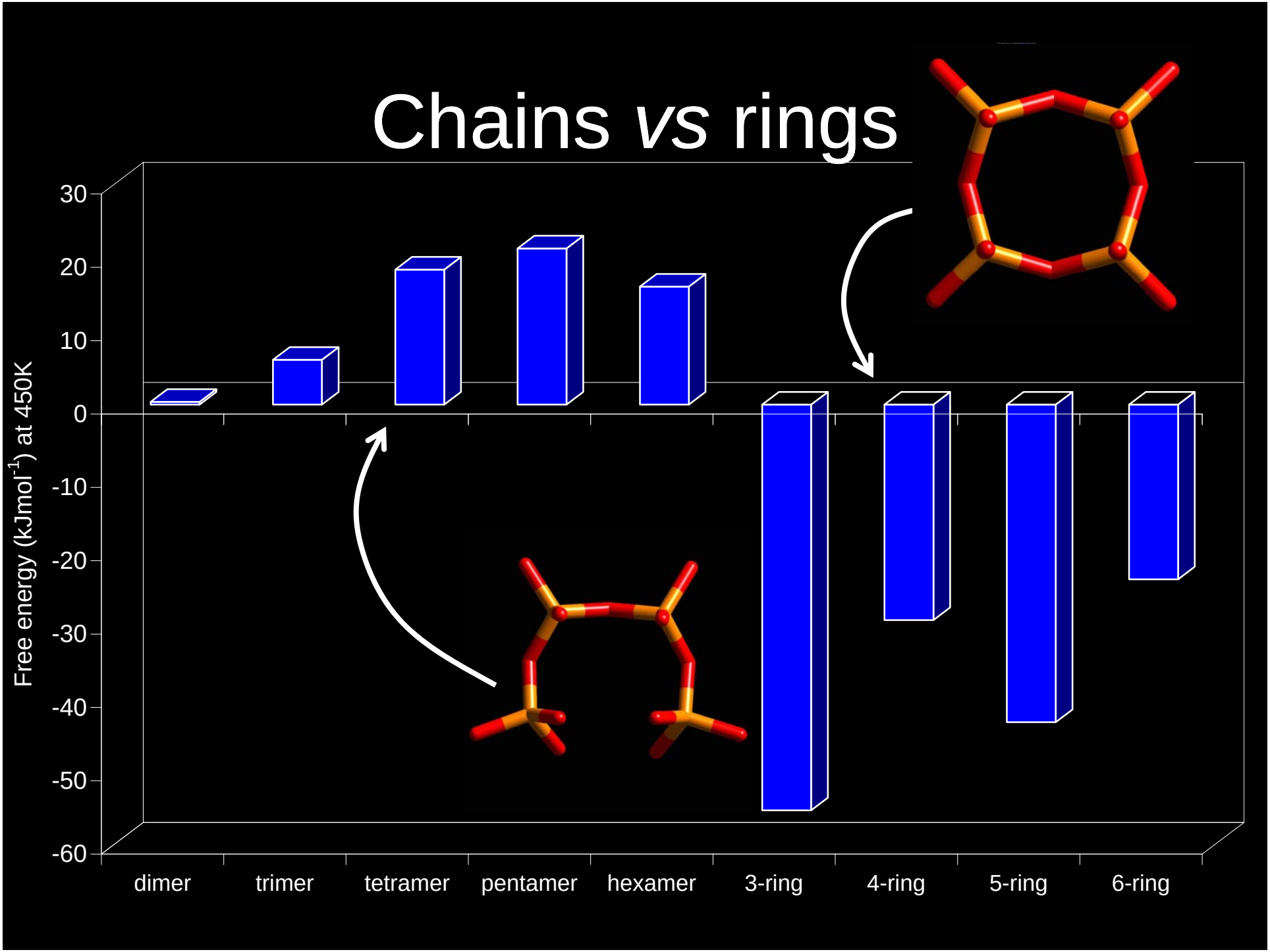
- Method Accuracy
- Rings vs Chains
- Ring specificity
- Physical interactions

The Big Nano-jigsaw!



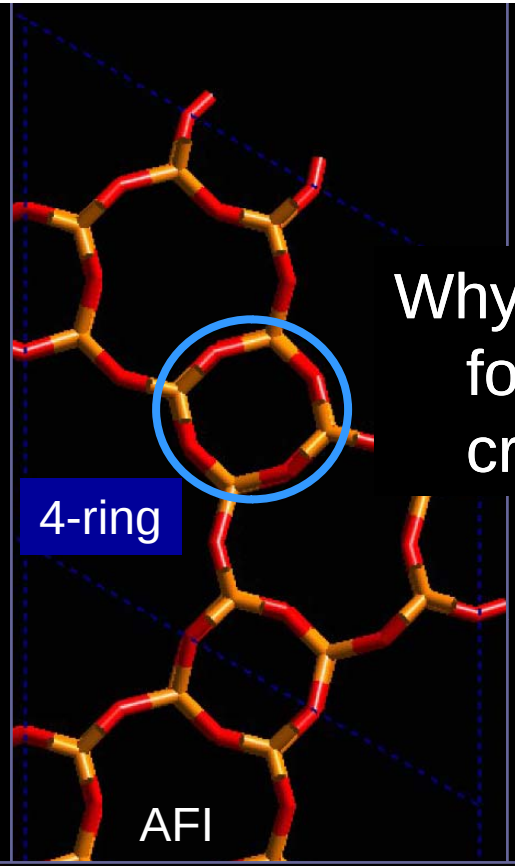

Accuracy
Free energy (kJmol-1)
300
100
50
0
-50
-100
-150
-200
-250
-300
-550
-1050
Gas phase
COSMO
Explicit water, cation and COSMO
Experiment
R. K. Iler, 1979.
J. Seffik, A. V. McCormick, 1997
Water autoprotolysis
monomer 1st deprotonation
monomer 2nd deprotonation
dimer 1st deprotonation
dimer 2nd deprotonation
dimerization

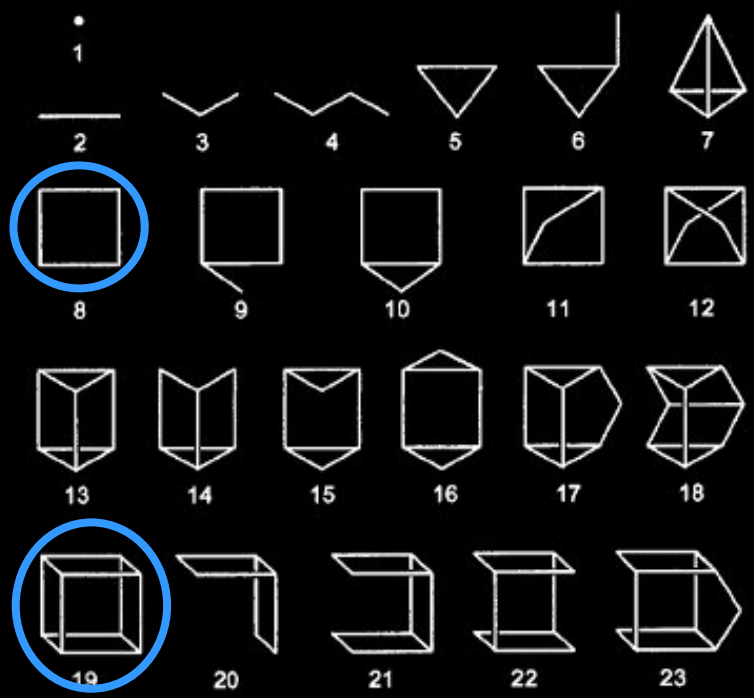
Chains *vs* rings



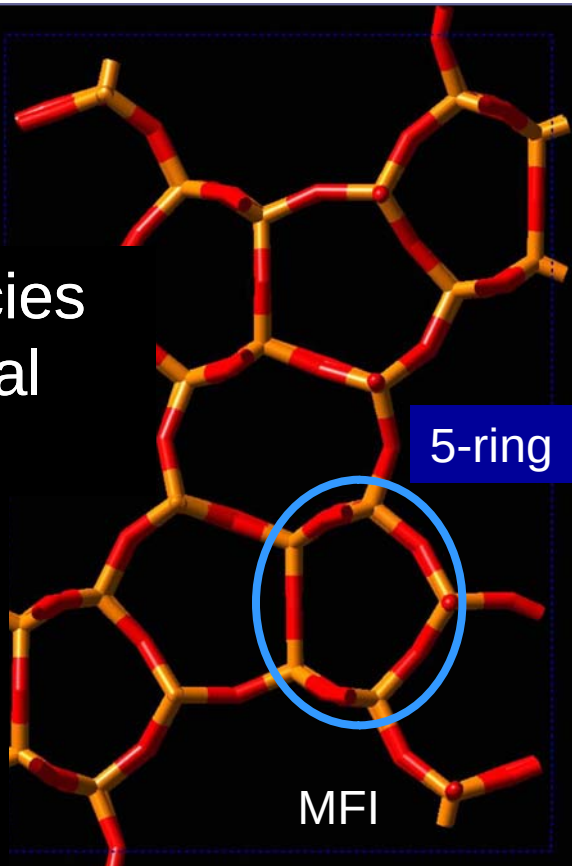
Which ring?

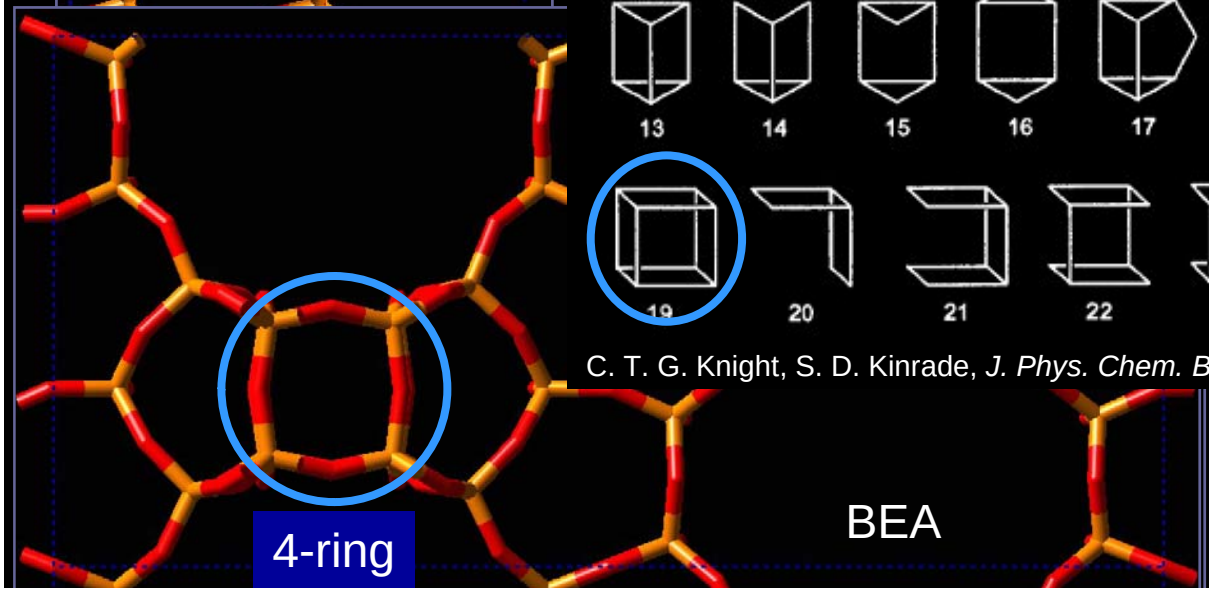
Why are some of the cyclic species found in solution not in the final crystal?

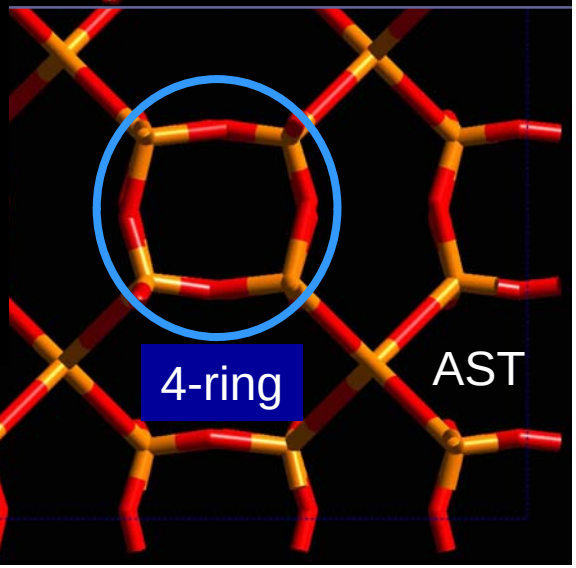




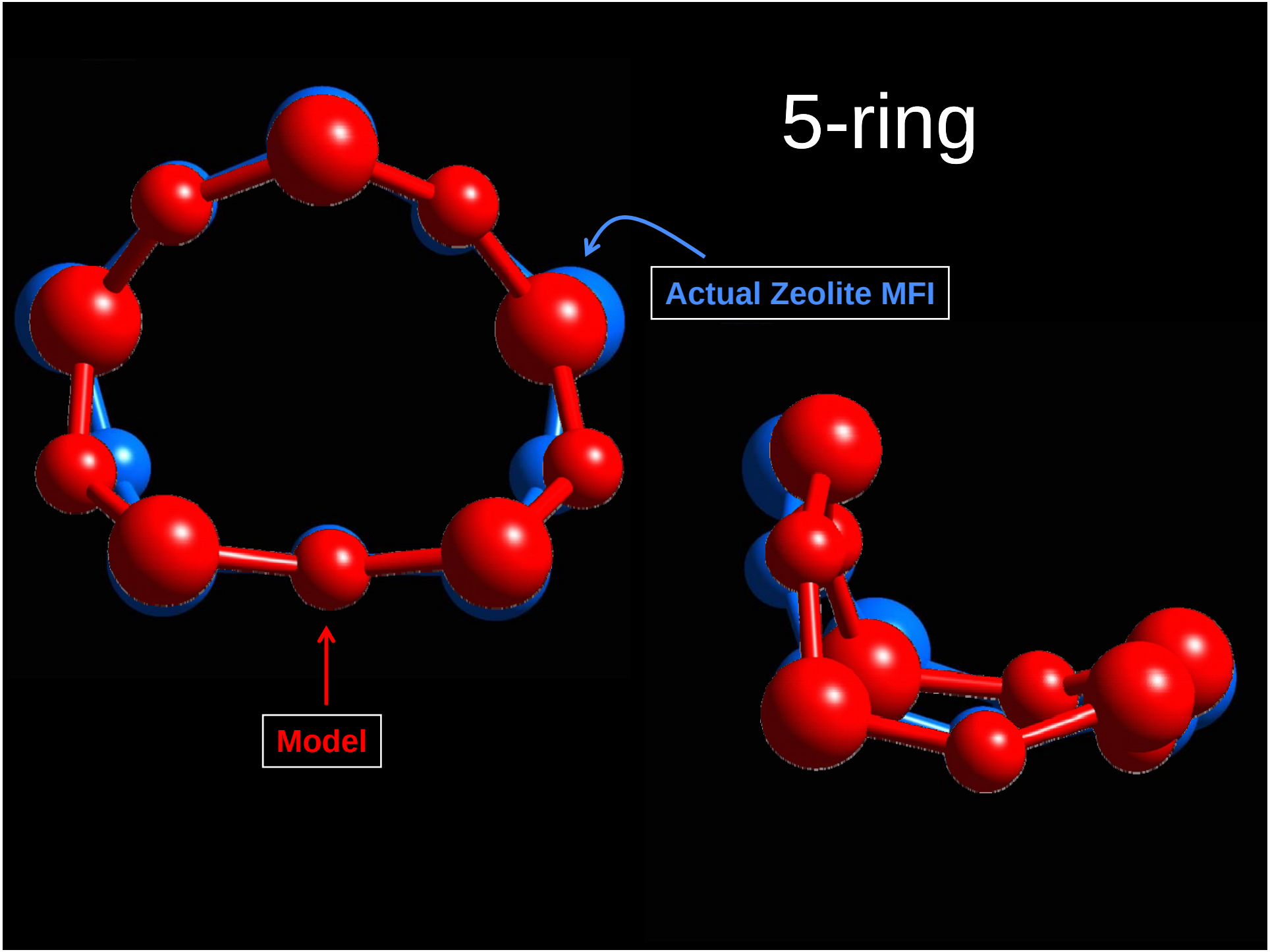
C. T. G. Knight, S. D. Kinrade, *J. Phys. Chem. B.* **2002**.



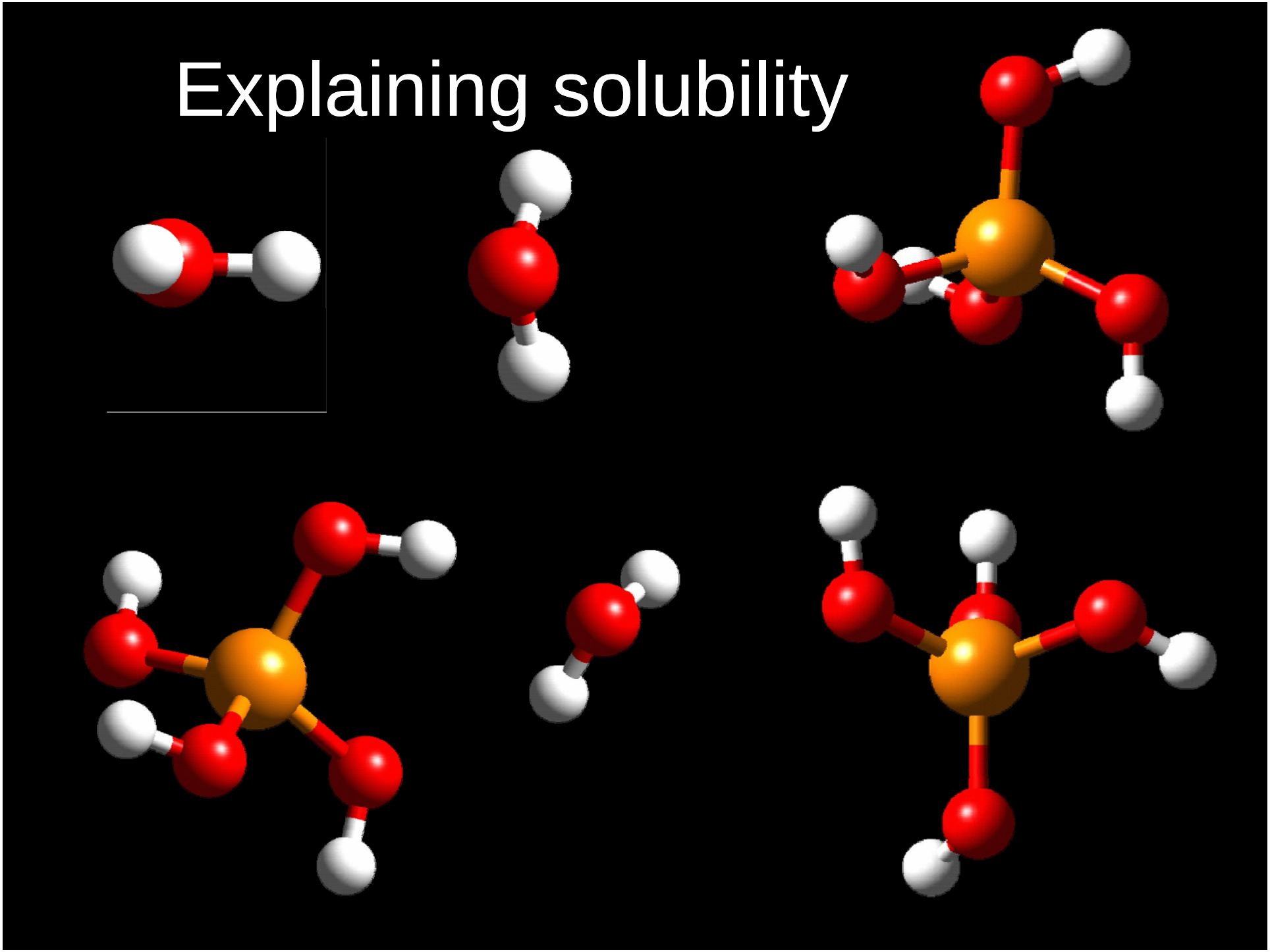




5-ring



Explaining solubility



Conclusions

- Theoretical methods reproduce experimental results accurately.
- Ring formation more favourable than linear, depending free energy and alkalinity.
- Type of ring structure formed during zeolite nucleation dependent on alkalinity and temperature.
- Computational approach models zeolite nucleation reliably.

M. J. Mora-Fonz, C. R. A. Catlow, D. W. Lewis, *Angewandte Chemie,* 2005, *44*, 3082.
M. J. Mora-Fonz, S. Hamad, C. R. A. Catlow, *Molecular Physics* 2007, *105*, 177.
M. J. Mora-Fonz, C. R. A. Catlow, D. W. Lewis, *Journal of Physical Chemistry C* 2007, *111*, 18155.
M. J. Mora-Fonz, C. R. A. Catlow, D. W. Lewis, *Physical Chemistry Chemical Physics* 2008.

Acknowledgements

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