

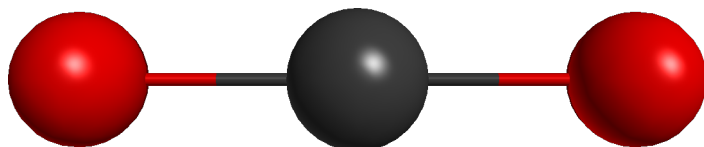
Alexander V. Zakharov

## **Experimental Equilibrium Structures**

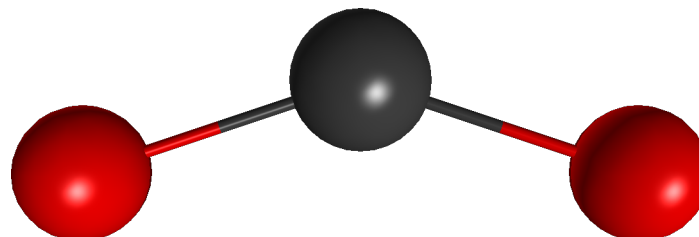
Application of Molecular Dynamics Simulations to Vibrational  
Corrections for Gas Electron Diffraction

Gas-phase electron diffraction (GED) is one of the most powerful methods to study the structure of molecules in gases, where they are free and undistorted by intermolecular interaction. However, structures determined by means of gas-phase electron diffraction are not equilibrium, but thermally averaged.

So-called *shrinkage effect*, caused by thermal motion of the atoms:



Equilibrium



Thermally averaged

Thermally averaged ( $r_g$ ) distance between non-bonded atoms is smaller than the equilibrium ( $r_e$ ) distance. Thermally averaged structure is *geometrically inconsistent*. Therefore, we need to apply vibrational corrections  $k = r_g - r_e$  to build a geometrically consistent model.

## Harmonic approximation with rectilinear treatment of nuclear movement

- Oldest and simplest method
- Force field (Hessian) from a theoretical calculation is necessary
- Works well only for molecules with small amplitudes of vibrations

## Harmonic approximation with curvilinear treatment of nuclear movement

- Force field (Hessian) from a theoretical calculation is necessary
- Works well for molecules with large amplitudes of vibrations
- Vibrational corrections are significantly different from actual  $k = r_g - r_e$
- The determined structure is *not* equilibrium

## Anharmonic approximation

- Third derivatives of potential energy (cubic force field) are necessary
- Computation is difficult or impossible for large molecules
- Not always works well for molecules with large amplitudes of vibrations
- Vibrational corrections are the best approximation of actual  $k = r_g - r_e$
- The determined structure can be considered equilibrium

## Application of molecular dynamics (MD) simulations

- MD simulation is necessary
- Linear or close to linear scaling – good for large molecules
- Works well for molecules with large amplitudes of vibrations
- Corrections are similar to those yielded by anharmonic approximation
- The determined structure can be considered equilibrium

D. A. Wann, A. V. Zakharov, A. M. Reilly, P. D. McCaffrey, D. W. H. Rankin, *J. Phys. Chem. A*, 2009, **113**, 9511.

$$r_{g,ij} = \langle r_{ij} \rangle = \frac{1}{N} \sum_{k=1}^N r_{ij,k}$$

$$u_{ij} = \left( \frac{1}{N} \sum_{k=1}^N (r_{ij,k} - \langle r_{ij} \rangle)^2 \right)^{\frac{1}{2}}$$

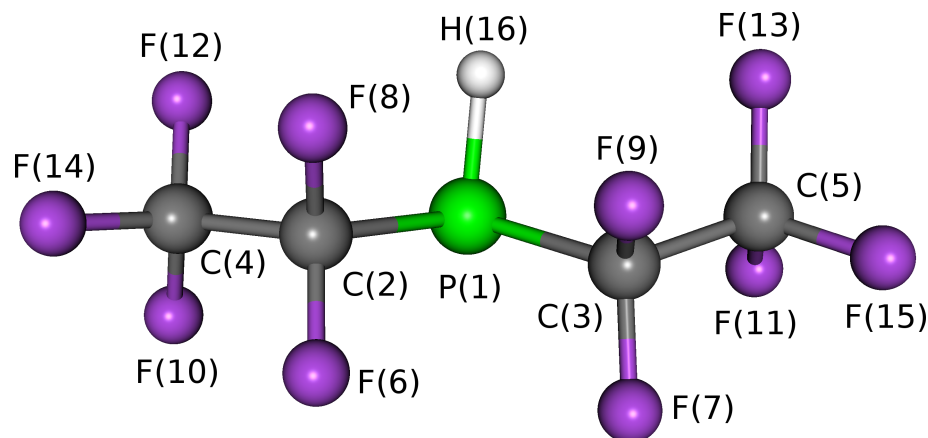
## **Multi-conformer models**

- The structure of each conformer should be described separately
- Vibrational corrections should be computed separately
- MD trajectory contains several conformers existing at the given temperature

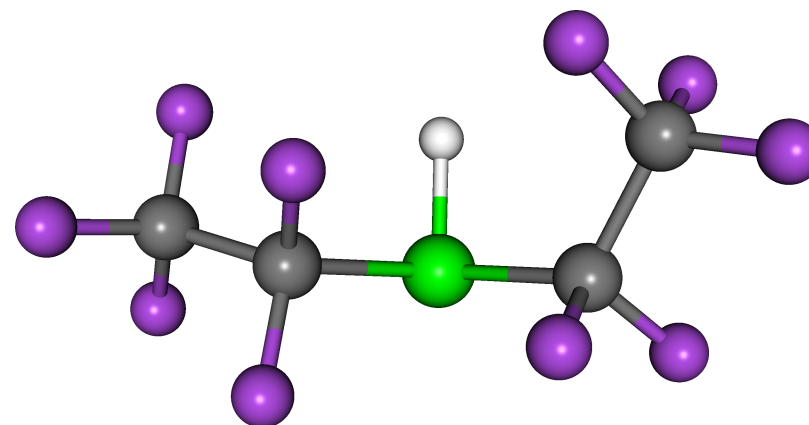
## **Solution:**

Geometries from the trajectories are classified according to the value of a dihedral or torsional angle which determines the conformation and vibrational corrections are computed for each conformer using only geometries that were determined to belong to this particular conformation.

## Bis(pentafluoroethyl)phosphane



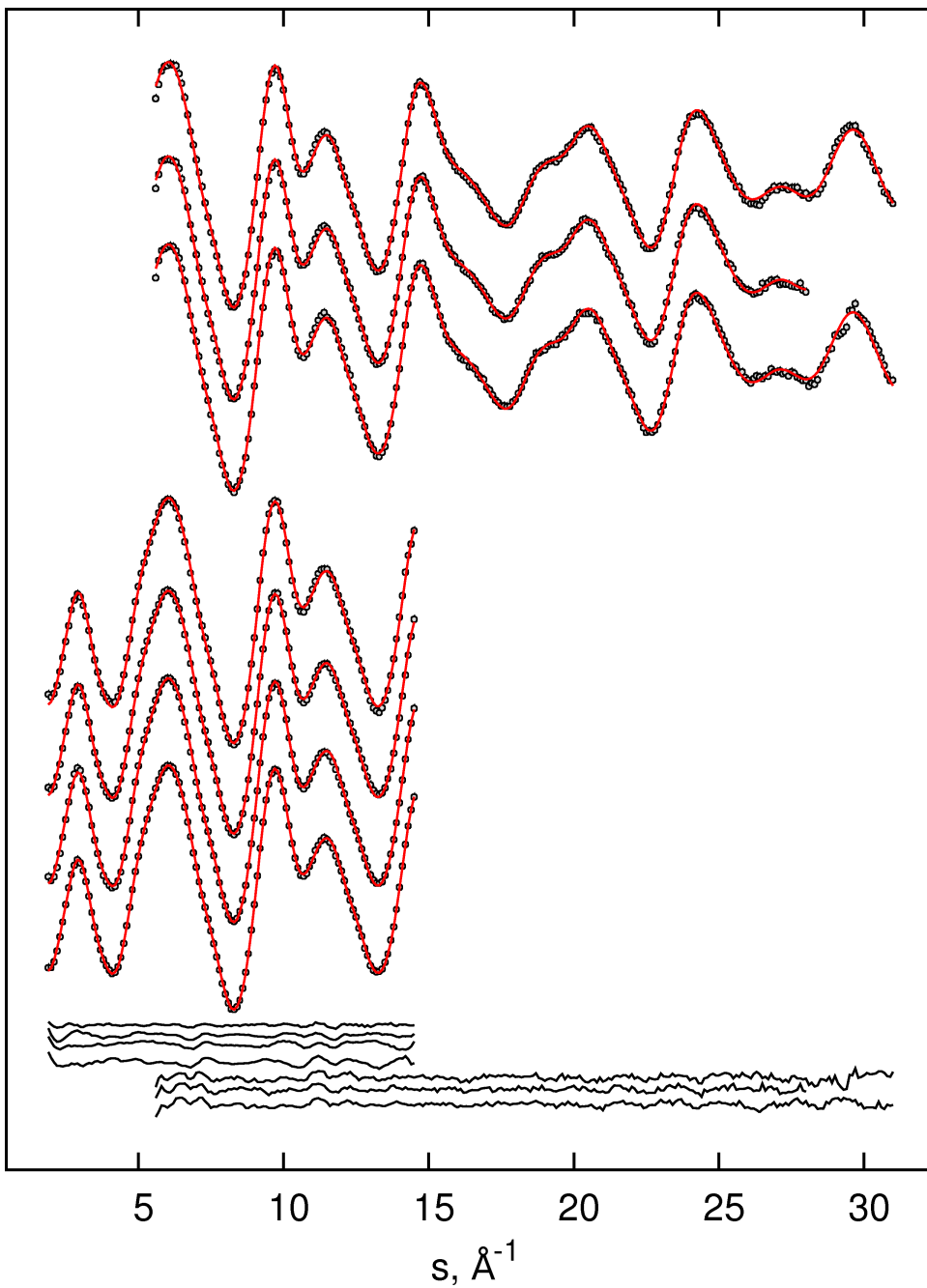
Conformer 1



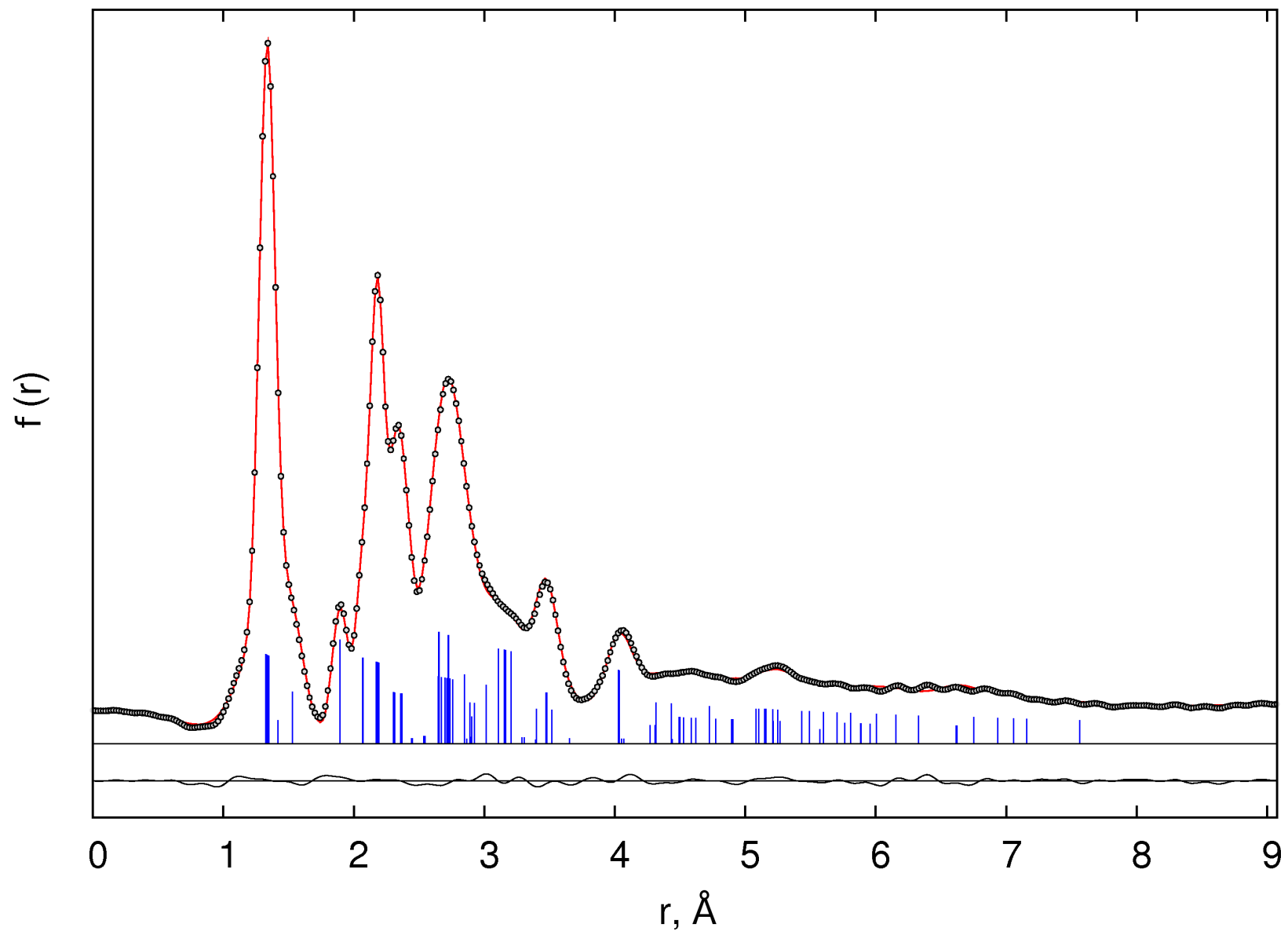
Conformer 2

Refinement with varying the conformer ratio (starting with 80% of the first conformer) resulted in 92(7)% abundance of the first conformer with its parameters being very close to those found by the single-conformer model refinement.

The first conformer is dominating, but the actual ratio cannot be detected from the GED data with sufficient accuracy.



Experimental (dots) and theoretical (lines) molecular intensities  $sM(s)$  curves and difference curves (below) for short (upper curves) and long (lower curves) camera distances



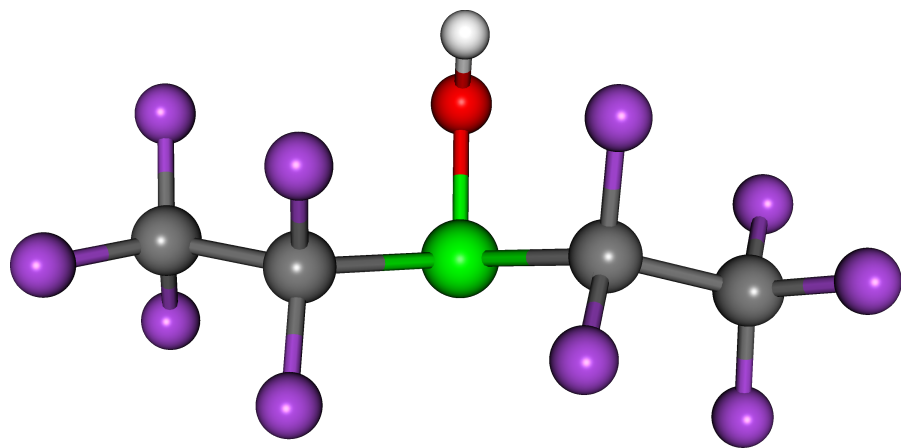
Experimental (dots) and theoretical (line) radial distribution  $f(r)$  curves and difference curve (below)



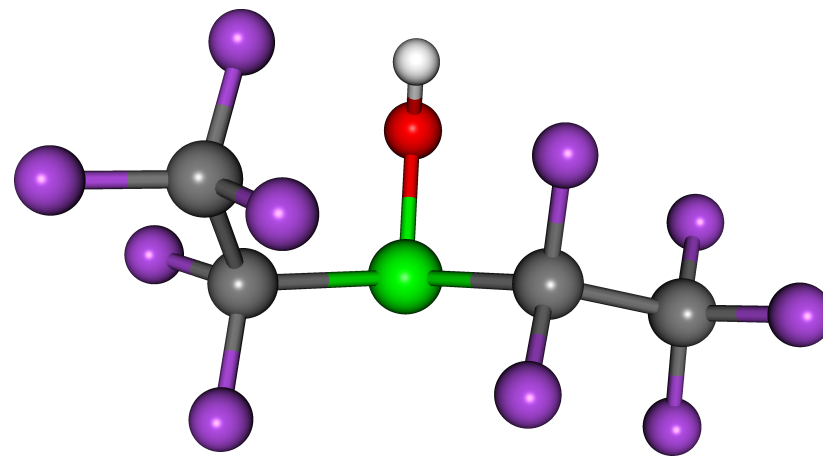
## Major geometrical parameters of (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>PH molecule

	GED $r_e$ ( $k_{MD}$ )	O3LYP/ aug-cc-pVTZ	MP2/ aug-cc-pVTZ
$r(\text{P1-C2})$	1.884(3)	1.905	1.886
$r(\text{P1-C3})$	1.880(3)	1.900	1.881
$r(\text{C2-C4})$	1.517(3)	1.547	1.529
$r(\text{C3-C5})$	1.518(3)	1.549	1.531
$r(\text{C2-F6})$	1.346(1)	1.345	1.350
$r(\text{C2-F8})$	1.344(1)	1.343	1.348
$r(\text{C3-F7})$	1.347(1)	1.347	1.352
$r(\text{C3-F9})$	1.344(1)	1.343	1.349
$r(\text{C4-F10})$	1.326(1)	1.327	1.328
$r(\text{C4-F12})$	1.333(1)	1.334	1.336
$r(\text{C4-F14})$	1.321(1)	1.323	1.324
$r(\text{C5-F11})$	1.328(1)	1.329	1.332
$r(\text{C5-F13})$	1.330(1)	1.331	1.333
$r(\text{C5-F15})$	1.321(1)	1.323	1.324
$\angle(\text{C2-P1-C3})$	98.5(8)	97.4	95.1
$\angle(\text{C4-C2-P1})$	111.9(2)	110.2	110.2
$\angle(\text{C5-C3-P1})$	112.8(2)	111.2	111.2
$\tau(\text{C4-C2-C1-C3})$	-176(3)	-172.8	-168.4
$\tau(\text{C5-C3-P1-C2})$	-165(3)	-162.4	-159.9

## Hydroxobis(pentafluoroethyl)phosphane



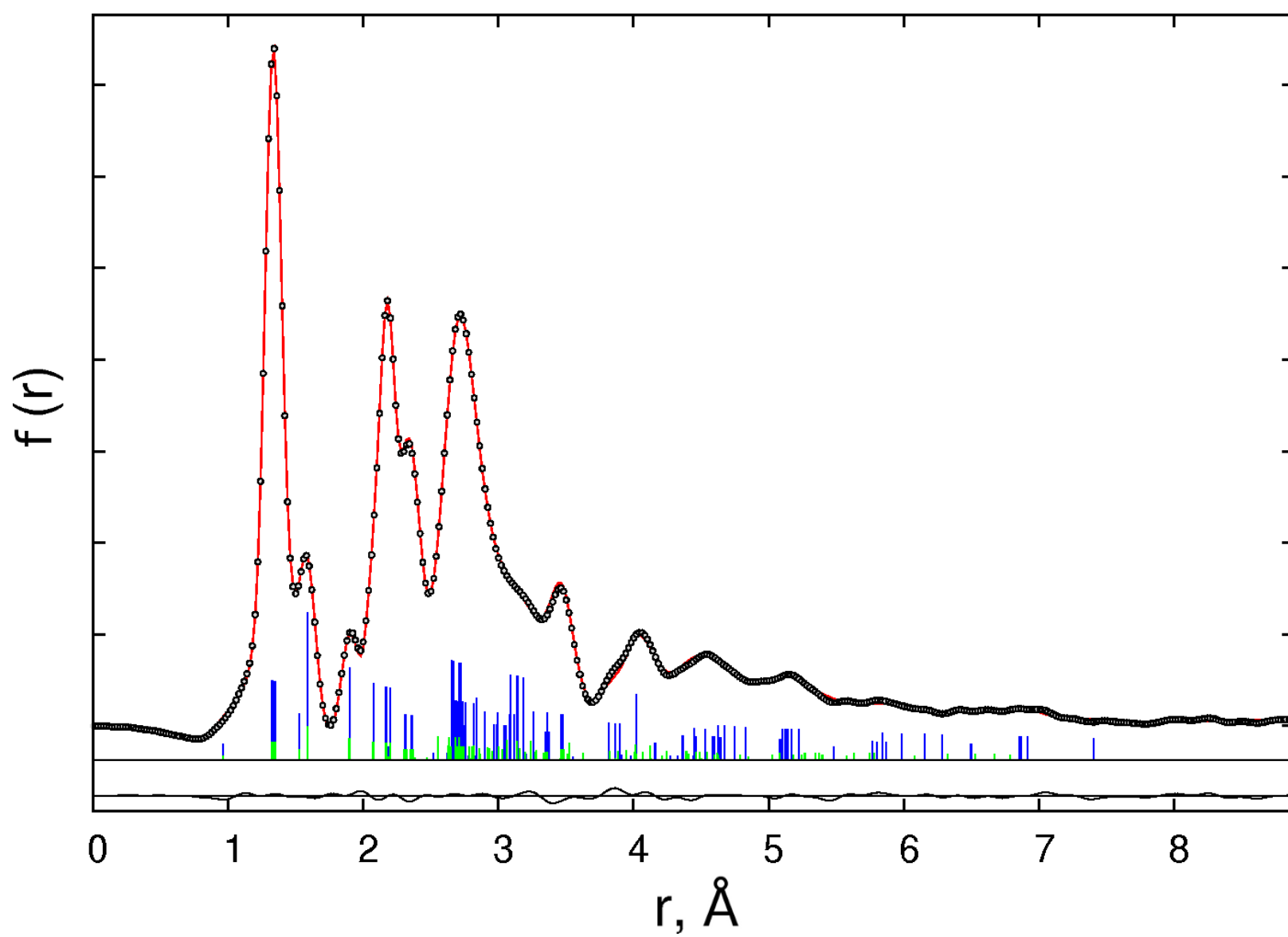
Conformer 1



Conformer 2

Refinement with varying the conformer ratio (starting with 75% of the first conformer) resulted in 81(5)% abundance of the first conformer.

Final analysis *in progress*



Experimental (dots) and theoretical (line) radial distribution  $f(r)$  curves and difference curve (below)