Two-to-three dimensional transition in neutral gold clusters: the crucial role of van der Waals interactions and temperature

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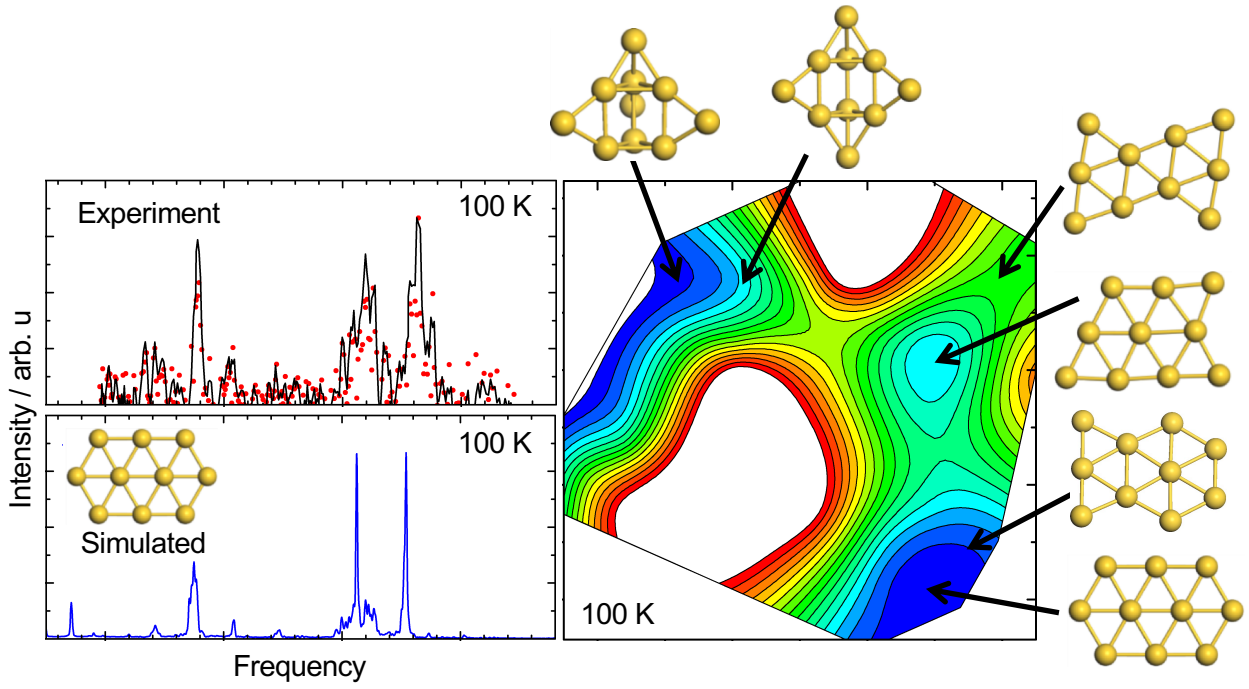
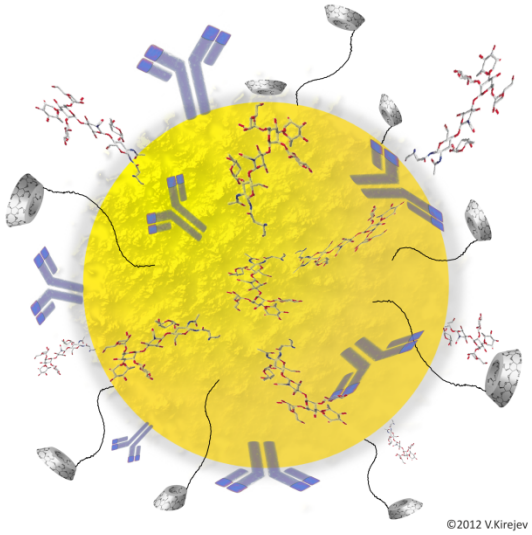
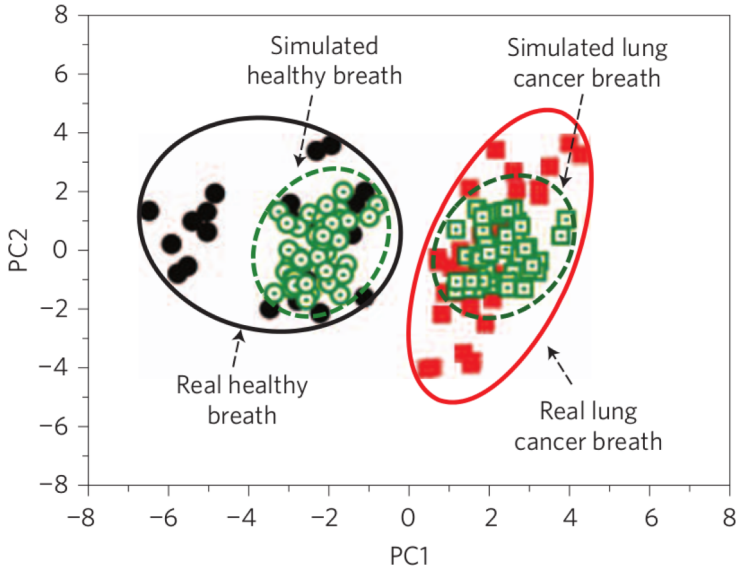


Metal clusters display interesting phenomena and are technologically useful

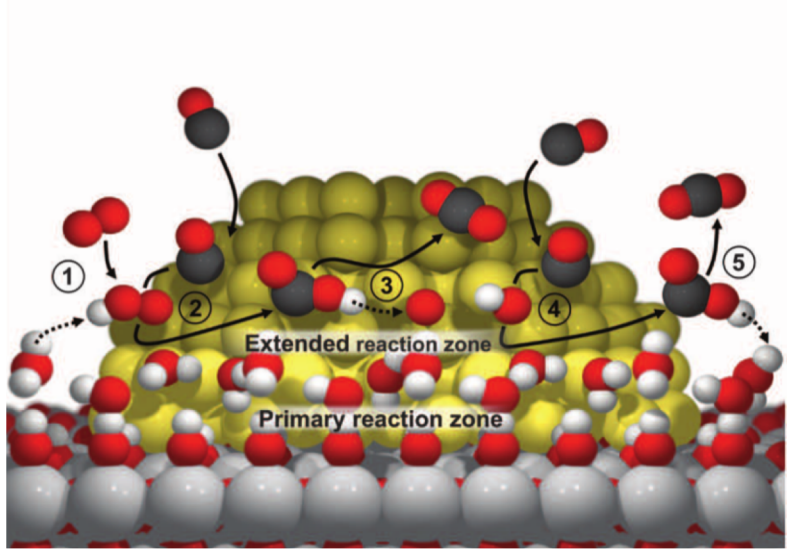
J. West and N. Halas, *Annu. Rev. Biomed. Eng.* 5, (2003)



P. Ghosh *et al., Adv. Drug Deliv. Rev.* 60, (2008)

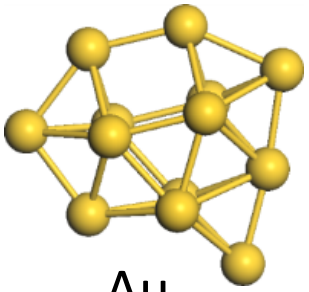


G. Peng *et al.*, *Nature Nano.* 4, (2009)



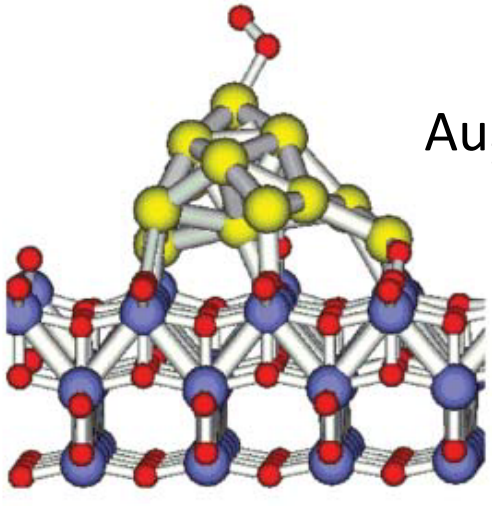
J. Saavedra *et al., Science* 345, (2014)

Knowledge of free clusters gives insight into fundamental processes



Au_{13}

Structure-property relationships
Catalytic properties
Charge state
Relativistic effects



$Au_{13} / TiO_2 + O_2$

Support affects cluster reactivity and other properties

[1] S. Arrii *et al., J. Am. Chem. Soc.* 126, (2014)
[2] L. M. Ghiringhelli *et al., New J. Phys.* 15, (2013)
[3] M. Boronat and A. Corma, *Dalton Trans.* 39, (2010)
[4] A. Fielicke *et al.*, *J. Chem. Phys.* 122, (2005)

In this talk, we address a number of questions:

1) What gold cluster structures are present at finite temperature (Au_5 to Au_{14})?

2) At what size do gold clusters turn three-dimensional?

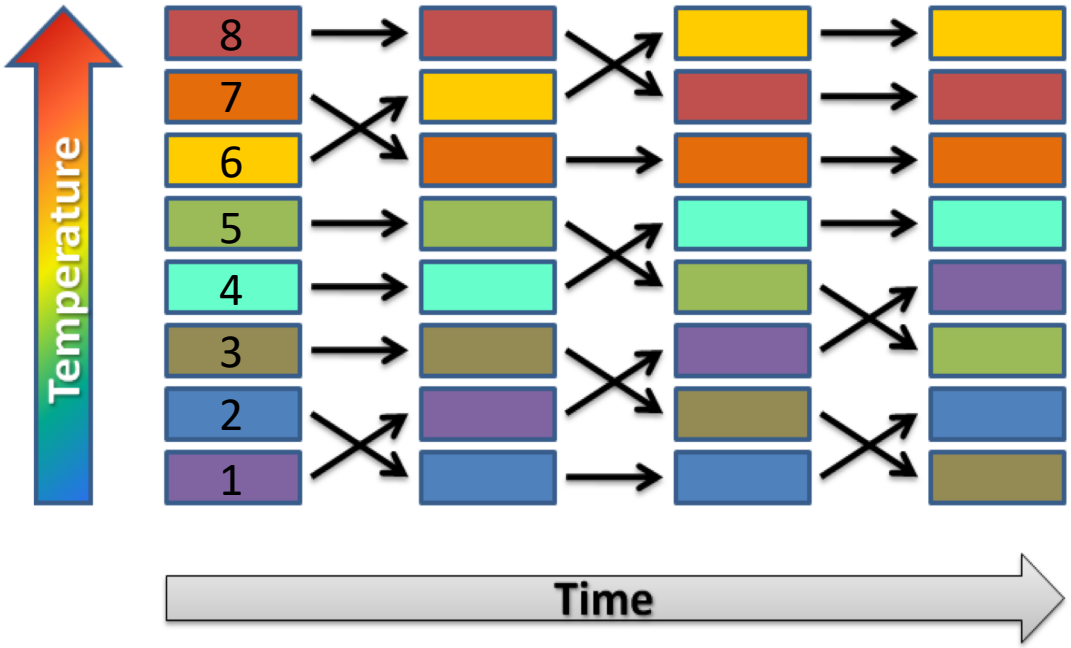
3) Influence of *intramolecular* van der Waals on cluster stability?

4) Importance of temperature on isomer populations?

5) Assign gold cluster structures with IR (Au_9, Au_{10}, Au_{12})

[1] E. C. Beret, L. M. Ghiringhelli, M. Scheffler, *Faraday Discuss*., 152, (2011)
[2] R. Zwanzig, *Acc. Chem. Res.* 23, (1990)

Replica Exchange Molecular Dynamics



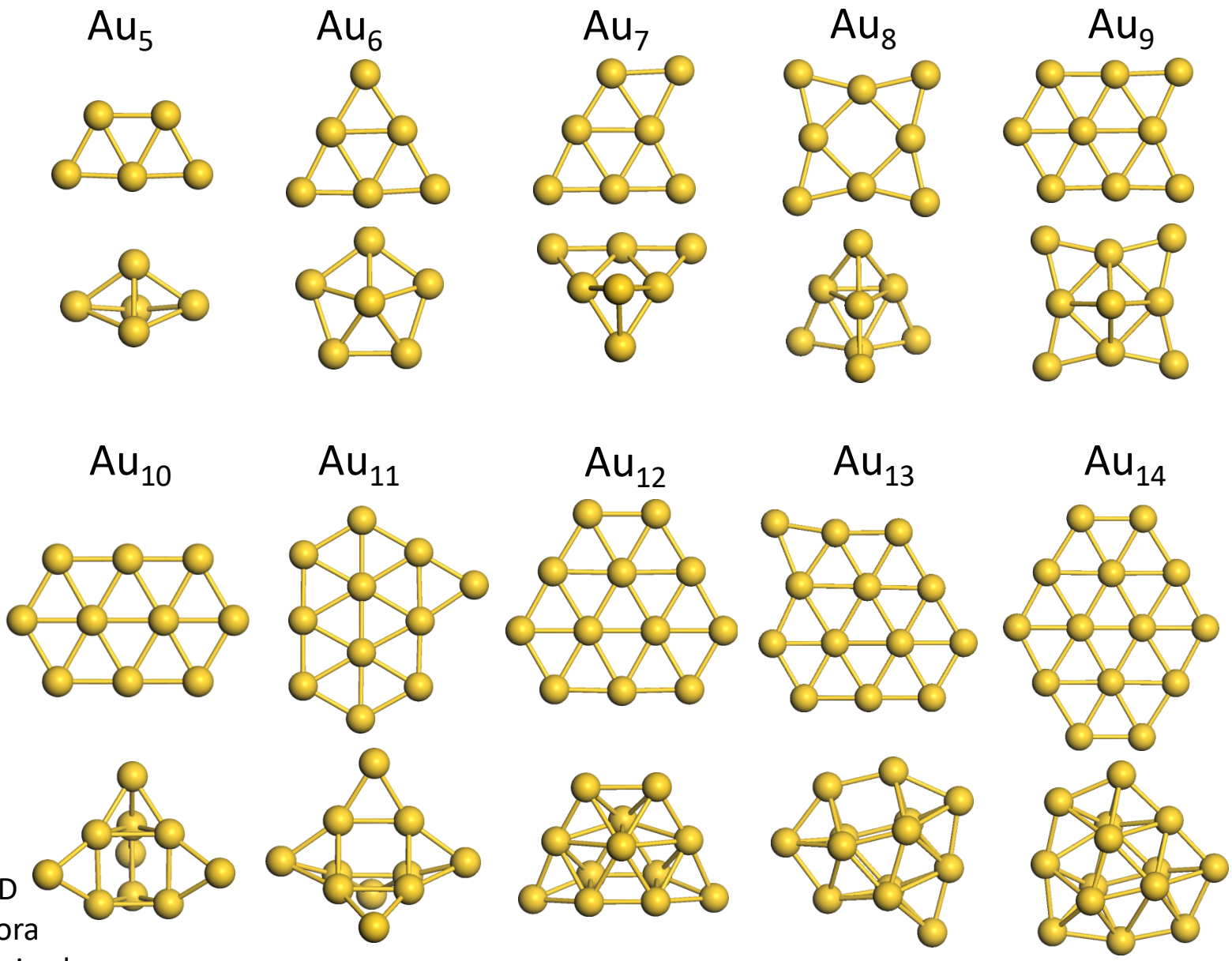
An enhanced, unbiased, sampling method

Simulated in the generalized canonical (NVT) ensemble

$$P_{exchange} = \min\left[1, \exp\left(-\left(\frac{1}{k_B T_i} - \frac{1}{k_B T_j}\right)(U_i - U_j)\right)\right]$$

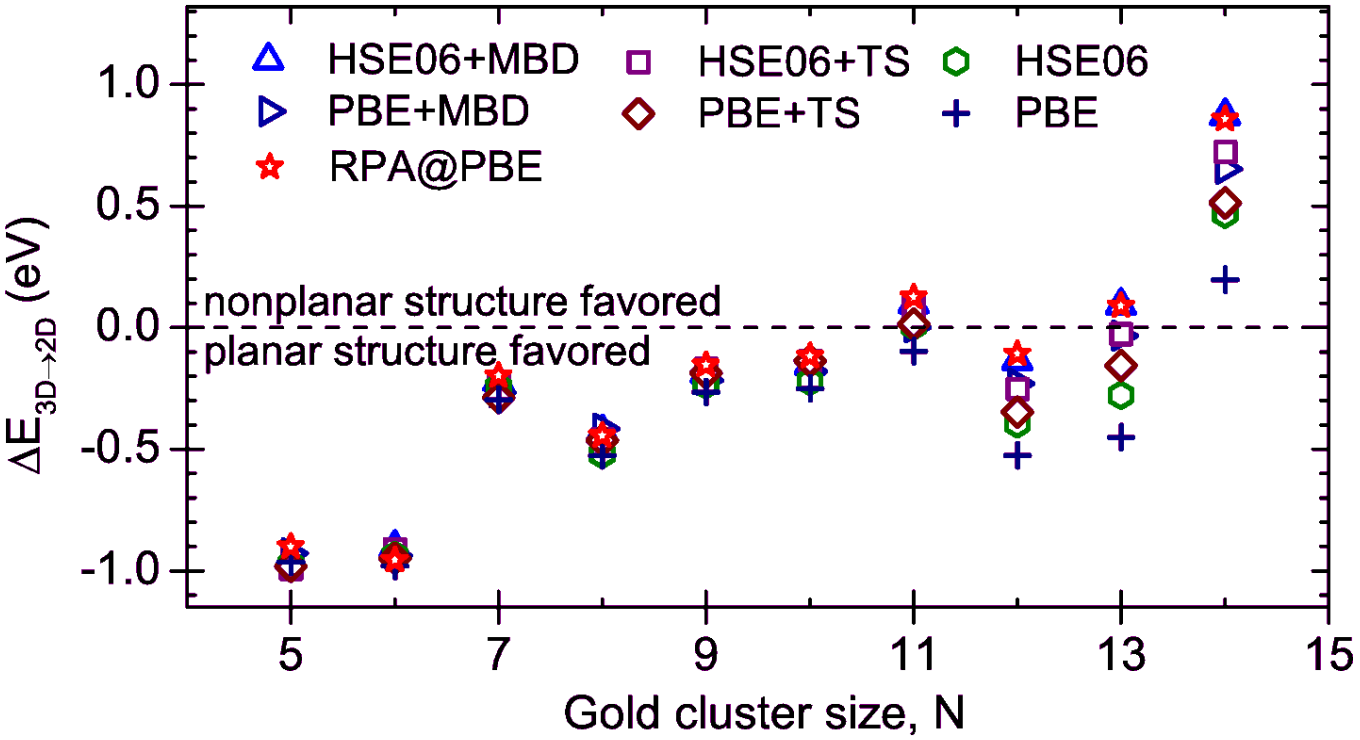
PBE + many body dispersion
atomic zora scalar relativistic correction
spin polarized, ‘light-tier 1’ settings

Lowest energy planar and nonplanar structures found at 0 K



PBE+MBD
atomic zora
spin polarized

Planar to three-dimensional ground state transition is size 11 at 0 K for neutral gold clusters



PBE+MBD agrees well with HSE06+MBD and RPA until Au_{13}

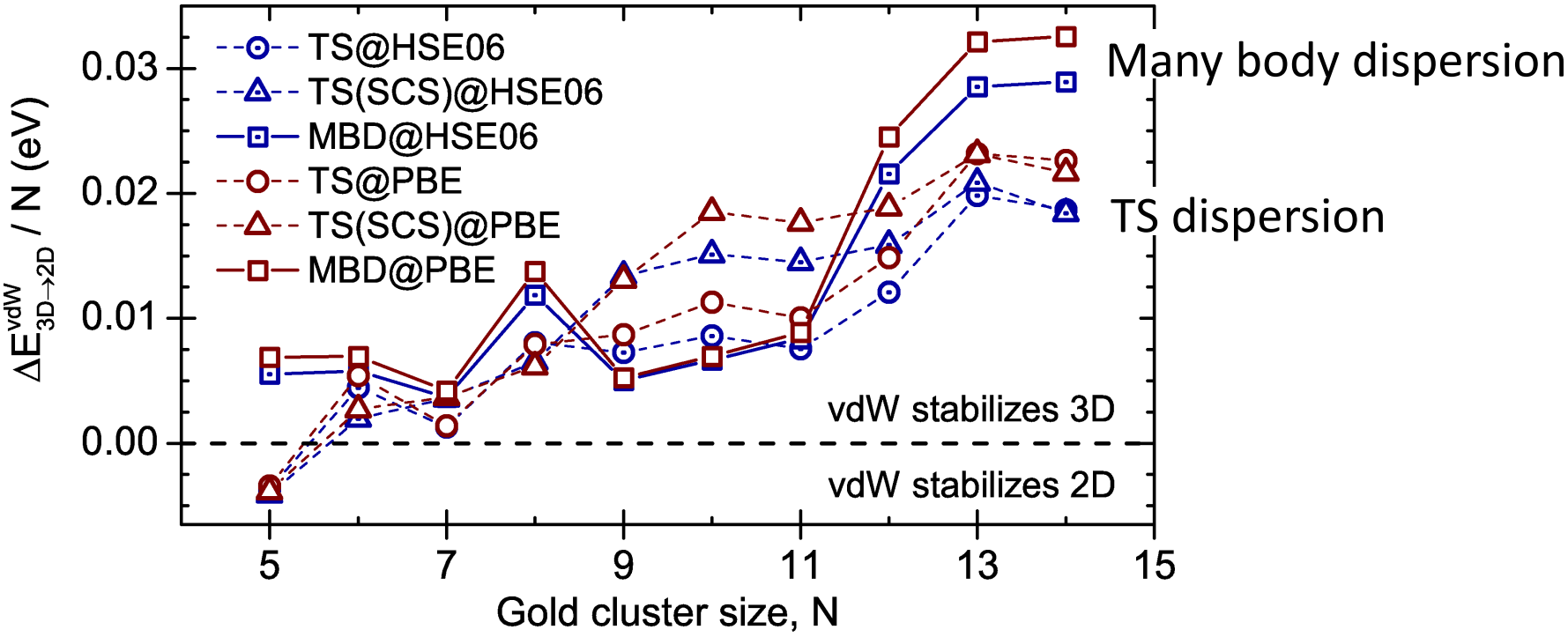
Crossover predicted at size 11 previously using RPA@TPSS[1]

MBD: Many body dispersion (screened long-range many-body vdW)

TS: Tkatchenko-Scheffler dispersion (pairwise interactions only)

[1] M. P. Johansson *et al., J. Phys. Chem. C* 118, (2014)

Three-dimensional isomers are more stabilized by *intra-cluster* dispersion than planar isomers

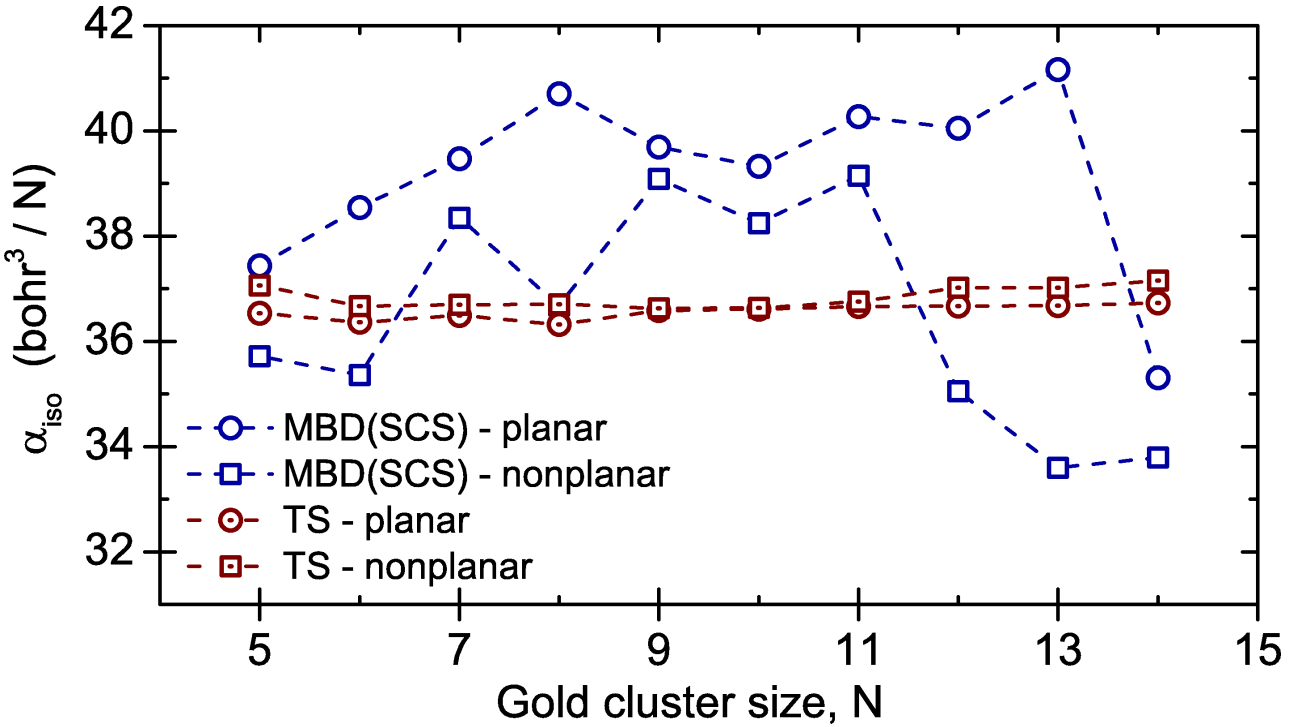


Dispersion is critical to predict correct isomer energetic ordering

Influence of dispersion on $\Delta E_{3D\rightarrow 2D}$ is larger than going from PBE to HSE06

TS: A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* 102, (2009)
MBD(rsSCS): A. Ambrosetti, A. M. Reilly, R. A. DiStasio Jr. and A. Tkatchenko, *J. Comp. Chem.* 140, (2014)

Planar isomers are more polarizable, but less stabilized by dispersion



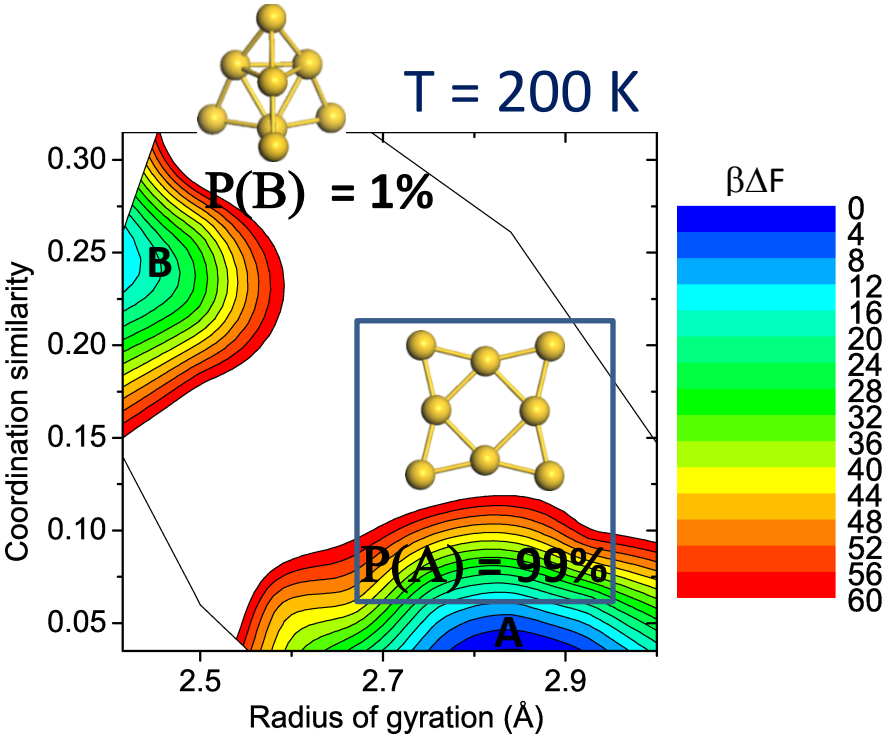
3D structures have more screening than 2D structures

Compact 3D structure leads to greater vdW stabilization

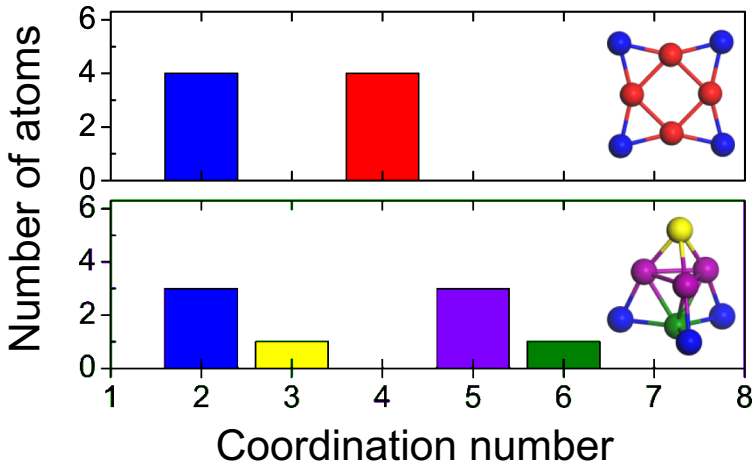
$$E_{\text{disp}} = -\sum_{j>i} f_{\text{damp}}\left(R_{ij}\right)\frac{C_{6ij}}{R_{ij}^{6}}$$

Screening of interior atoms in Na clusters
[1] Li Ma *et al. Phys. Rev. B* 89, 035429, (2014)

Au_8 free energy surface from replica-exchange MD



Coordination similarity

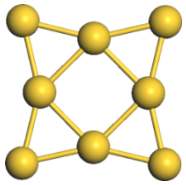


Mean relative bin error = 7.6%

Mean bin error = 1.1 k_BT = 19 meV

3 ns total per simulation

Boltzmann Probability, P



Structure experimentally assigned at 100 K

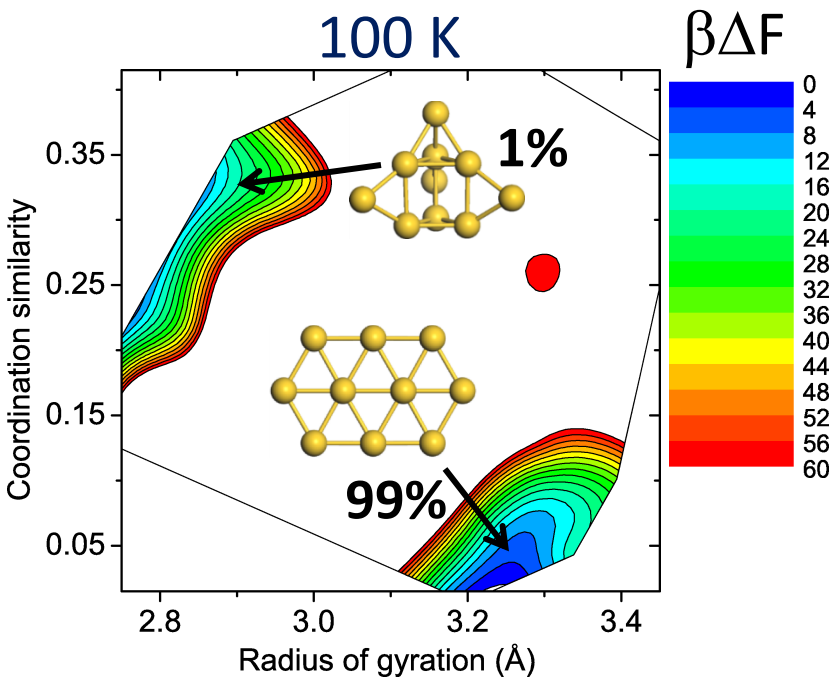
P. Gruene *et al Z. Phys. Chem.* 228, (2014)

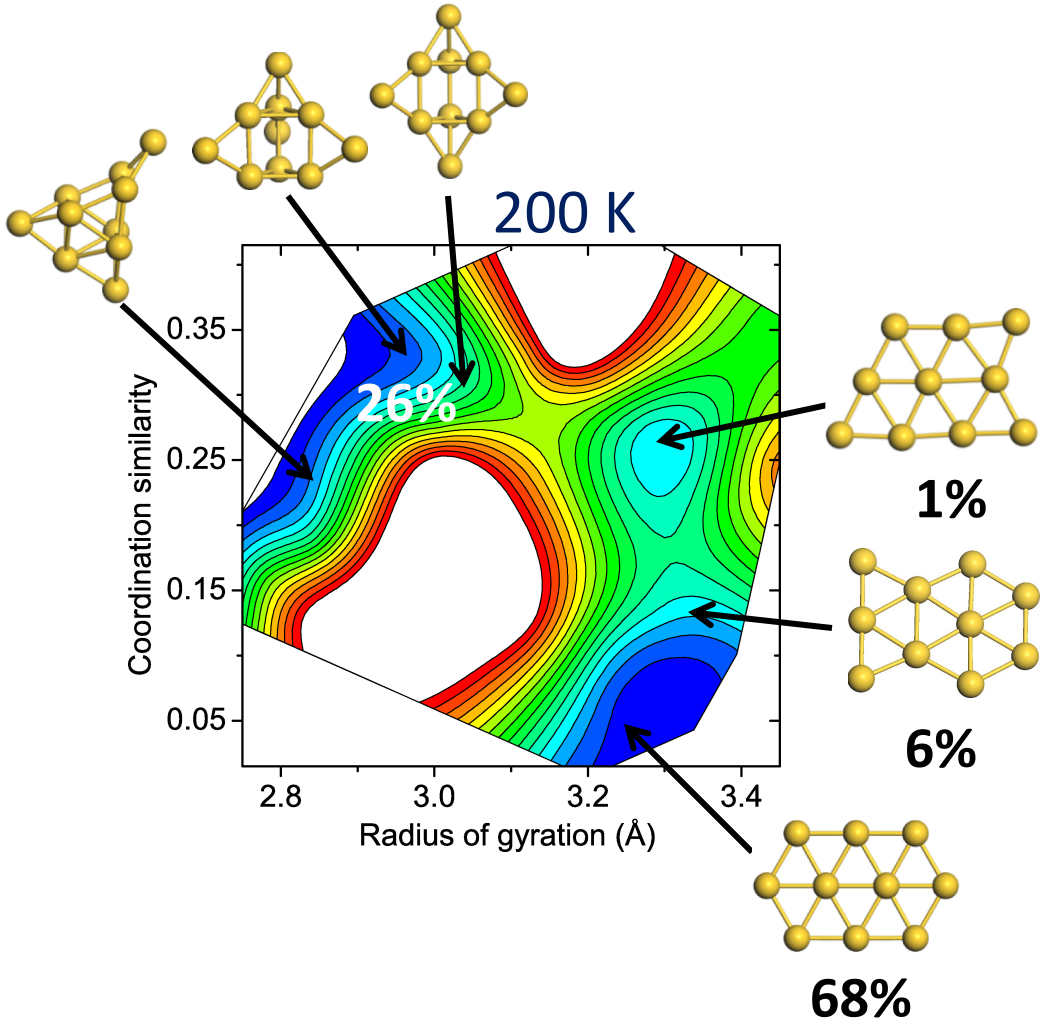
[1] *Multistate Bennett Acceptance Ratio:* M. R. Shirts and J. D. Chodera, *J. Chem. Phys*. 129, (2008)

[2] *Coordination similarity:* A. R. Oganov and M. Valle, *J. Chem. Phys.* 130, (2009)

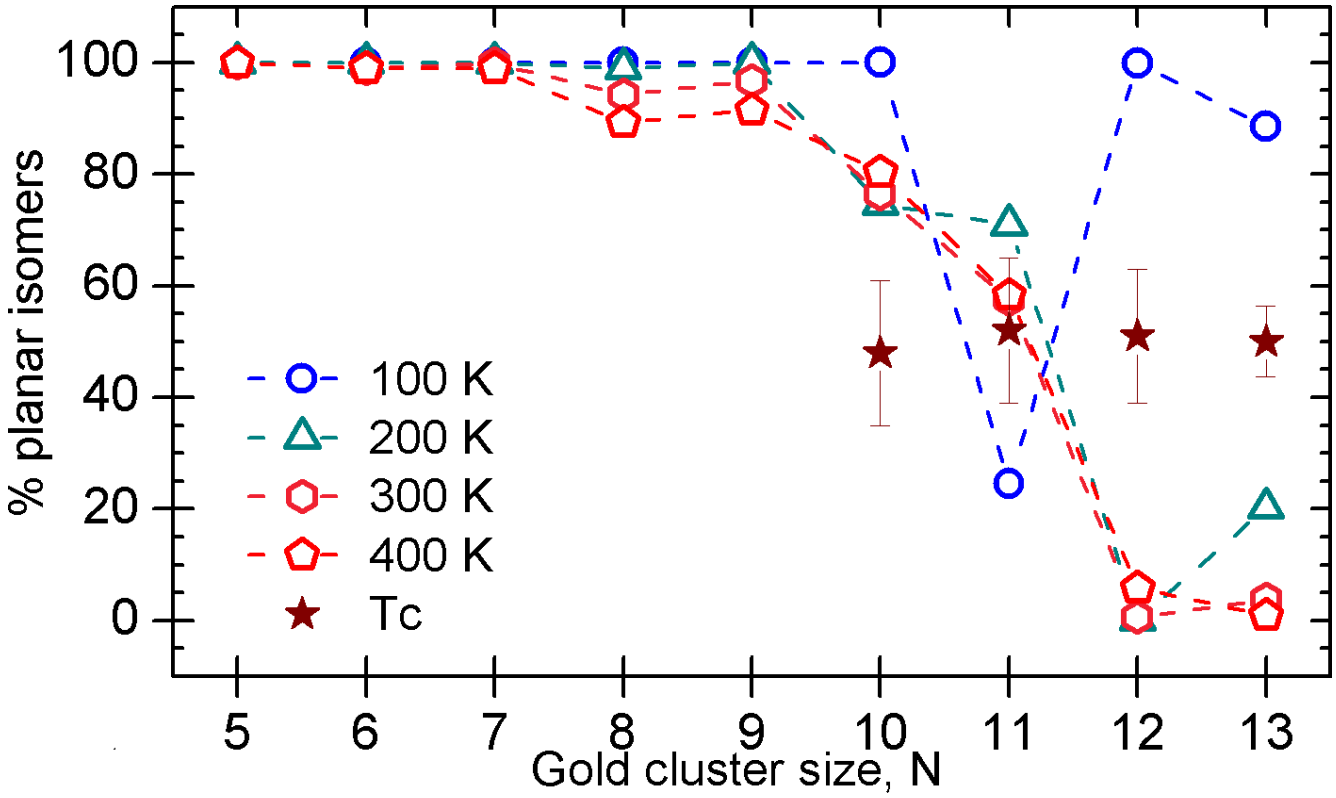
[3] *Radius of gyration:* G. Santarossa *et al., Phys. Rev. B.* 81, (2010)

Free energy surface of Au_{10} displays multiple isomers above 100 K





The configurational entropy of 3D structures is typically larger compared to planar structures



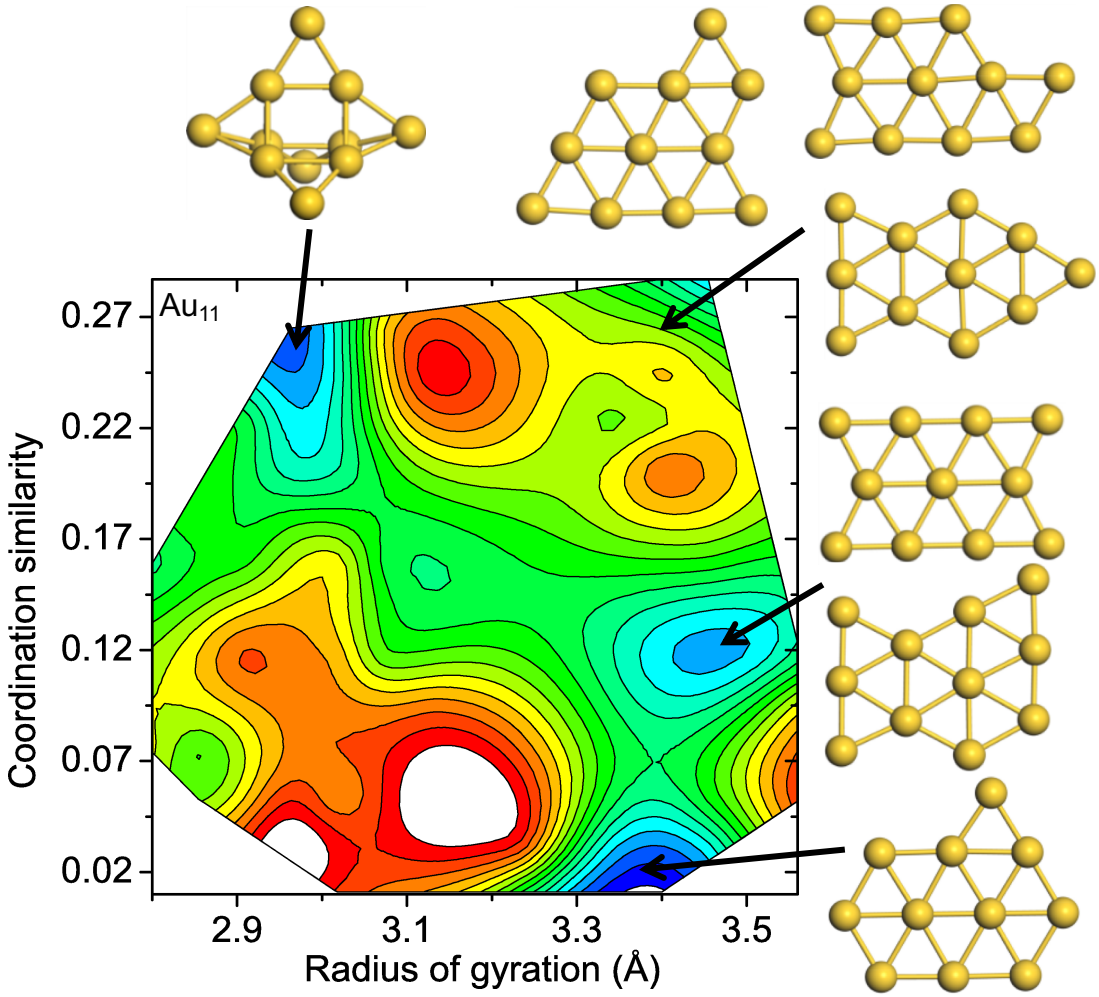
Au_{11} is exceptional case due to conformational entropy of planar structures

Typically fraction of 3D structures increases as size ↑ and temperature ↑

Au_{12} is ~50% planar at 300 K [1]

[1] G. Santarossa *et al., Phys. Rev. B.* 81, (2010)

The configurational entropy of 3D structures is typically larger compared to planar structures



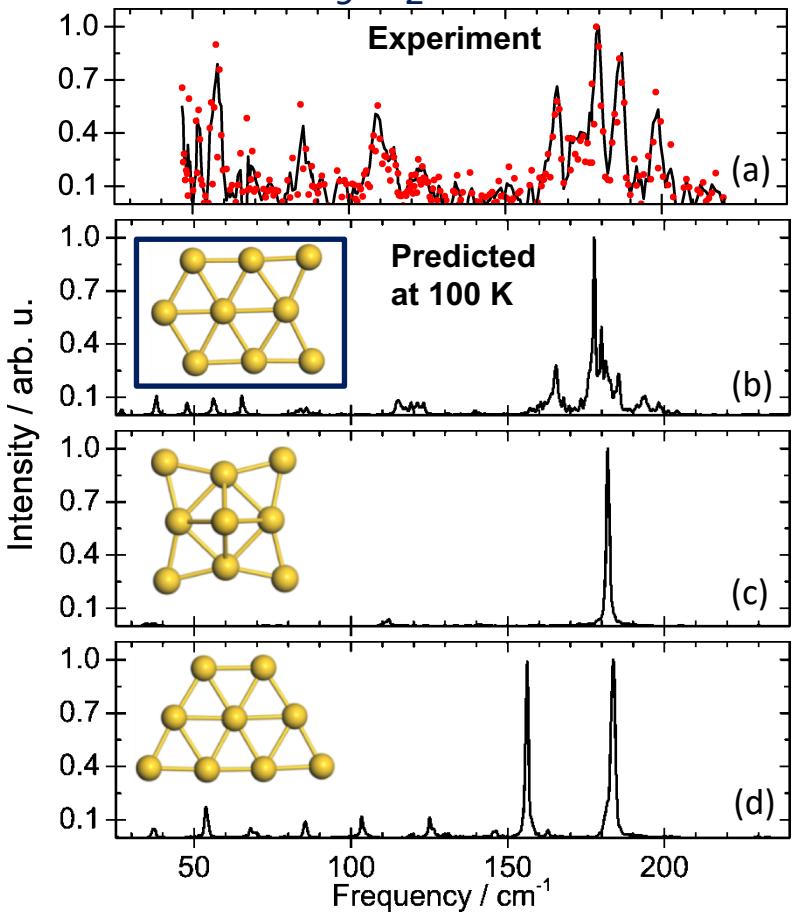
IR structural assignment of Au_9 via experiment and theory

Past experimental structure determination

Au_4-Au_8: P. Gruene *et al. Z. Phys. Chem.* 228, (2014)

Au_7, Au_{19}, Au_{20}: P. Gruene *et al. Science* 321, (2008)

Au_9Kr_2 at 100 K

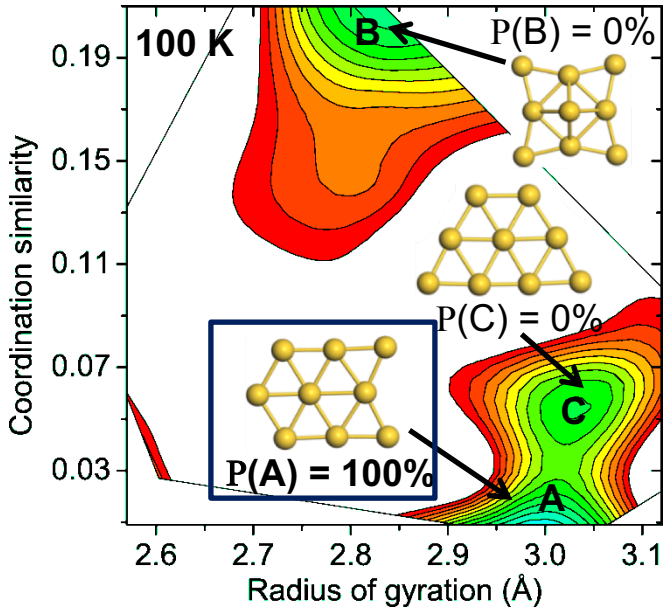


Free Kr atom not shown

100 ps/trajectory, PBE+MBD, 'tier2-tight'

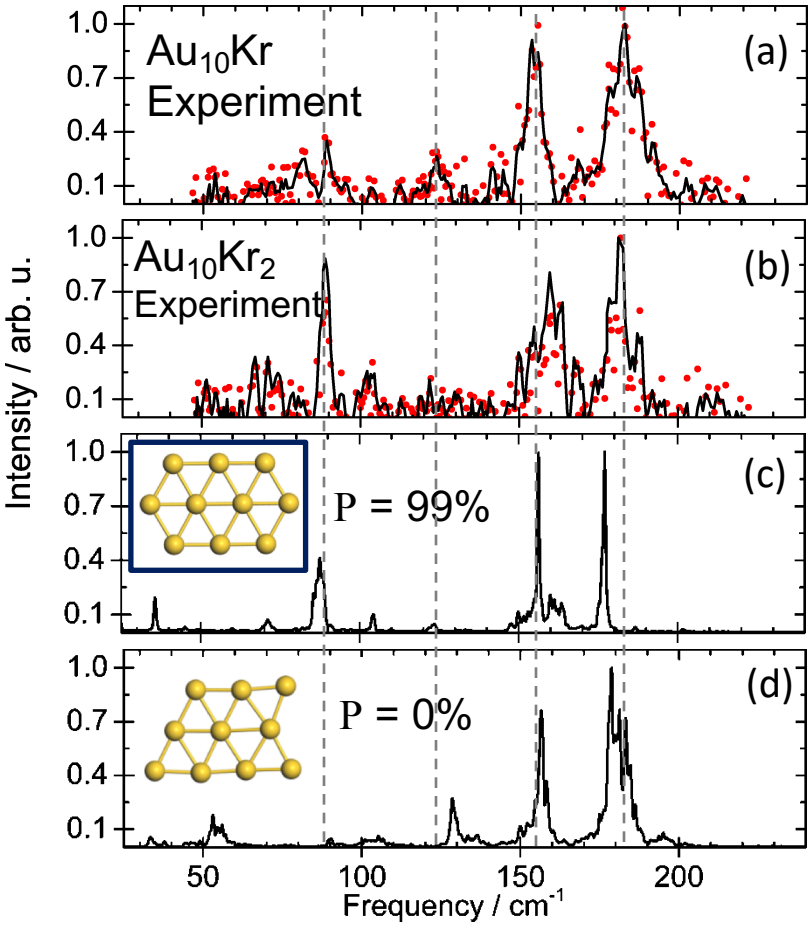
IR spectra obtained via molecular dynamics

$$I(\omega) \propto \beta\omega^2 \int_0^\infty \mathrm{d}t \left\langle \vec{M}(t) \cdot \vec{M}(0) \right\rangle_{NVT} \exp(\mathrm{i}\omega t)$$

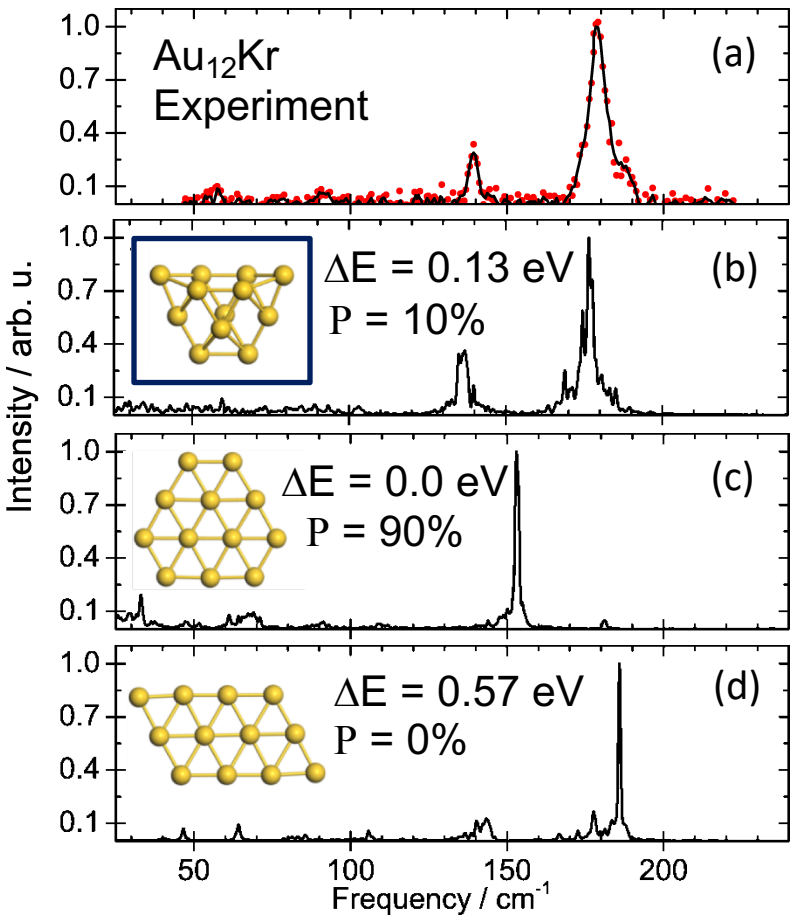


Structural assignment of Au_{10} and Au_{12}

T = 100 K



T = 100 K



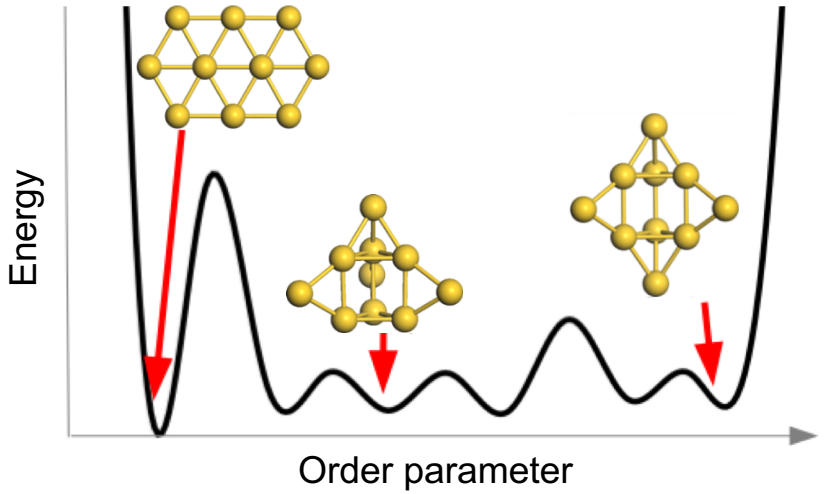
Is (b) trapped in metastable state?

van der Waals and temperature are important for predicting nanocluster isomer (meta)stability

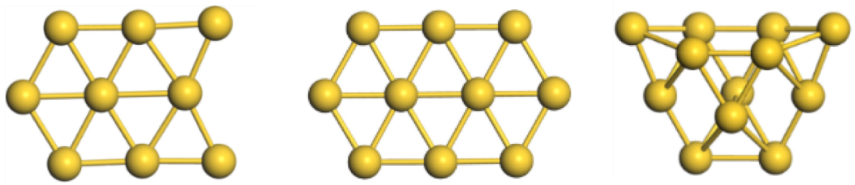
Accurate description of dispersion in clusters is needed

Conformational entropy typically stabilizes nonplanar isomers

<u>2D to 3D crossover</u>
Au_{11} at 0 K
Au_{10} or Au_9 at elevated T



Molecular Dynamics → Free energy surface
→ isomer populations » IR spectra assignment of Au_9, Au_{10}, Au_{12}



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