

The Structural Beauty of Nanoparticles. The so far Largest Crystal Structure of a Gold Nanoparticle: $\text{Au}_{133}(\text{SC}_6\text{H}_4^t\text{Bu})_{52}$

Kristin Kirschbaum,¹ Chenjie Zeng,²

Yuxiang Chen,² Kannatassen Appavoo,³ Matthew Y. Sfeir,³ Rongchao Jin²

¹Instrumentation Center, Department of Chemistry, The University of Toledo, Toledo, OH 43606, USA ²Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA.

³Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA.

Abstract

Significant efforts have been exerted to uncover the structure of nanoparticles, because many applications (such as catalysis and biomedicine) and fundamental studies of quantum size effect in nanoparticles require structural details at the atomic level.

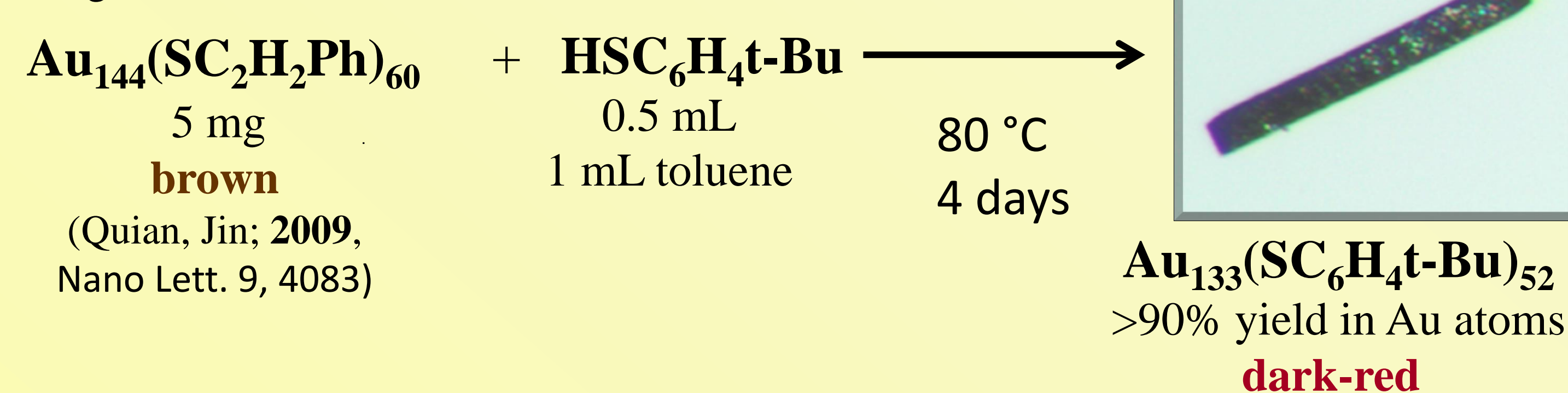
Single crystal X-ray diffraction remains the best tool to determine the structure of the metal and ligand core as well as the packing, while theoretical calculations can be somewhat unreliable (e.g. Mednikov, Dahl **2008**, Small, *4*, 534).

A breakthrough in the structural characterization of very large nanoparticles was achieved in 2007, when Kornberg et al. first reported the – although not unproblematic - high resolution structure of $\text{Au}_{102}(\text{SPhCOOH})_{44}$ (Jadzinsky *et al.* **2007**, Science, *318*, 430). However, it still remains a daunting task to elucidate even larger structures of gold nanoparticles—which are critically important to understand the growth pattern, surface structural ordering, and the emergence of metallic properties.

We report here the largest crystallographic structure of the chiral gold nanoparticle having 133 gold atoms and 52 surface-protecting thiolate ligands (Zeng *et al.* **2015**, Science Advances, *1*, e1500045). Almost parallel and independent of this work, the crystal structure of a polymorph was solved by Noll (Dass *et al.* **2015**, J. Am. Chem. Soc., *137*, 4610).

The X-ray structure analysis has been performed in-house using a Bruker Apex Duo ($\text{I}\mu\text{S CuK}\alpha$, 170 K) diffractometer and Oxford Cryosystem 700.

Synthesis

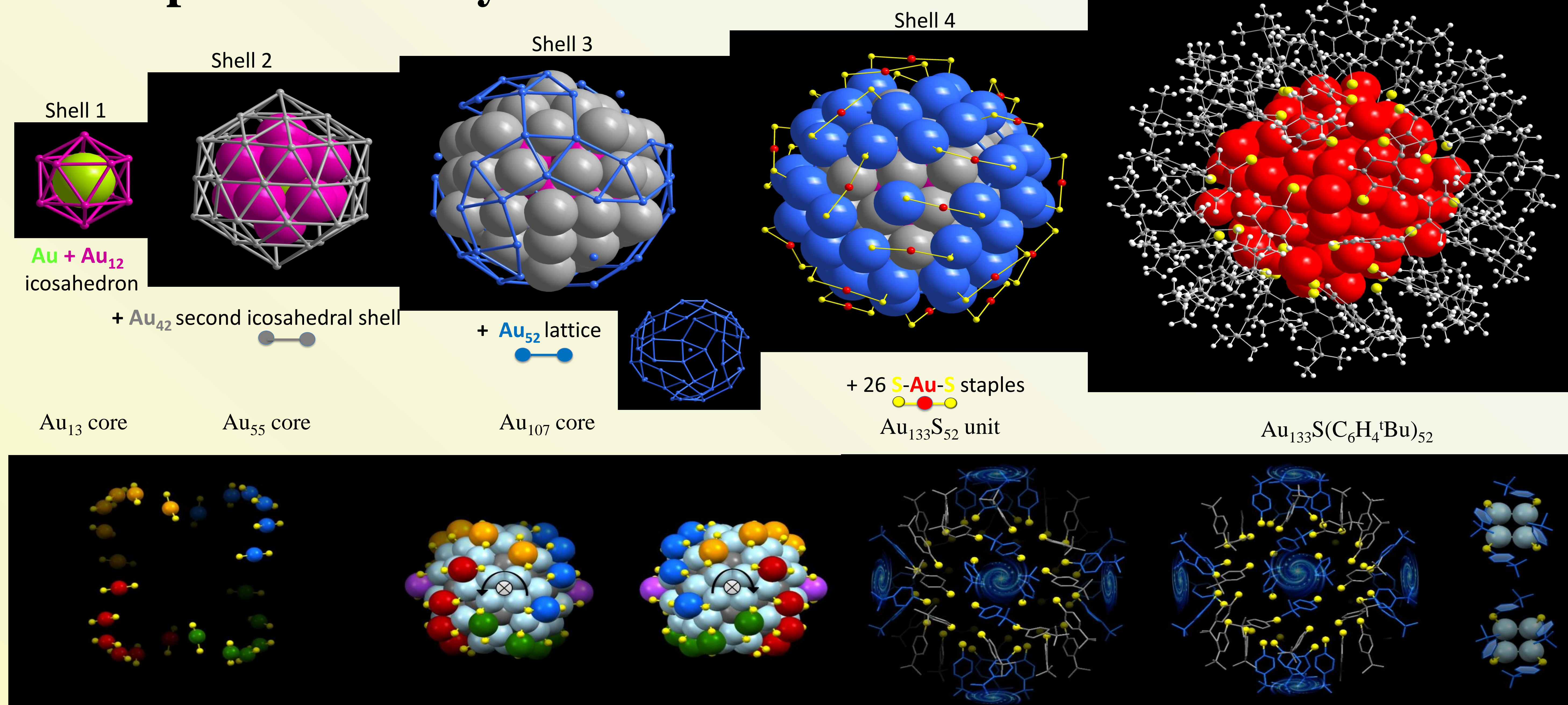


Single crystals were obtained through vapor diffusion of CH_3CN into a toluene solution of Au_{133} nanoparticles.

Crystallographic Data

Formula weight, Density	34,790.23 3.031 g/cm ³
Temperature	170(2) K
Cu Bruker $\text{I}\mu\text{S}$; 2 θ max; res.	1.54178 Å; 94°; 1.05 Å
Crystal size	0.01 x 0.035 x 0.266 mm
Space Group	P-1
Theta range	1.52 to 47.00°
Unit cell dimensions	a = 30.1364(9) Å α = 87.789(2)° b = 30.4359(9) Å β = 83.9430(19)° c = 43.6892(13) Å γ = 73.0690(18)°
Volume; Z	38,121(2) Å ³ ; 2
Reflections collected, independent	10,5010 53820 [R(int) = 0.0638]; 79% completeness
Absorption coefficient correction	48.285 mm ⁻¹ multi-scan and face absorption
Data / restraints / parameters	53820 / 321 / 3719
Final R indices	31436 data; I>2 σ (I) R_1 = 0.086, w R_2 = 0.228 all data; R_1 = 0.155, w R_2 = 0.294
Largest diff peak and hole	4.038 and -5.081 e/Å ³

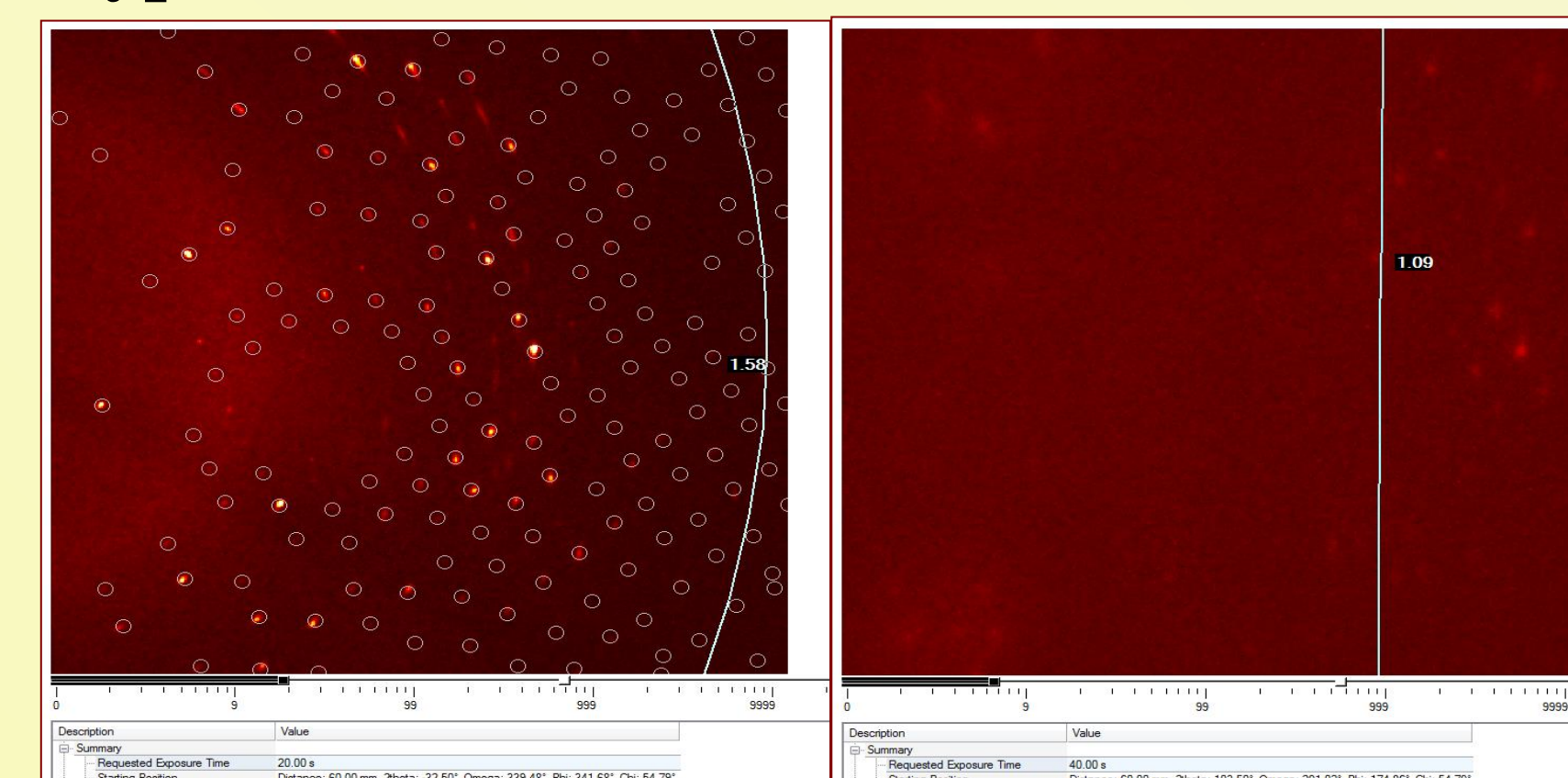
Description of the crystal structure



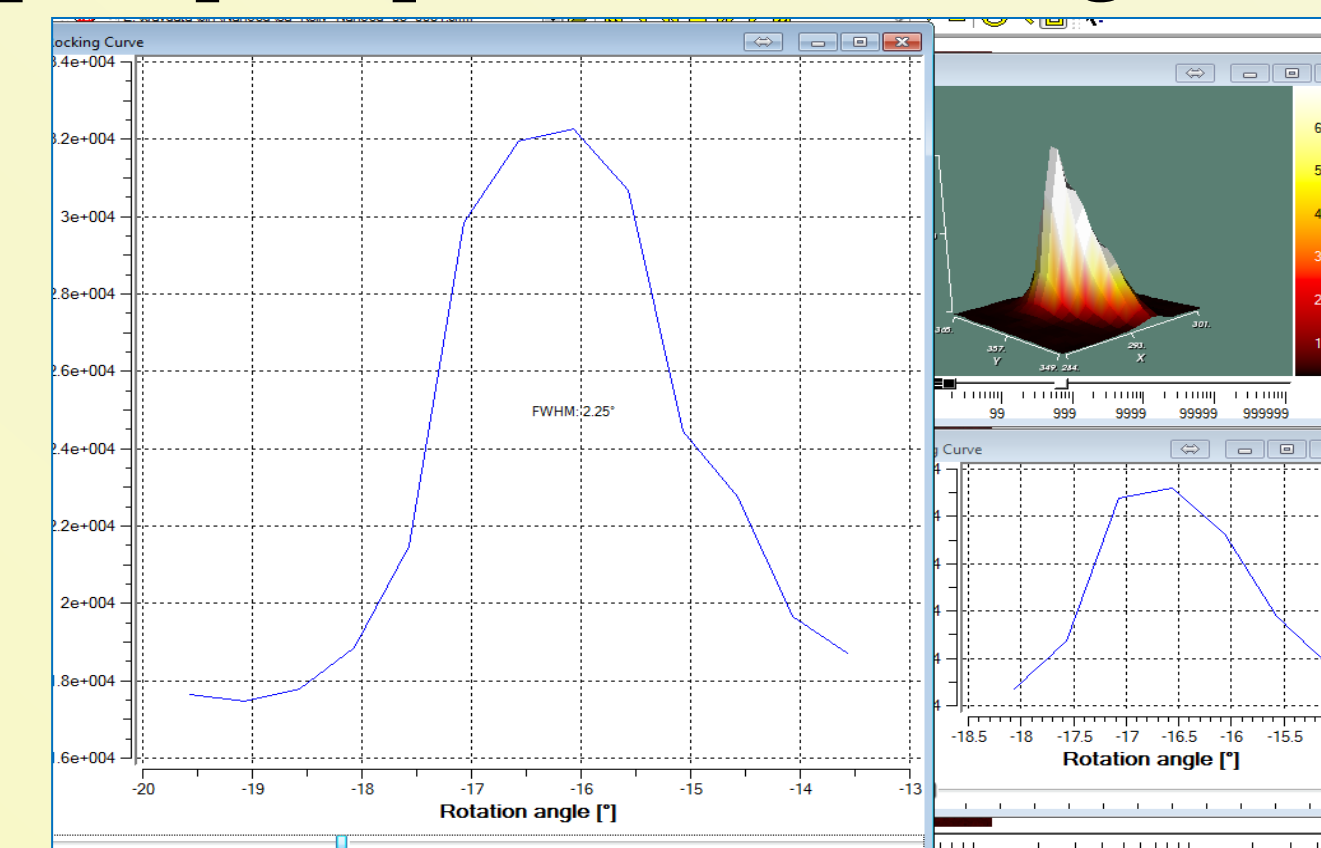
- Gold kernel Au₁₀₇ consists of a central atom + 2 shelled icosahedron + transition shell
- Gold-thiolate interface exhibits a helical chiral “stripe” pattern (2 isomers) in which the S–Au–S motifs stack into ladders in the curved space; The carbon tails of thiolates form “swirl” patterns that are different from the underlying S–Au–S stripe patterns

Crystallographic Challenges

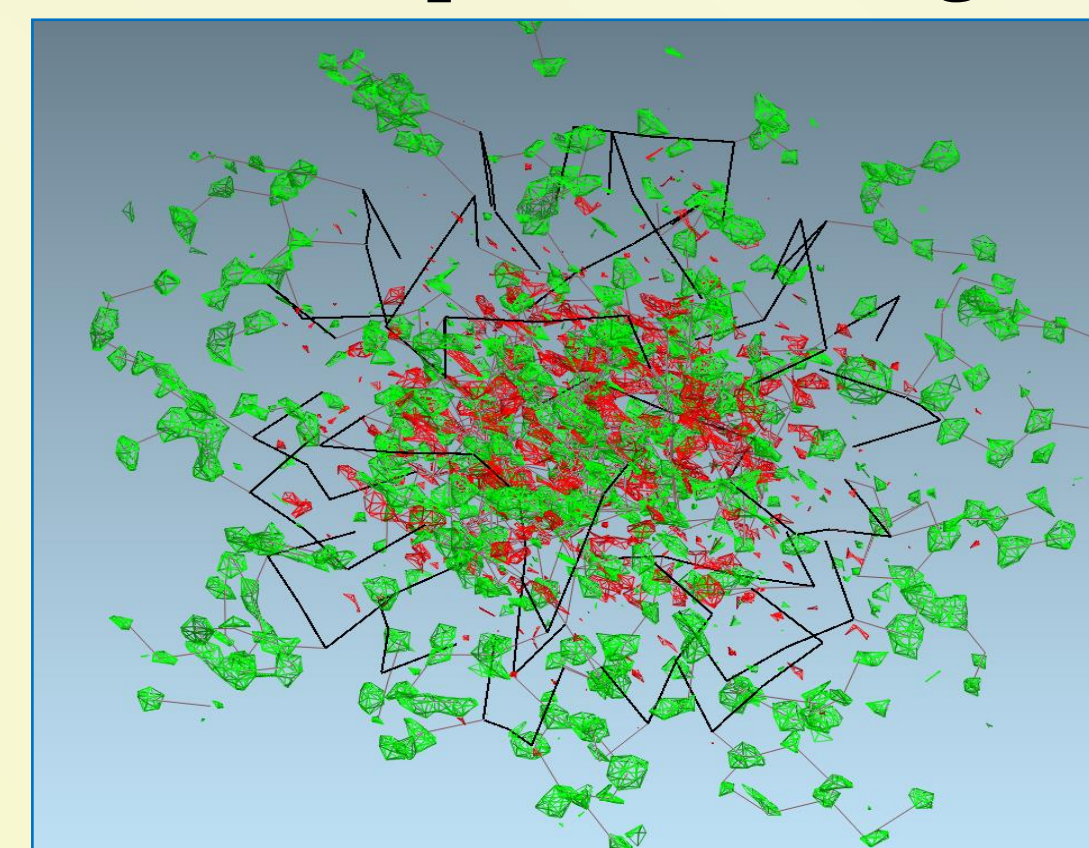
Typical Frames:



Typical peak profiles and rocking curves:



Fo-Fc map after locating all Au and S atoms:

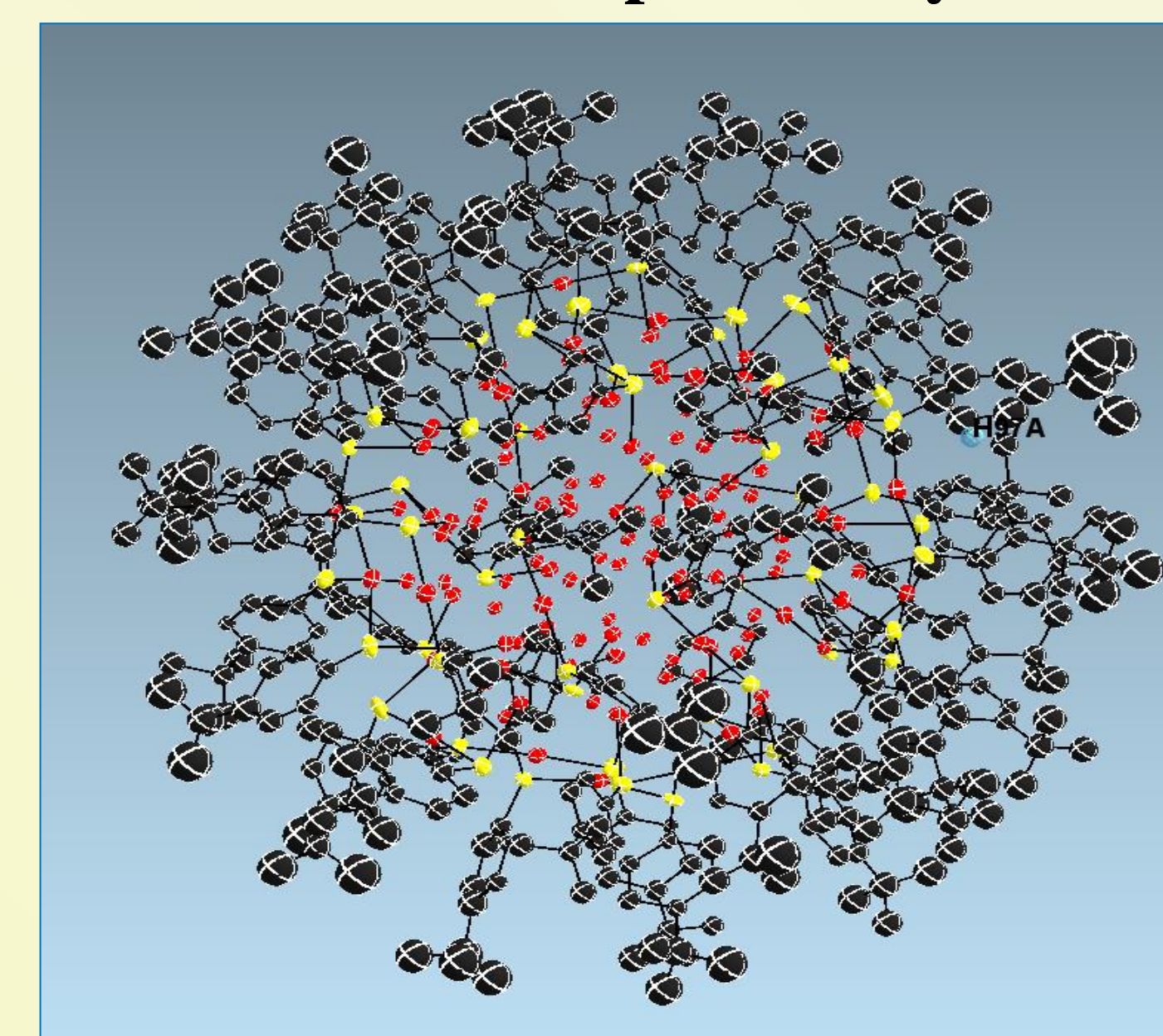


- Low resolution data
- Poor data quality
- Significant amount of disordered solvent
- Low data/parameter ratio
- Heavy atoms dominate the diffraction pattern
- Most of the residual electron density is located within the Au₁₃₃ cluster

Refinement

- Solved by direct methods; Au- and S- atoms were refined with anisotropic ADPs
- Analytical (face absorption) and multi-scan absorption correction
- A high amount of residual electron density is observed in the Au-core, a disordered model for the Au core could not be identified
- Initial refinements were severely (~6500) restrained/constrained (DFIX, AFIX, SAME, SADI, ISOR, FLAT, SIMU, BUMP)
- 95 % of the initial restraints and constraints were very slowly (iteratively) released or changed from constraints to restraints (DFIX to SADI)
- C-atoms were refined with isotropic ADPs; 3 of the 52 C-rings and 3 of the 52 t-Bu needed SIMU restraints; 5 of the aromatic rings needed planar restraints; all other restraints are C-C distance similarity restraints (total of 321).
- Nine C-atoms of three t-Bu groups, which were calculated on geometrically idealized positions
- The solvent molecules could not be identified from the X-ray structure data
- PLATON (Spek **2009**, Acta Cryst. D65, 148) was used to calculate the total accessible void to be ~28 % (10,600 Å³) and an electron count of 4,000 e/cell. Refinement against solvent reduced data did not show any improvement.

ORTEP with 30% probability ADPs



Acknowledgement

We thank T. Li for early trials on the crystal structure and K.J. Lambright for assistance with the crystallographic experiments.