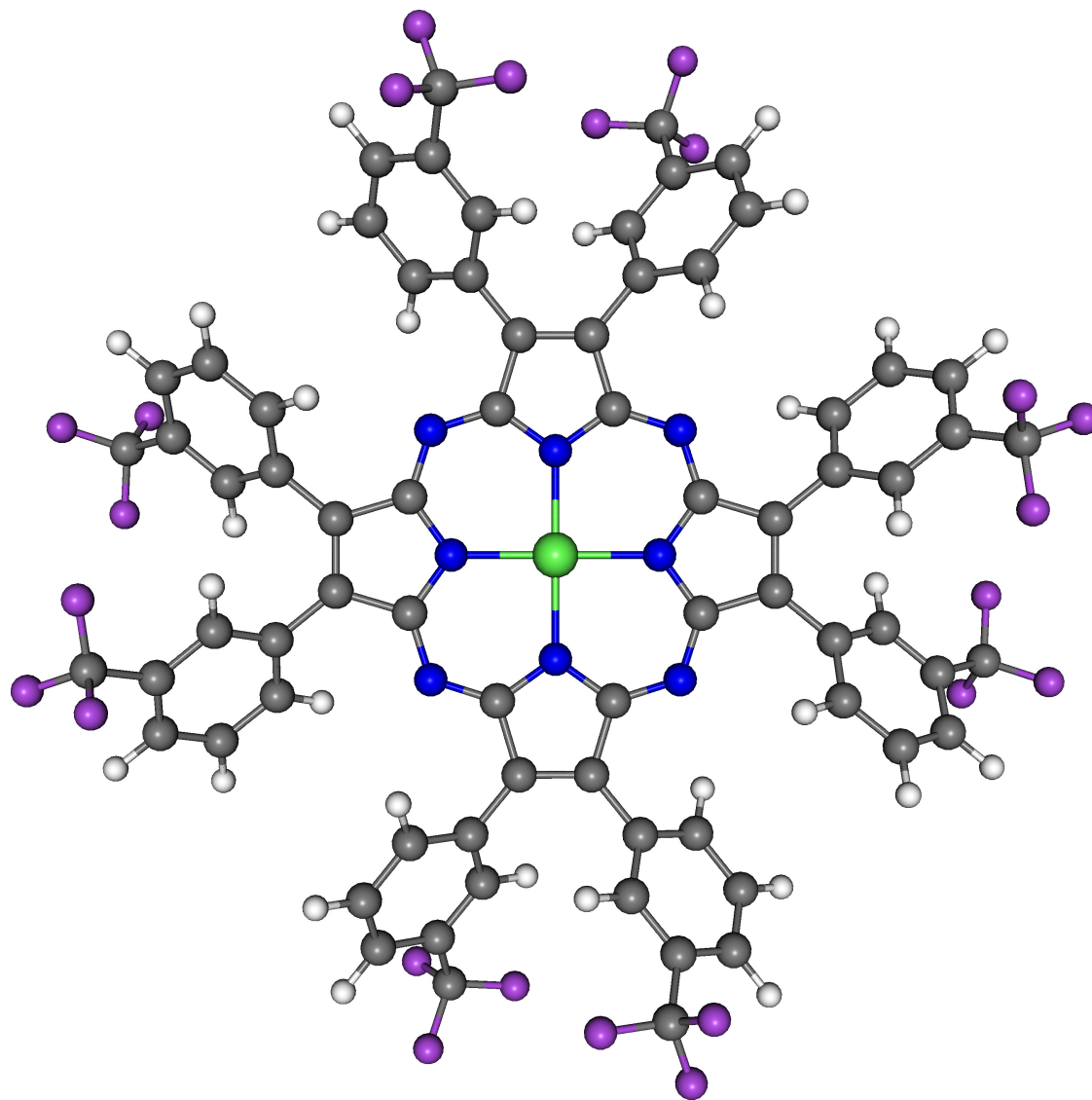**Alexander V. Zakharov, Yuriy A. Zhabanov, Sergei A. Shlykov, Nina I. Giricheva, Oscar I. Koifman and Georgiy V. Girichev**

Moleculare structure of magnesium octa(m-trifluoromethylphenyl)porphyrazine and application of molecular dynamics for computation of vibrational corrections

Department of Physics

Ivanovo State University of Chemistry and Technology

1

Magnesium octa(m-trifluoromethylphenyl)porphyrazine ($MgC_{72}H_{32}N_8F_{24}$)

2

Thermal-average structures obtained from GED experimental data are the weighted (Boltzmann) averages over all electronic, vibrational and rotational states populated at the temperature of the experiment and, therefore, are geometrically inconsistent.

This shrinkage effect, caused by thermal motion of the atoms, can be accounted for by calculating vibrational corrections $k = r_a - r_e$.

- Harmonic approximation with rectilinear treatment of nuclear movements

- Harmonic approximation with curvilinear treatment of nuclear movements

- Anharmonic approximation

- Application of molecular dynamics (MD) simulations

Harmonic approximation with rectilinear treatment of nuclear movement

- Oldest and simplest method, imlemented in ASYM40 and SHRINK (k_{h0})
- Requires force field (Hessian) from a theoretical calculation
- Works well only for molecules without low (less than 50 cm^{-1}) vibrational frequencies

For molecules with low vibrational frequencies this approach yields very large corrections for bonded distances. For example, for C-C bond (r = 1.510 Å) in Mg(acac)$_2$ it gave the amplitude of 0.0554 Å and correction of -0.0465 Å (A. V. Zakharov, M. Dakkouri, A. V. Krasnov, G. V. Girichev, I. G. Zaitzeva. *J. Mol. Struct.*, 2004, **701**, 1)
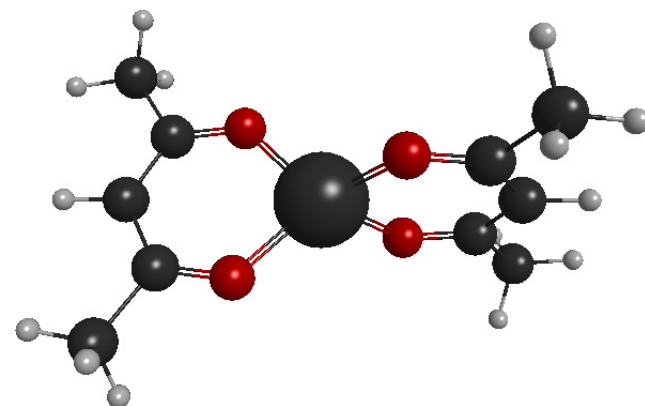
Not sutable for studies of large, floppy molecules

Harmonic approximation with curvilinear treatment of nuclear movement

- Requires force field (Hessian) from a theoretical calculation
- Works well for molecules with low vibrational frequencies (even for ones with several frequencies of 10-20 cm^{-1}
- Vibrational corrections are significantly different from actual $k = r_a - r_e$; the determined structure is *not* equilibrium structure

A. V. Zakharov, S. A. Shlykov, E. A. Danilova, A. V. Krasnov, M. K. Islyaikin, G. V. Girichev. *Phys. Chem. Chem. Phys.*, 2009, **11**, 8570.

Current state of the art, used in several studies of large macroheterocyclic molecules
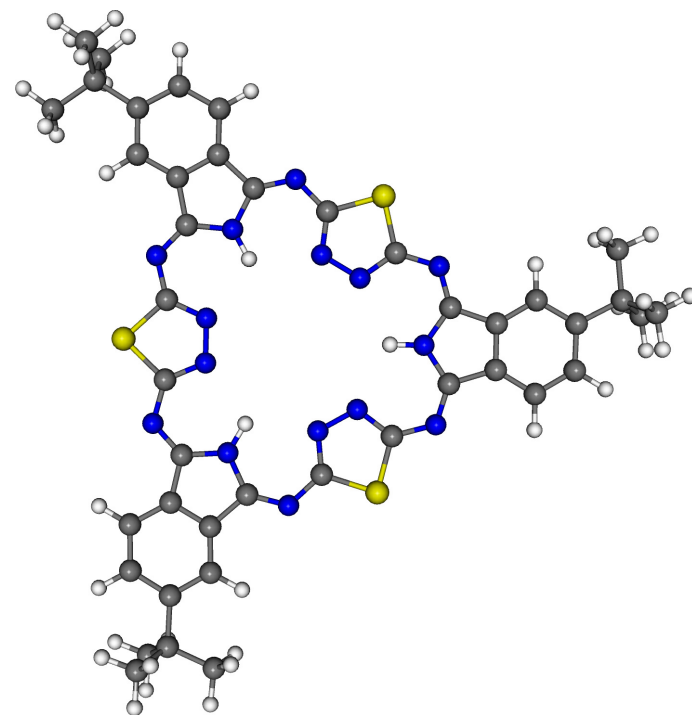
Anharmonic approximation

- Requires third derivatives of potential energy (cubic force field)
- Computation is difficult or impossible for large molecules
- Vibrational corrections are the best approximation of actual $k = r_a - r_e$
- The determined structure can be considered equilibrium

For example, this approach was used in the following study for comparison with the MD method:
A. V. Zakharov, Yu. V. Vishnevskiy, N. Allefeld, J. Bader, B. Kurscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, R. J. F. Berger, N. W. Mitzel. *Eur. J. Inorg. Chem.*, 2013, 3392.
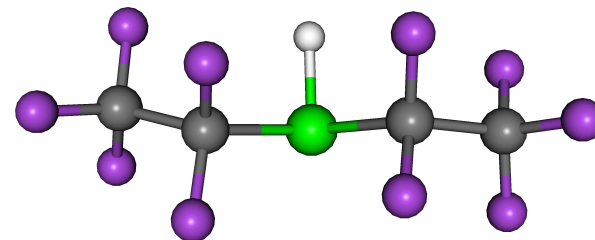
Good for smaller molecules

Application of molecular dynamics (MD) simulations

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

D. A. Wann, R. J. Less, F. Rataboul, P. D. McCaffrey, A. M. Reilly, H. E. Robertson, P. D. Lickiss, D. W. H. Rankin, *Organometallics*, 2008, **27**, 4183.

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

$$r_{a,ij} = \left(\frac{1}{N} \sum_{k=1}^{N} (r_{ij,k})^{-1} \right)^{-1} \; ; \qquad r_{g,ij} = \langle r_{ij} \rangle = \frac{1}{N} \sum_{k=1}^{N} r_{ij,k}$$

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

The major deficiency of standard molecular dynamics simulations is the inability to incorporate the quantum dynamics of the nuclei. This results in underestimation of the amplitudes of vibration for the shorter distances that involve high-frequency vibrations (C-H).

Possible solutions:
- Path-integral molecular dynamics (PIMD) − computationally intensive
- Refinement of the amplitudes using starting values from MD
- Usage of amplitudes from SHRINK (any approximation)

Comparison of anharmonic vibrational corrections calculated using molecular dynamics trajectories (k_{MD}) and using third derivatives via SHRINK (k_3)
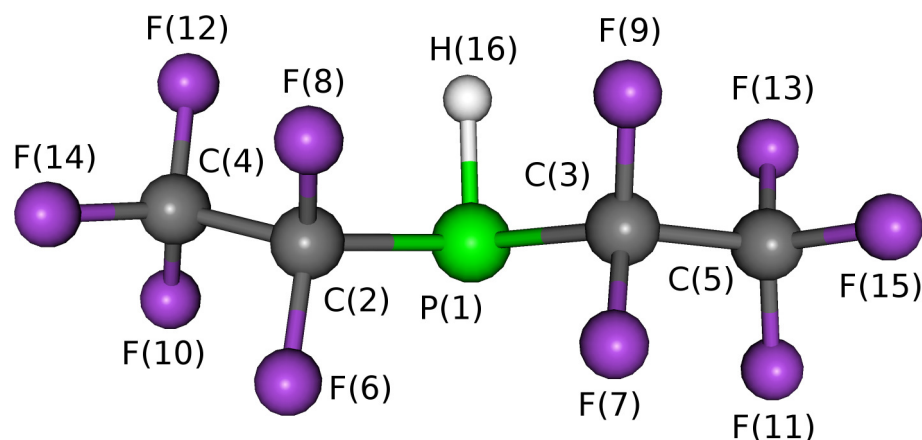
A. V. Zakharov, Yu. V. Vishnevskiy, N. Allefeld, J. Bader, B. Kurscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, R. J. F. Berger, N. W. Mitzel. *Eur. J. Inorg. Chem.*, 2013, 3392.

|	k_{MD}	k_3
r(P1–C2)	-0.00907	-0.00830
r(P1–C3)	-0.01425	-0.01450
r(C2–C4)	-0.01335	-0.01340
r(C3–C5)	-0.01067	-0.01280
r(C2–F6)	-0.00353	-0.00680
r(C2–F8)	-0.00340	-0.00590
r(C3–F7)	-0.00164	-0.00530
r(C3–F9)	-0.00371	-0.00460
r(C4–F10)	-0.00624	-0.00710
r(C4–F12)	-0.00097	-0.00500
r(C4–F14)	-0.00287	-0.00580
r(C5–F11)	-0.00327	-0.00500
r(C5–F13)	-0.00501	-0.00740
r(C5–F15)	-0.00329	-0.00580
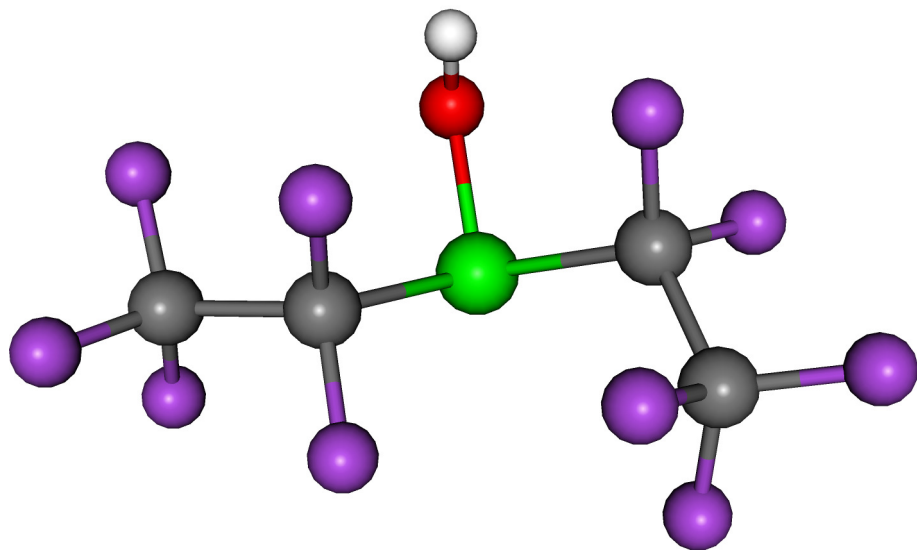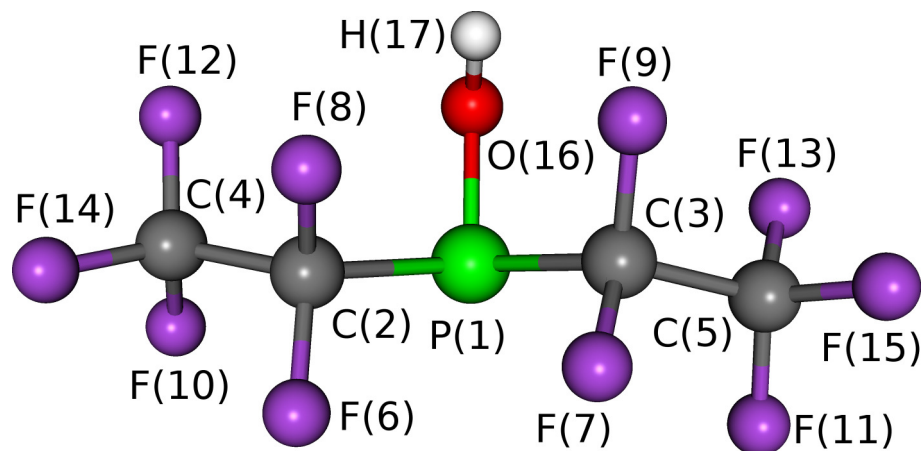
Multi-conformer models

- The structure of each conformer should be described separately
- Vibrational corrections should be computed separately
- MD trajectory contains several con-fromers 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.

10

Magnesium octa(m-trifluoromethylphenyl)porphyrazine
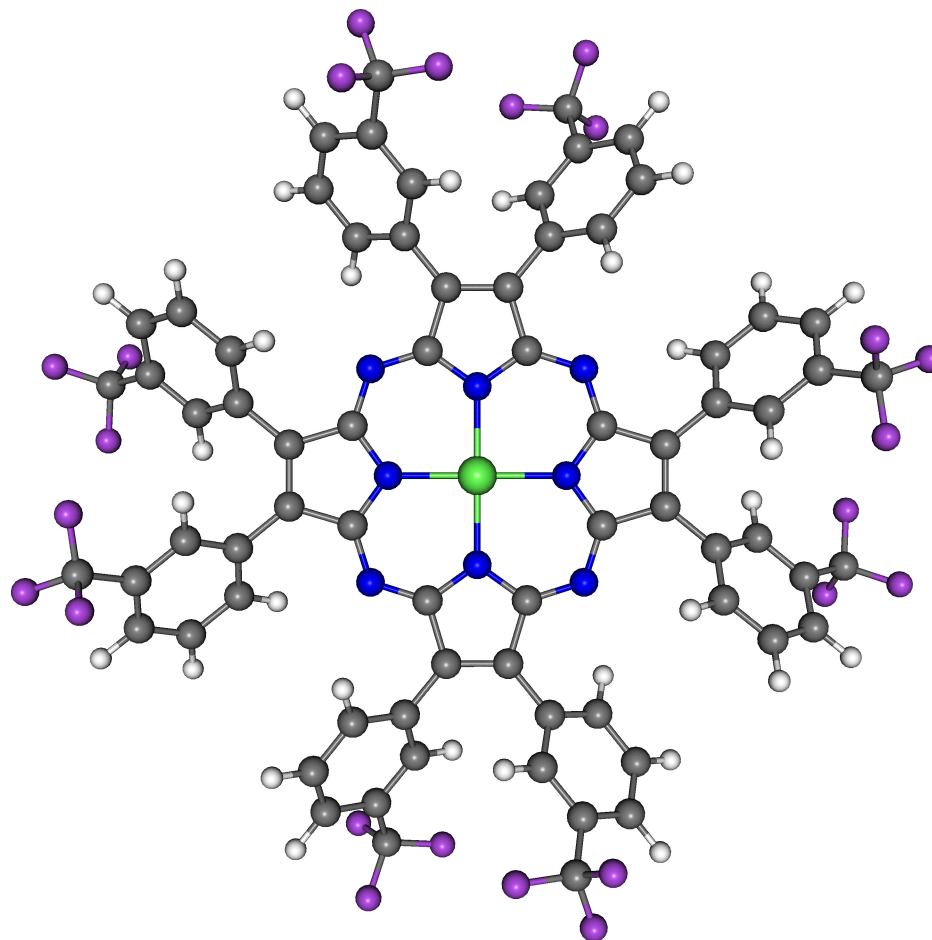
Studied by DFT computations (B3LYP/cc-pVTZ) and synchronous GED and MS experiment using "second approximation" (k_{h1}) and MD (k_{MD}) vibrational corrections.

Experimental

- Synchronous gas electron diffraction (GED) and mass spectrometric (MS) experiment carried out using the EMR-100/APDM-1 unit

- The sample was evaporated at temperature $T = 667(10)$ K from a graphite cell with a cylindrical effusion nozzle of 0.6×1.6 mm size (diameter $\times$ length)

- Three peaks in the mass spectra during recording of the diffraction patterns: the molecular ion $MgC_{72}H_{32}N_8F_{24}^+$, an ion corresponding to the break-off of a single CF_3 group, and a doubly charged molecular ion $MgC_{72}H_{32}N_8F_{24}^{++}$, with relative abundances of 100:19:17

- Electron diffraction patterns were obtained from short ($L_1 = 338$ mm, two experiments) and long ($L_2 = 598$ mm) camera distances at accelerating voltages of ca. 92 kV; accurate wavelengths of electrons calibrated using polycrystalline ZnO

- The diffraction patterns were recorded using Kodak SO-163 electron image films, which were scanned by a calibrated scanner

Computational

- Geometry optimzation and force field calculations were performed using the B3LYP functional and the cc-pVTZ basis sets in Gaussian 09

- Molecular dynamics calculations were performed using the CP2K code

- A single molecule was simulated in a cubic supercell with the size of 25 Å

- The BLYP exchange-correlation functional, GTH pseudopotentials and corresponding DZVP basis sets were used

- The simulation was performed in the canonical (NVT) ensemble using a chain of five Nose-Hoover thermostats with time constant of 4 fs, simulation temperature $T = 670$ K

- Time step of 0.5 fs, the simulation lasted for 25 ps (50000 time steps)

	DFT	r_{h1}	r_e
$r(\text{Mg1–N2})$	1.983	1.979(5)	1.978(5)
$r(\text{N2–C10})$	1.360	1.363(3)	1.360(2)
$r(\text{C10–C18})$	1.467	1.466(3)	1.462(3)
$r(\text{N6–C10})$	1.331	1.334(4)	1.331(2)
$r(\text{C18–C24})$	1.376	1.380(7)	1.370(12)
$r(\text{C18–C26})$	1.470	1.469(3)	1.465(3)
$r(\text{C26–C34})$	1.399	1.400(1)	1.398(1)
$r(\text{C26–C42})$	1.399	1.400(5)	1.399(1)
$r(\text{C34–C50})$	1.388	1.390(1)	1.388(1)
$r(\text{C42–C58})$	1.387	1.389(1)	1.387(1)
$r(\text{C50–C66})$	1.387	1.389(1)	1.387(1)
$r(\text{C58–C66})$	1.392	1.394(1)	1.392(1)
$r(\text{C58–C98})$	1.505	1.510(5)	1.500(3)
$r(\text{C98–F106})$	1.348	1.349(2)	1.347(2)
$r(\text{C98–F114})$	1.351	1.352(2)	1.349(2)
$r(\text{C98–F122})$	1.349	1.350(2)	1.348(2)
$r(\text{C34–H74})$	1.079	1.087(7)	1.078(7)
$r(\text{C42–H82})$	1.079	1.087(7)	1.078(7)
$r(\text{C50–H90})$	1.081	1.088(7)	1.080(7)
$r(\text{C66–H130})$	1.080	1.088(7)	1.079(7)
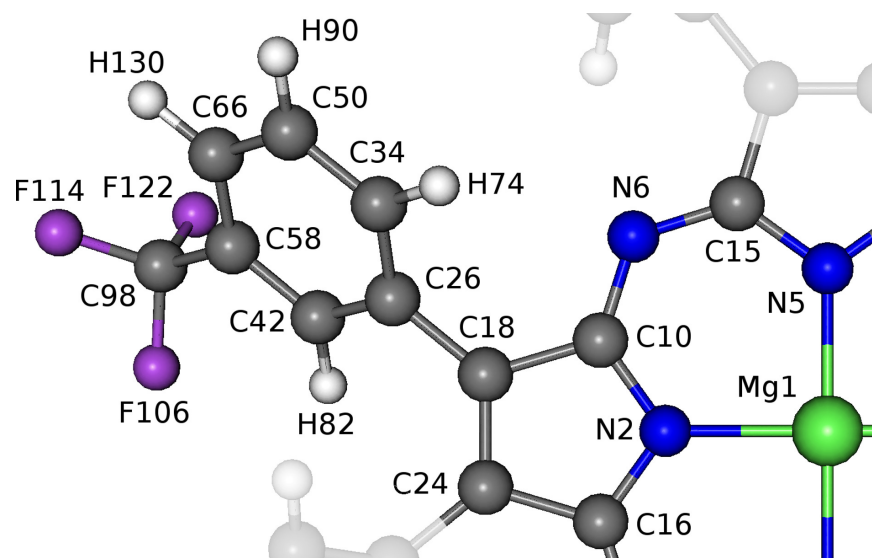
Numbering of atoms in the $MgC_{72}H_{32}N_8F_{24}$ molecule

Distance	k_{h1}	k_{MD}
r(Mg1-N2)	-0.0045	-0.0130
r(N2-C10)	0.0003	-0.0072
r(C10-C18)	0.0002	-0.0075
r(N6-C10)	0.0005	-0.0058
r(C18-C24)	0.0006	-0.0014
r(C18-C26)	-0.0009	-0.0121
r(C26-C34)	0.0005	-0.0050
r(C26-C42)	0.0006	-0.0039
r(C34-C50)	0.00002	-0.0065
r(C42-C58)	0.00004	-0.0080
r(C50-C66)	-0.0001	-0.0065
r(C58-C66)	-0.0001	-0.0061
r(C58-C98)	-0.0003	-0.0088
r(C98-F106)	0.0017	-0.0096
r(C98-F114)	0.0027	-0.0074
r(C98-F122)	0.0018	-0.0109
r(C34-H74)	0.0011	-0.0089
r(C42-H82)	0.0011	-0.0069
r(C50-H90)	0.0010	-0.0069
r(C66-H130)	0.0010	-0.0078
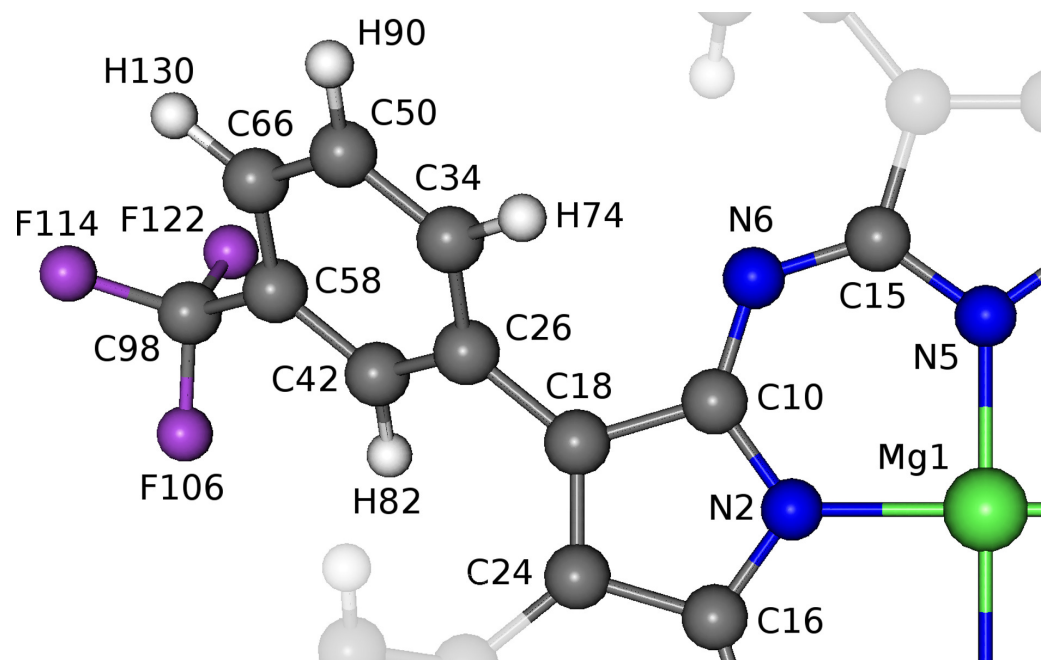
For bonded distances, k_{MD} are always smaller than k_{h1}, r_e are shorter than r_{h1}

15
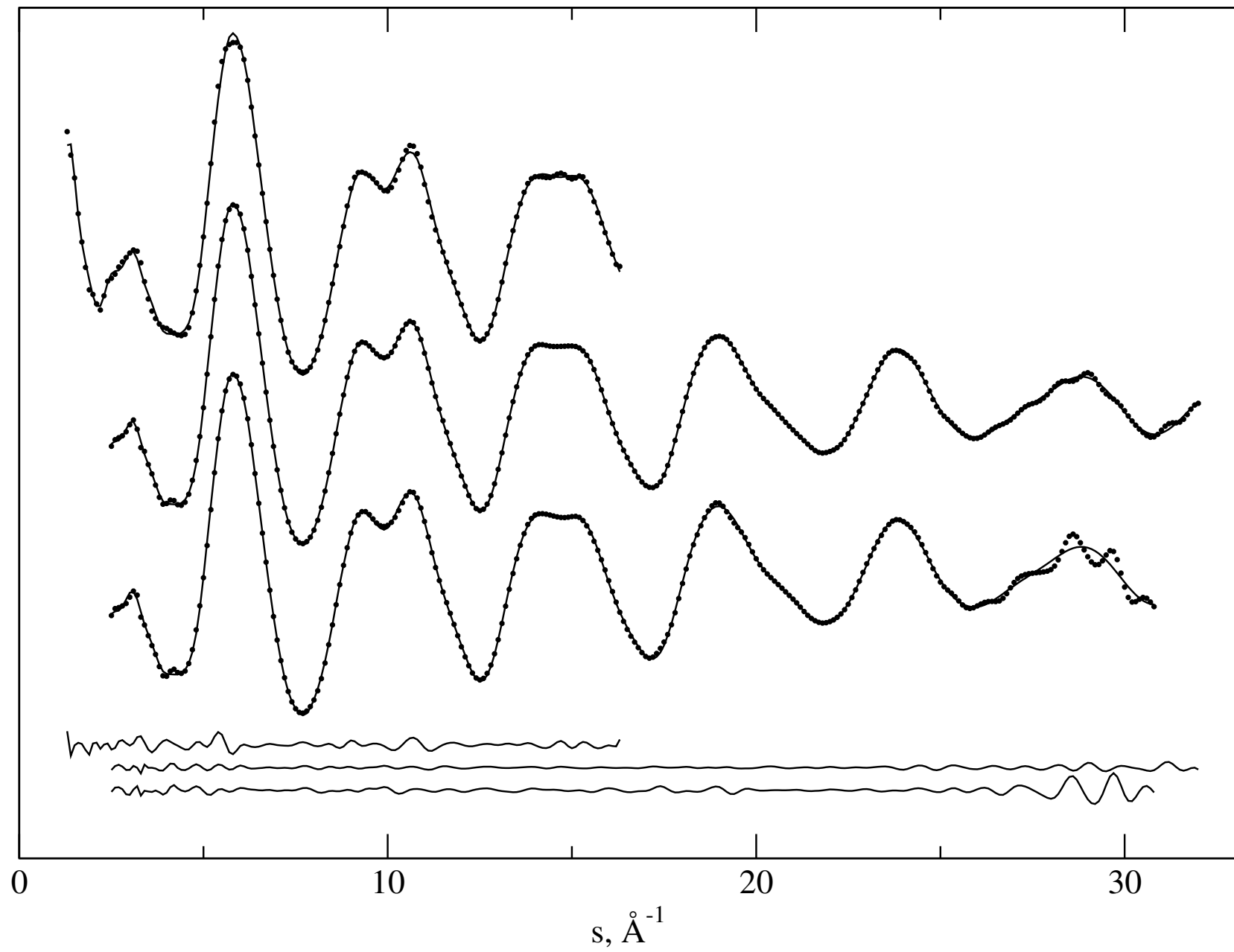
Experimental (dots) and theoretical (lines) $sM(s)$ curves. Total $R_f = 4.2\%$

16
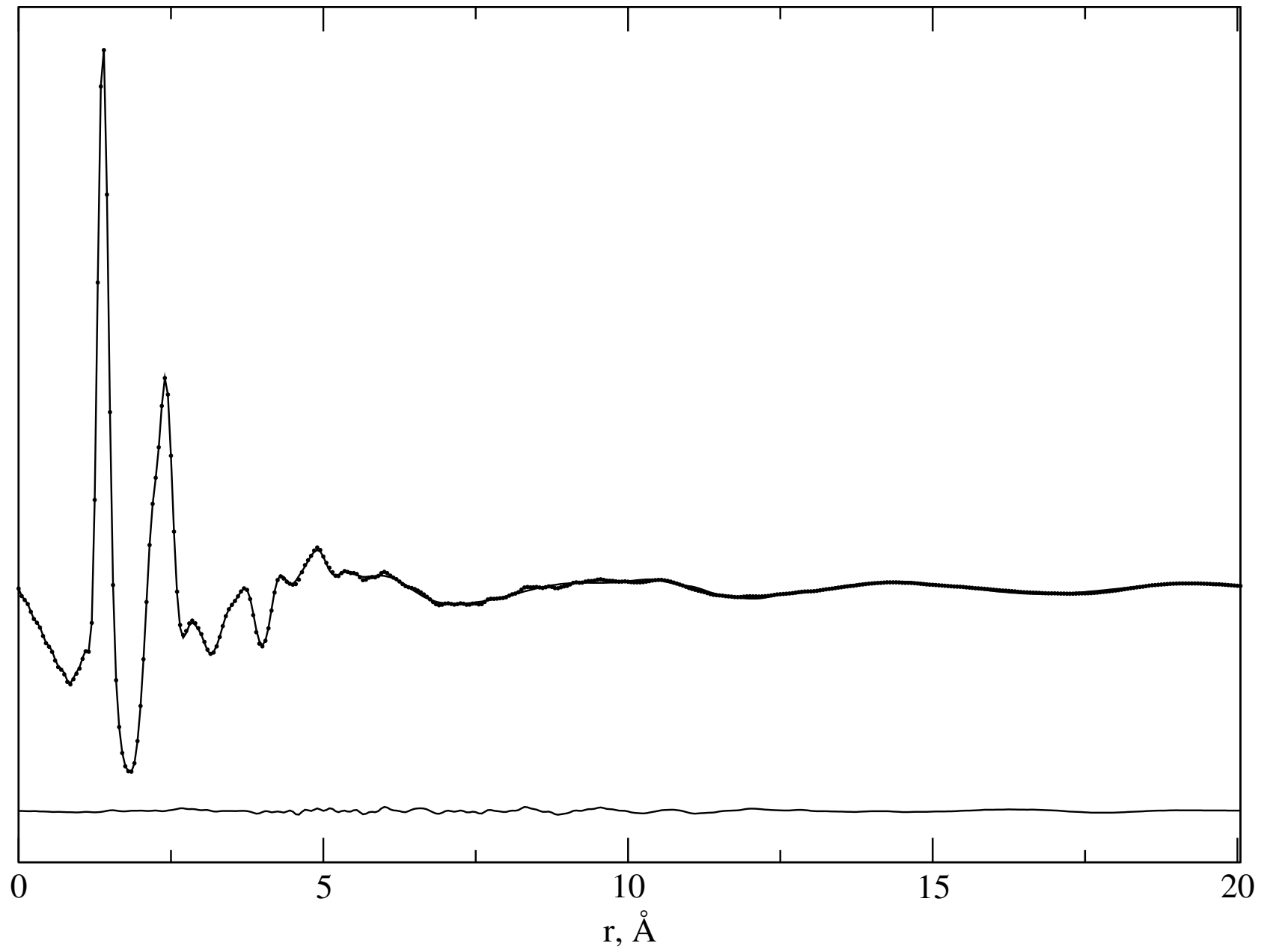
Experimental (dots) and theoretical (line) $f(r)$ curves