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Born-Oppenheimer Molecular Dynamics Studies of Ferroelectric Phase Transition in Ammonium Sulphate

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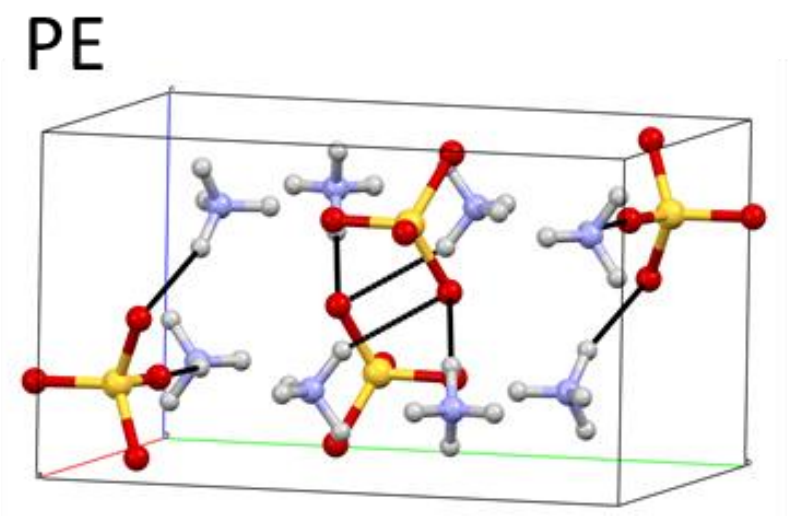
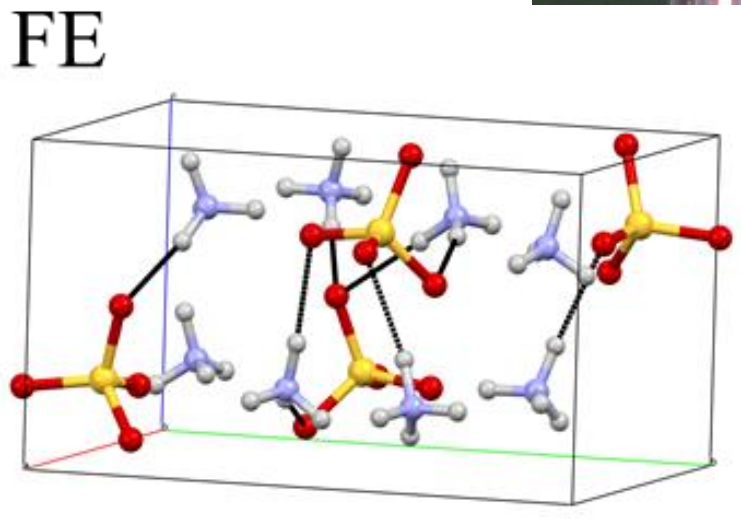
Ammonium Sulfate (AS) – $(NH_4)_2SO_4$

- Ionic, colorless crystal, obtained from aqueous solution.
- In paraelectric (PE) phase AS belongs to Pnam centrosymmetric space group.



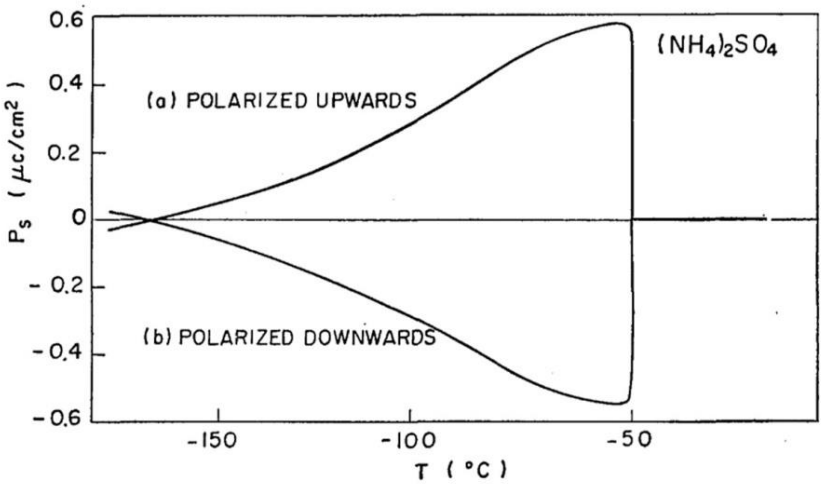


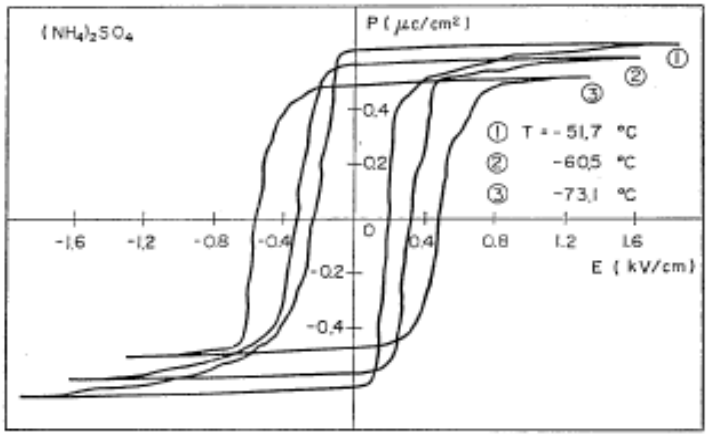
- In ferroelectric (FE) phase AS belongs to $Pna2_1$ polar space group.
- In both phases Z=4 and asymmetric unit contains two nonequivalent ammonium cations and one sulfate anion. [Schlemper, E. O.; Hamilton, W. C., *J. Chem. Phys.* 44, 4498 (1966)]

Why interesting?

- Structural phase transition to FE phase at 223 K was discovered in 1956.
[Matthias, B. T.; Remeika, J. P., *Phys. Rev.* 103, 262 (1956)]

- Atypical spontaneous polarization vs T dependence was found for AS.
[Unruh, H. G-. *Solid State Commu.* 8, 1951 (1970)]



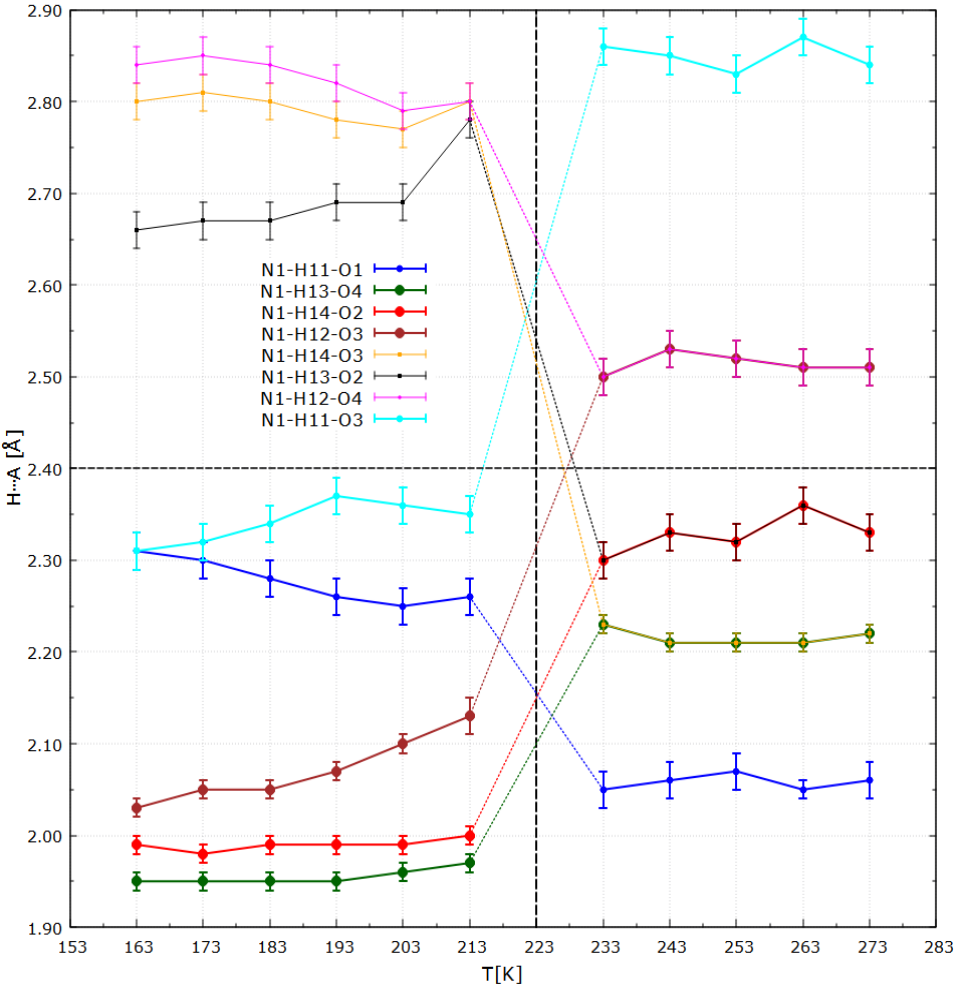


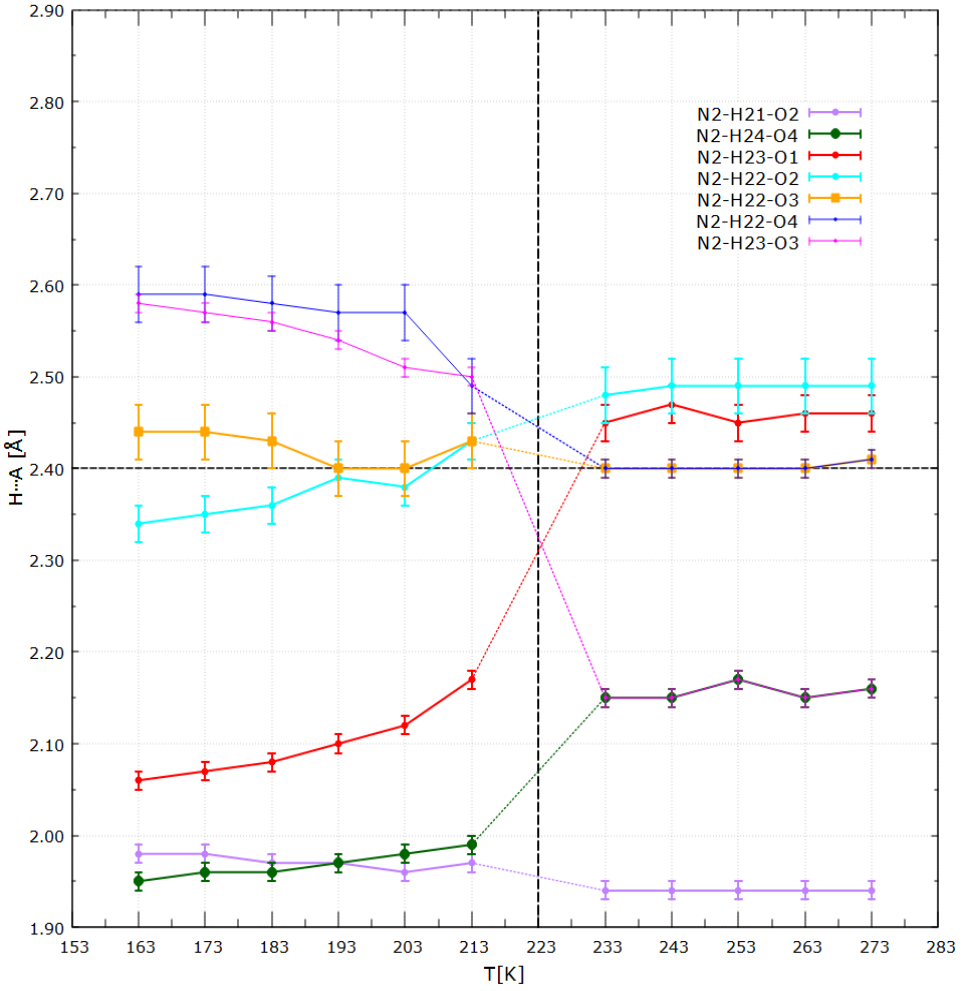
[Sawada, A.; Okaya, S.; Ishibashi, Y.; and Takagi, Y. *J. Phys. Soc. Jpn.* 38, 1408 (1974)]

- The phase transition mechanism is still unknown.

- The mechanism type with a possible use as the scheme one for the engineering of new MOF and hybrid inorganic – organic ferroelectrics.

H-bond lengths formed by ammonium cations N1 (left) and N2 (right)



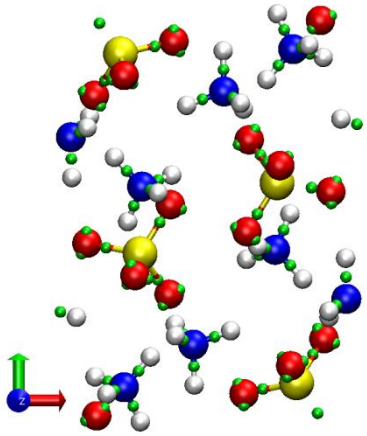


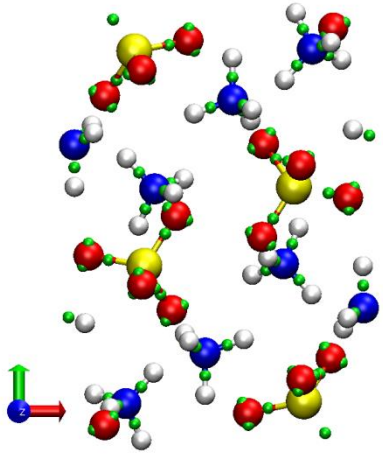
Malec, L. M.; Gryl, M.; Stadnicka, K. M. *in preparation* (2017)

Computational details

- BOMD calculations carried out using CPMD package. [http://www.cpmd.org/]
- Simulation performed for AS unit cell (60 atoms) with the NVT ensemble.

FE 148 K





PE 298 K

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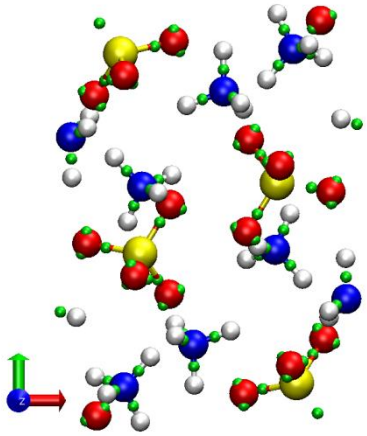

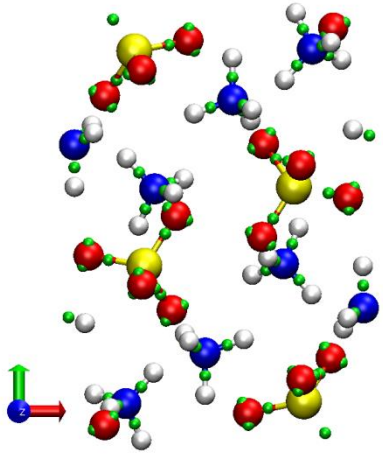

PE 298 K

- Temperature control provided by the Nose-Hoover thermostat.
- Time step 20 a.u. ⟶ 100 000 steps ⟶ 48.56 ps (for each simulation).
- The BLYP functional applied with plane wave basis set (cutoff = 250 Ry).
- Norm-conserving Goedecker pseudo-potentials applied for all atoms.

ACC CYFRONET AGH computational source usage

All calculations based on PL-Grid infrastructure at the Prometheus supercomputer.

Preliminary computations:

- the optimization for AS unit cells from 13 different temperatures.
- attempts of optimization and MD (1000 steps) of clusters build from 8 unit cells (2x2x2) (4 nodes – 96 cores).
- attempts of optimization of clusters build from 27 unit cells (3x3x3) (8 nodes - 192 cores).

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Main computations:

- for the PE phase with ***mmm*** point group applied at T= 298, 273, 263, 243 and 233K;
- for the FE phase with ***mm2*** point group applied at T= 213, 203, 173, 163 and 148K;
- for the FE phase with ***1*** point group at T= 213 and 148K
- for FE and PE phases with point group ***1*** at T= 298, 233, 213 and 148K, without the preceding geometry optimization;

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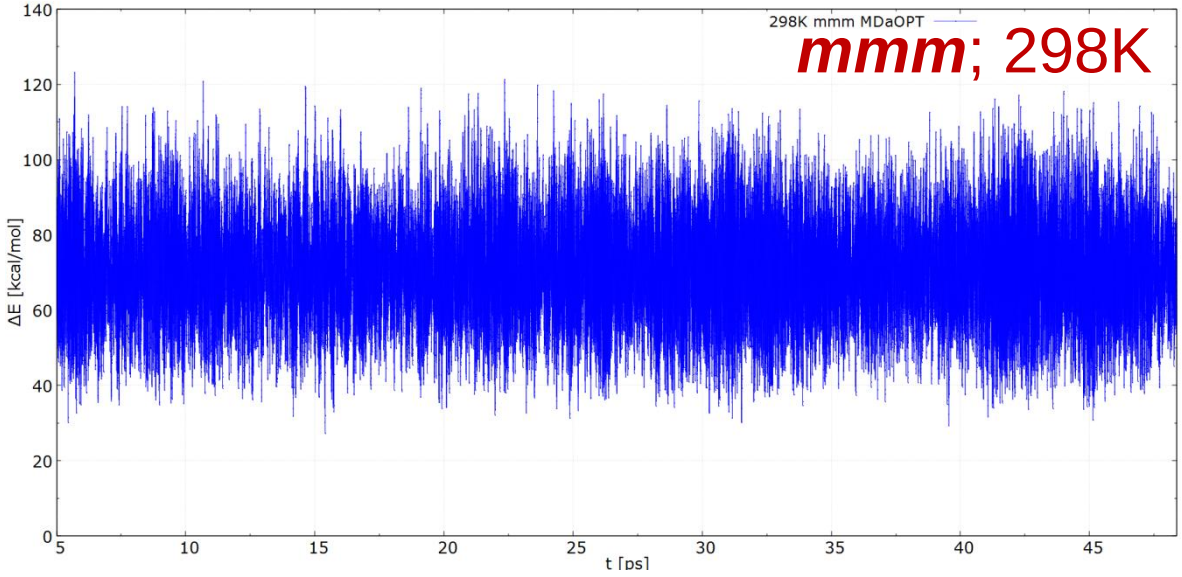
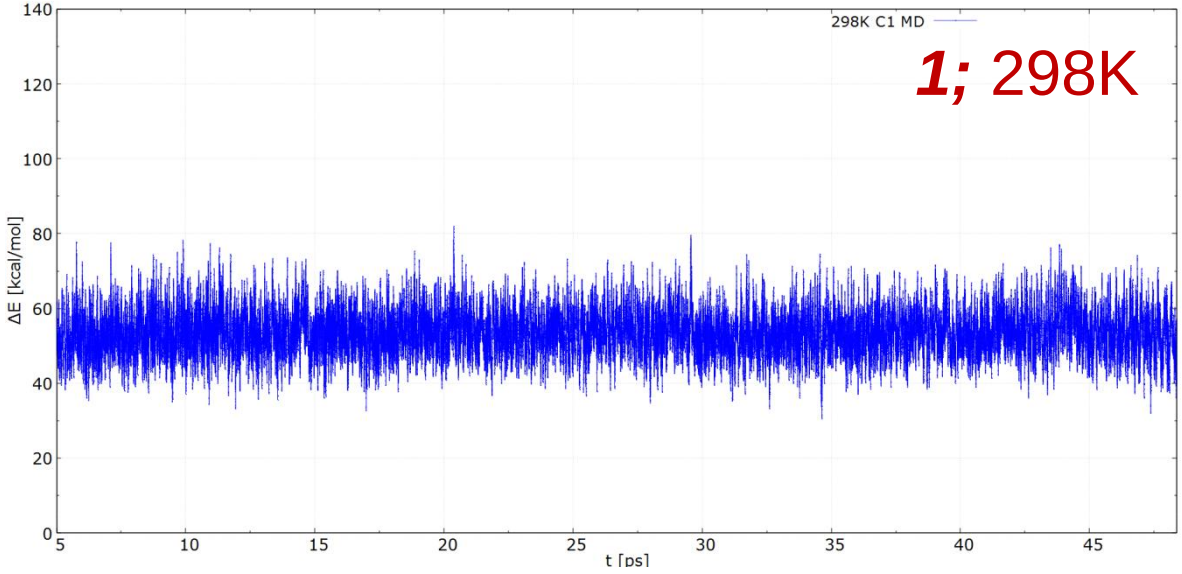
- for the FE phase with ***1*** point group at T= 213 and 148K
- for FE and PE phases with point group ***1*** at T= 298, 233, 213 and 148K, without the preceding geometry optimization;

One MD calculations for 60 atoms utilized c.a. 138 000 CPU hours (2 nodes – 48 cores).
The estimated total time of computations c.a. 3 500 000 CPU hours.

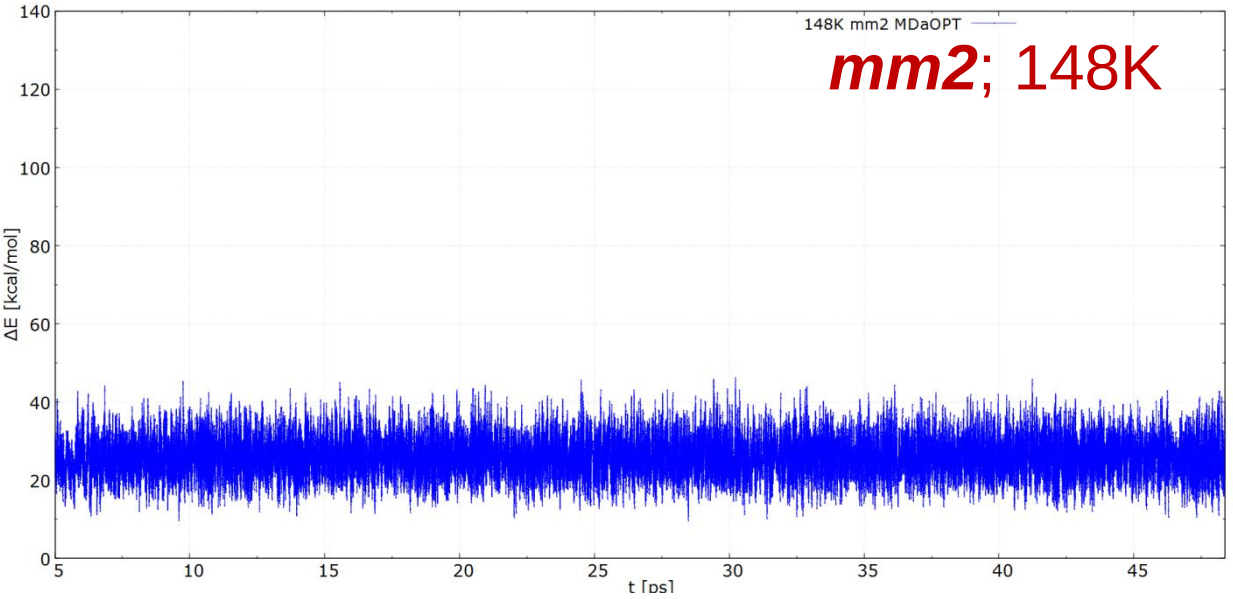
Potential energy analysis

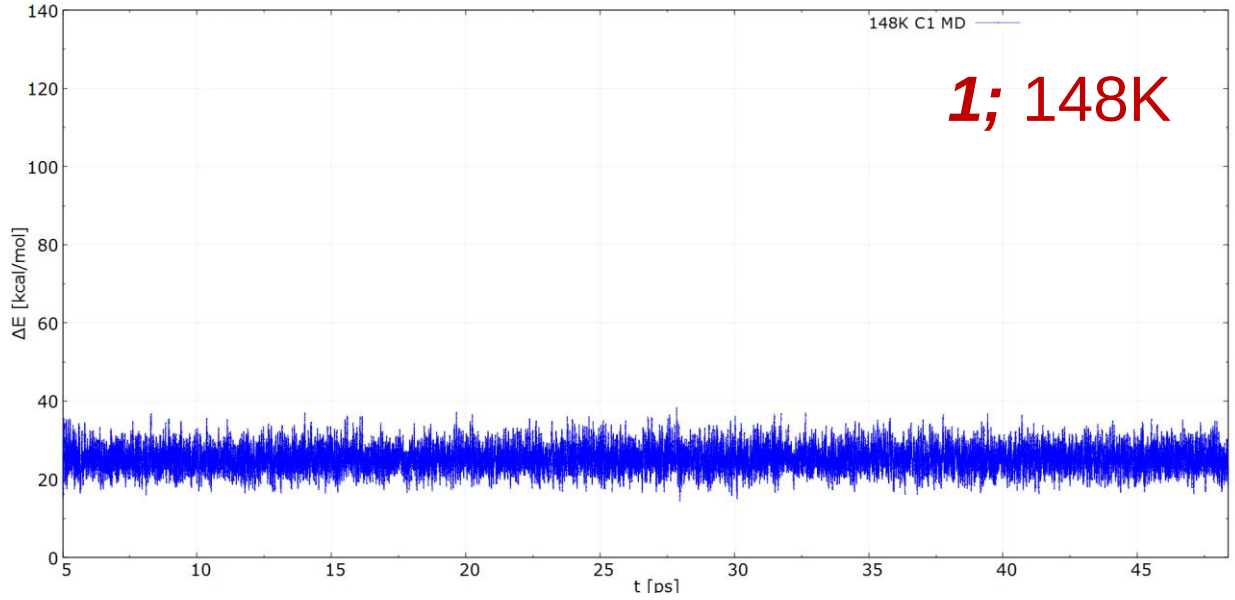




SYM	ΔEmin [kcal/mol]
mm2 148 K	**56**
mm2 163 K	**5**
mm2 173 K	**22**
mm2 203 K	**3**
mm2 213 K	**4**
mmm 233 K	**82**
mmm 243 K	**144**
mmm 263 K	**44**
mmm 273 K	**28**
mmm 298 K	**31**

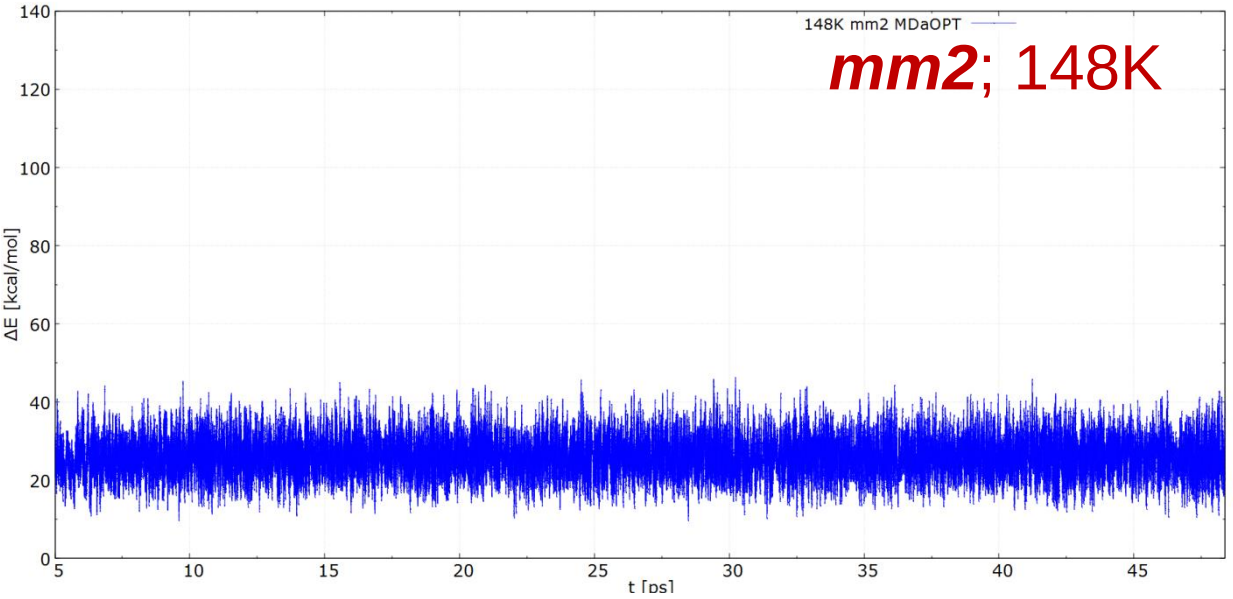
Potential energy analysis

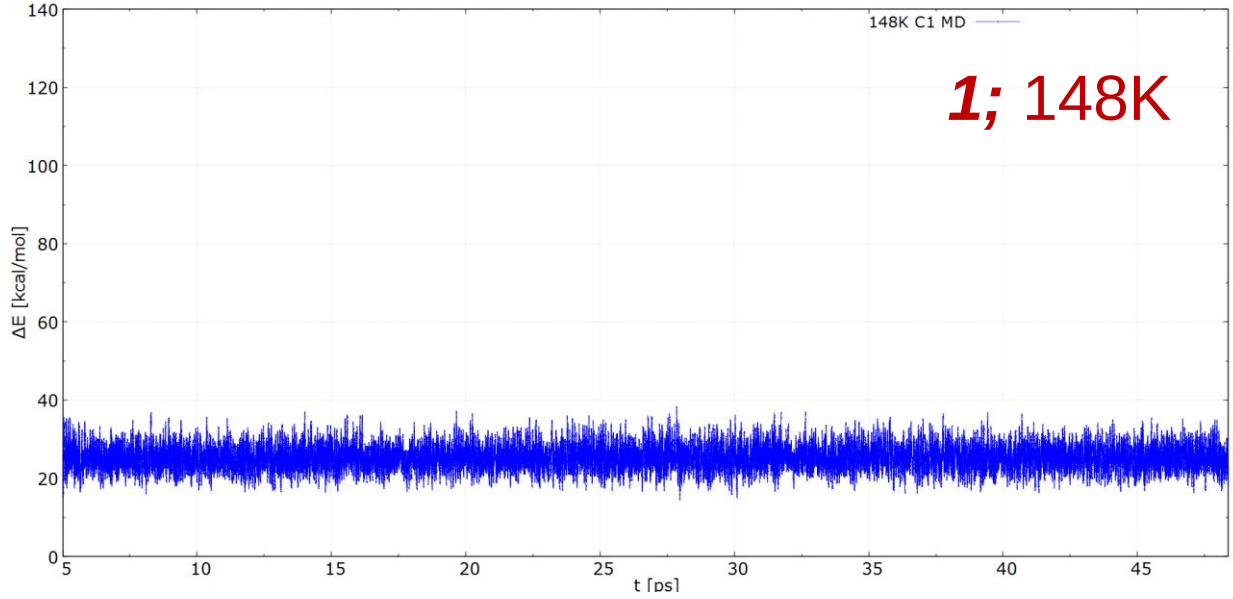




SYM	Amplitude of ΔE [kcal/mol]
mm2 148 K	**26**
mm2 163 K	**28**
mm2 173 K	**32**
mm2 203 K	**37**
mm2 213 K	**39**
mmm 233 K	**61**
mmm 243 K	**63**
mmm 263 K	**66**
mmm 273 K	**68**
mmm 298 K	**71**
1 148 K	**26**
1 213 K	**40**
1 233 K	**43**
1 298 K	**54**

Potential energy analysis





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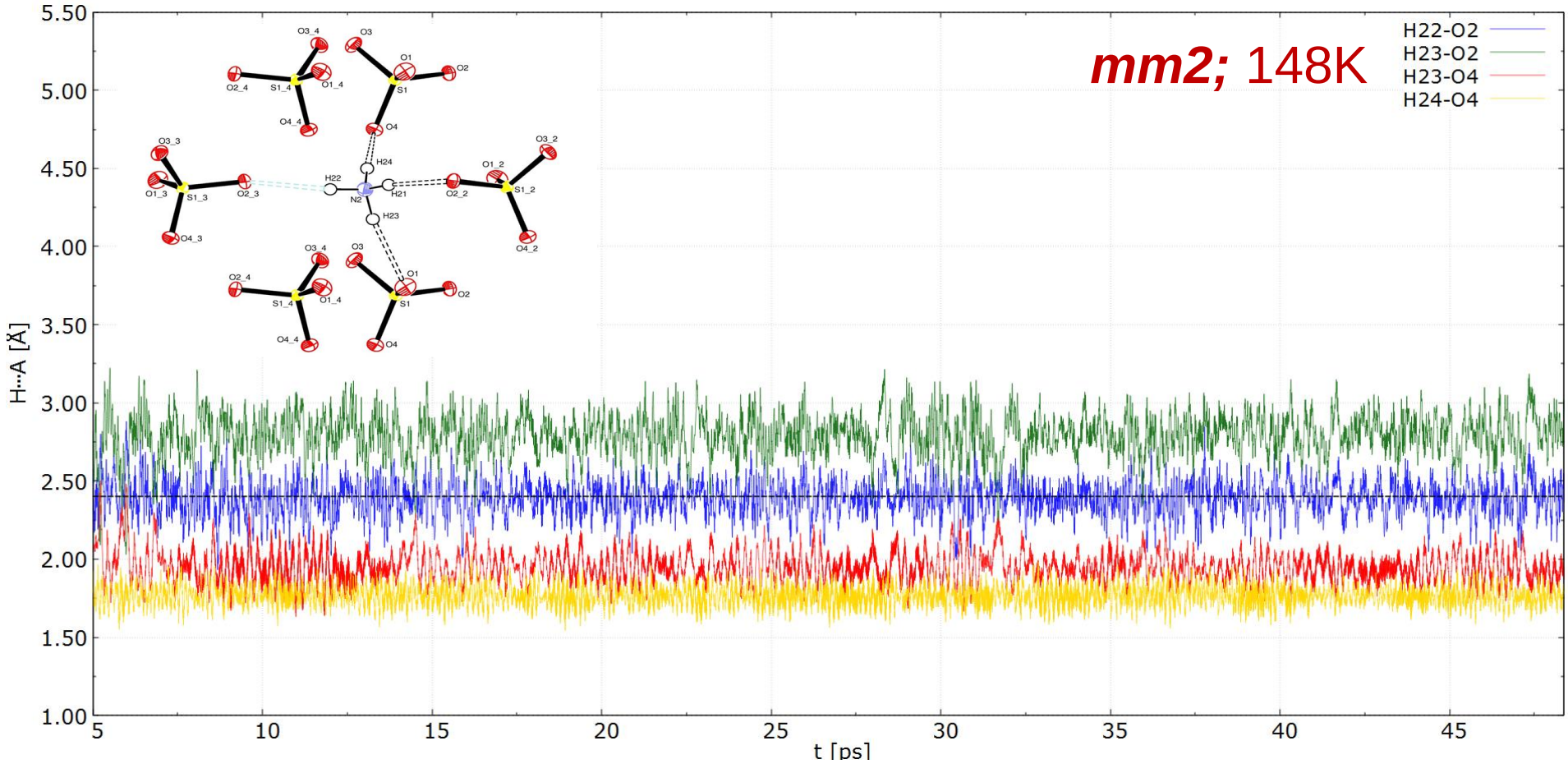
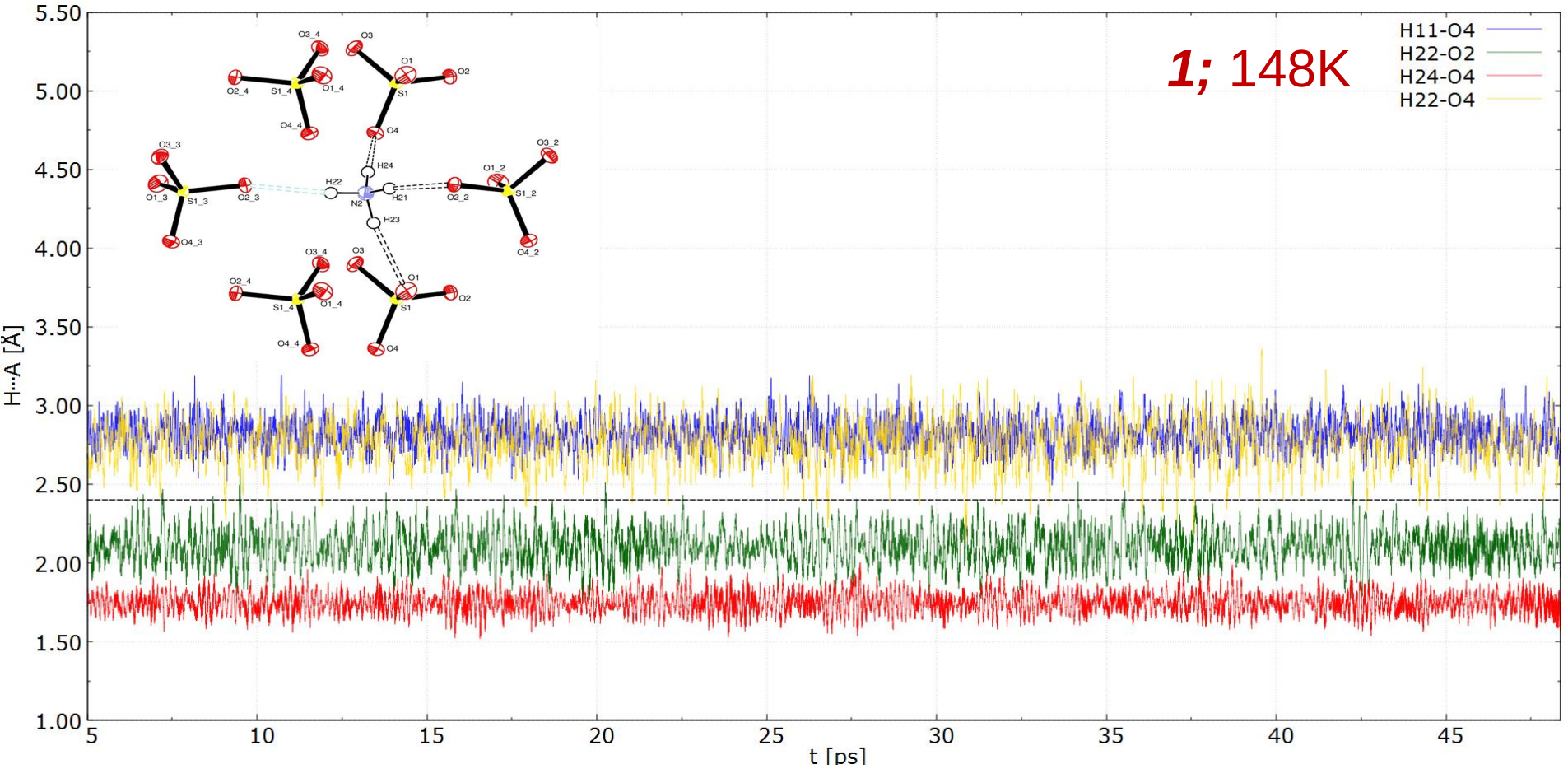
Analysis of geometrical parameters – FE

H···O	EXP	*mm2*	*1*	H···O	EXP	*mm2*	*1*
H13-O2	2.66	1.88	2.71	**H22-O2**	2.34	2.39	2.11
H13-O4	1.95	2.70	1.75	**H24-O4**	1.95	1.77	1.74
H12-O4	2.84	1.89	-	**H22-O4**	2.59	-	2.76
H12-O3	2.03	2.26	1.78	**H23-O1**	2.06	2.81	1.79
H13-O3	-	2.41	-	**H23-O3**	2.58	-	2.70
H14-O2	1.99	2.8	1.78	**H22-O3**	2.44	1.89	2.50
H14-O3	2.80	-	-	**H21-O2**	1.98	-	-
H11-O1	2.31	1.86	2.61	**H23-O2**	-	2.79	-
H11-O3	2.31	2.78	1.84	**H23-O4**	-	1.95	-
H14-O1	-	1.70	-	**H21-O1**	-	2.84	-
H11-O4	-	2.75	2.82	**H22-O1**	-	2.75	-

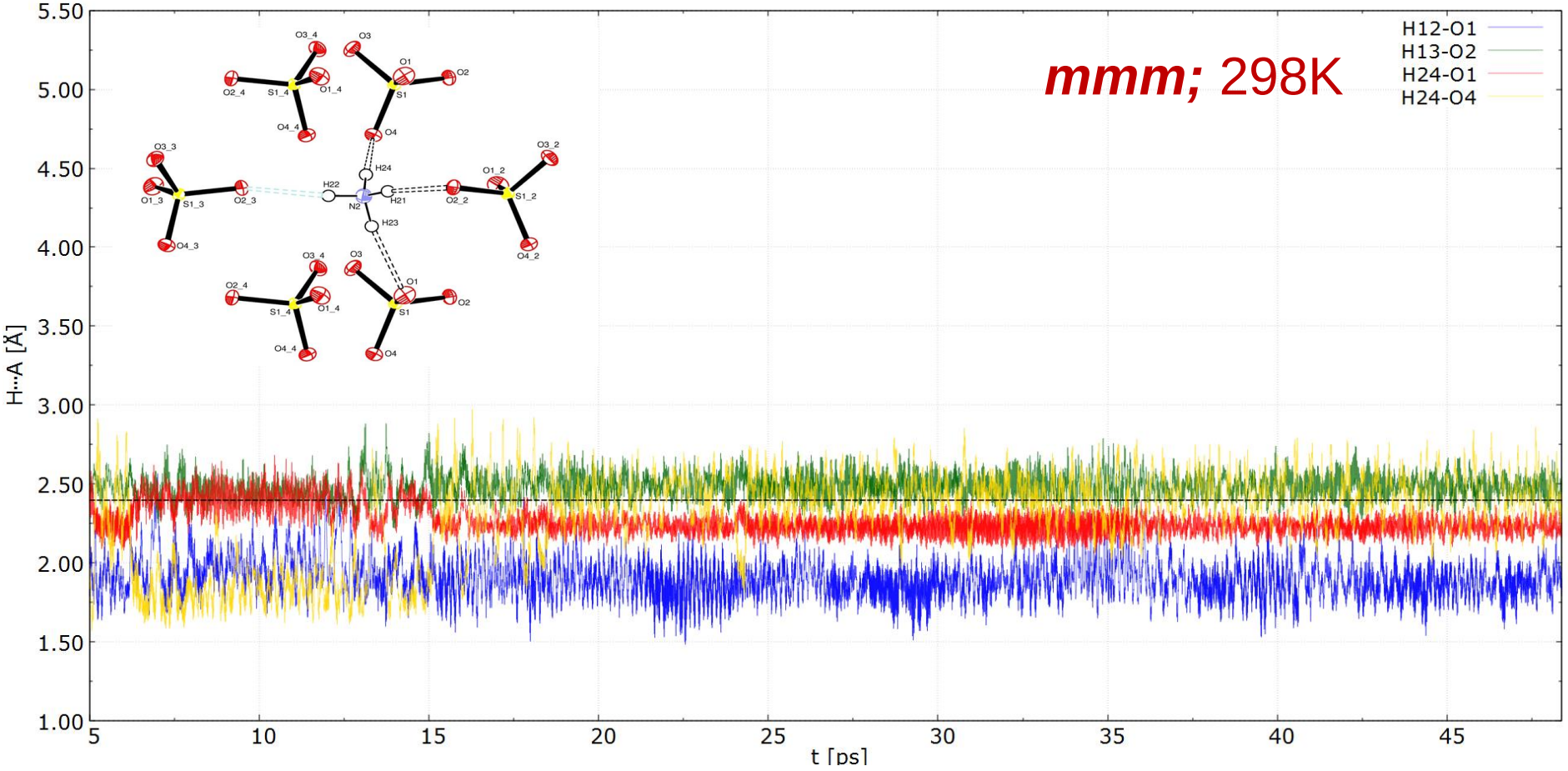
Analysis of geometrical parameters– FE



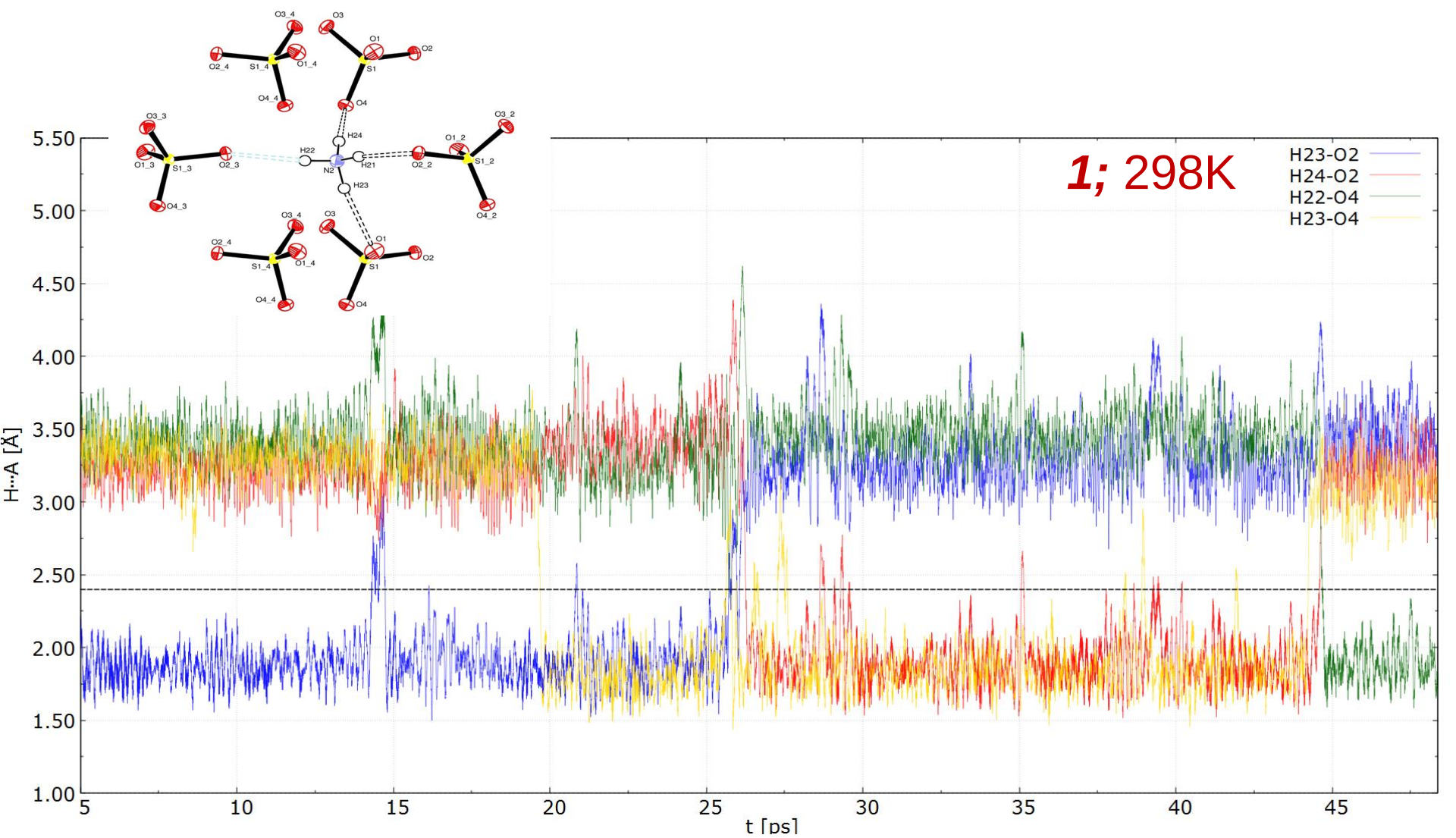
Analysis of geometrical parameters- FE



Analysis of geometrical parameters- PE



Analysis of geometrical parameters - PE



Conclusions

- The phase structure does not change during simulation

- Application of symmetry (***mmm*** and ***mm2***) in simulations restricts us to selected moderate and weak hydrogen bonds in the system. As a side effect of symmetry restrictions some additional moderate H-bonds appear in structures.

- The use of ***1*** symmetry provides reproduction of almost all moderate and weak hydrogen bonds.

- The reorientations of ions in simulations for temperatures above Tc in ***1*** have been observed.

Conclusions

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- The use of ***1*** symmetry provides reproduction of almost all moderate and weak hydrogen bonds.

- The reorientations of ions in simulations for temperatures above Tc in ***1*** have been observed.

The system ’ feels’ it’s true symmetry,

if we do not disrupt it with symmetry constraints.

Perspectives

- MD temperaturę ramping calculations starting from low temperature structure.

- Extension of the considered system by k-point approach.

- Calculation of IR spectra from autocorelation function of dipole moment (comparison with experimental spectra).

Acknowledgments:

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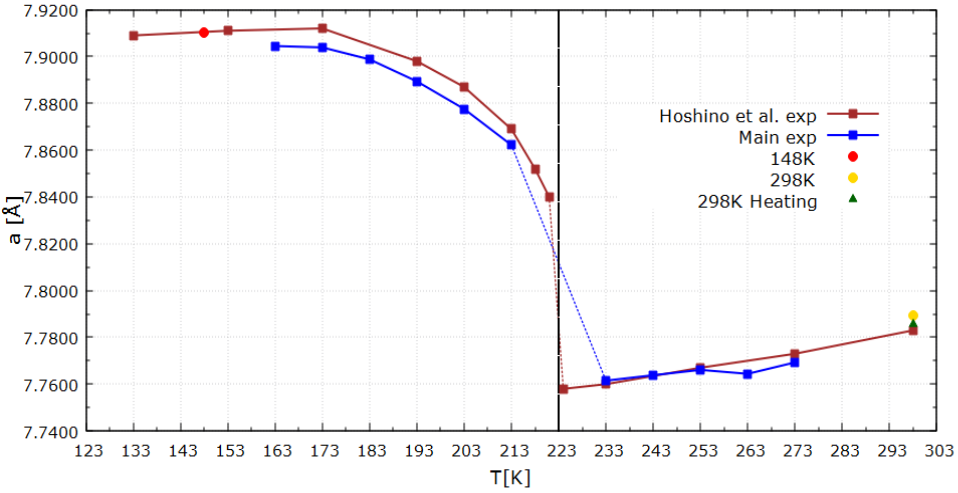
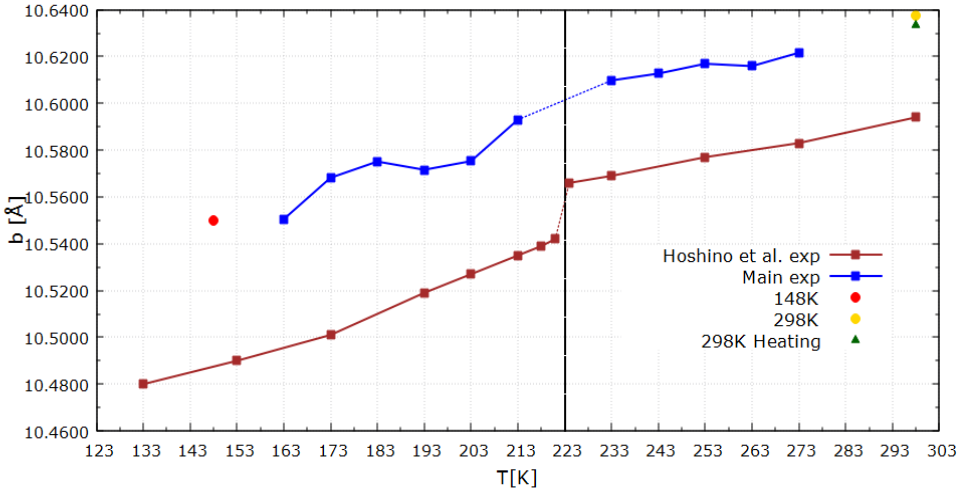
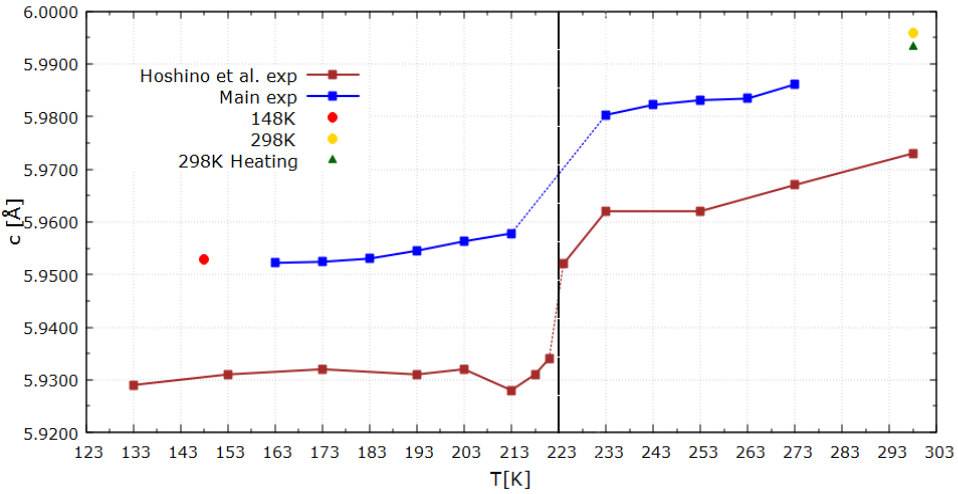
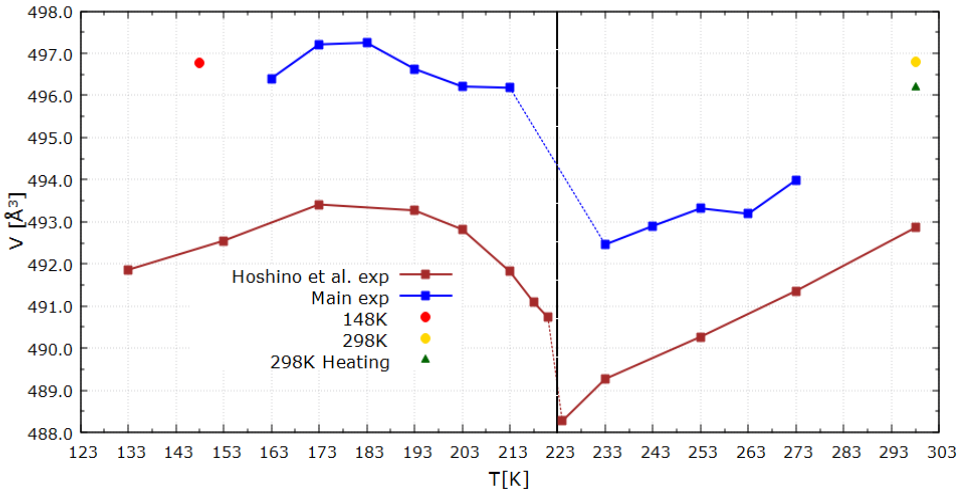
Thank you for your attention

Experimental lattice parameters and the unit cell volume vs temperature





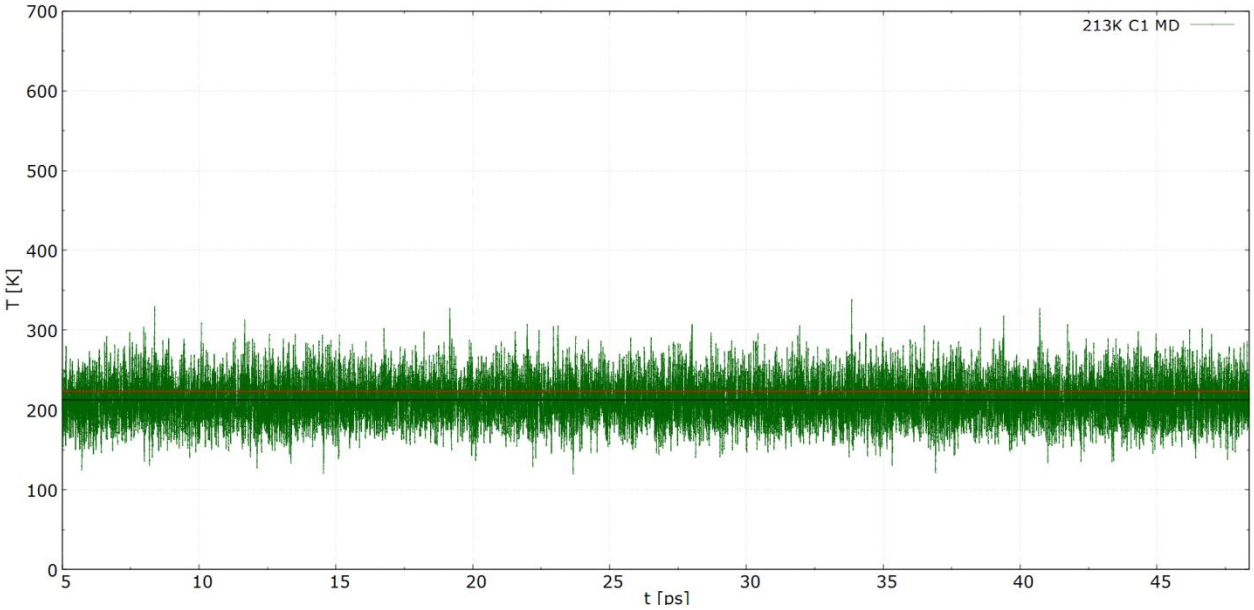


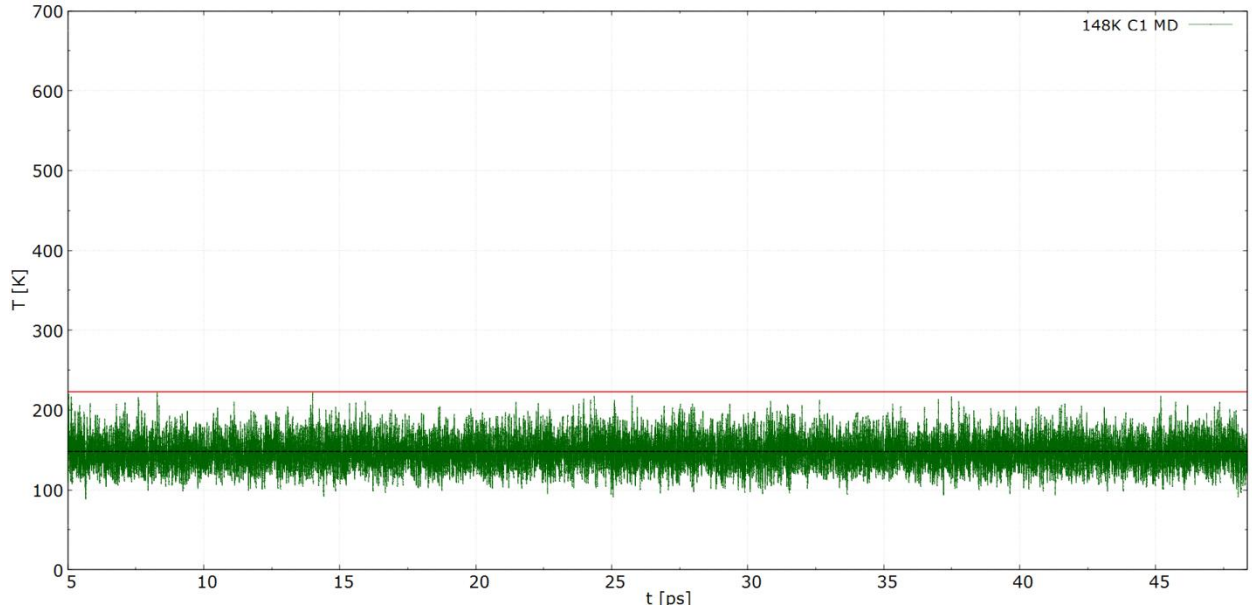


[Malec, L. M.; Gryl, M.; Stadnicka, K. M. *in preparation* (2017)]
[Hoshino, S.; Vedam, K.; Okaya, Y.; Pepinsky, R. *Phys. Rev.* 112, 405 (1958)]

Temperature control analysis

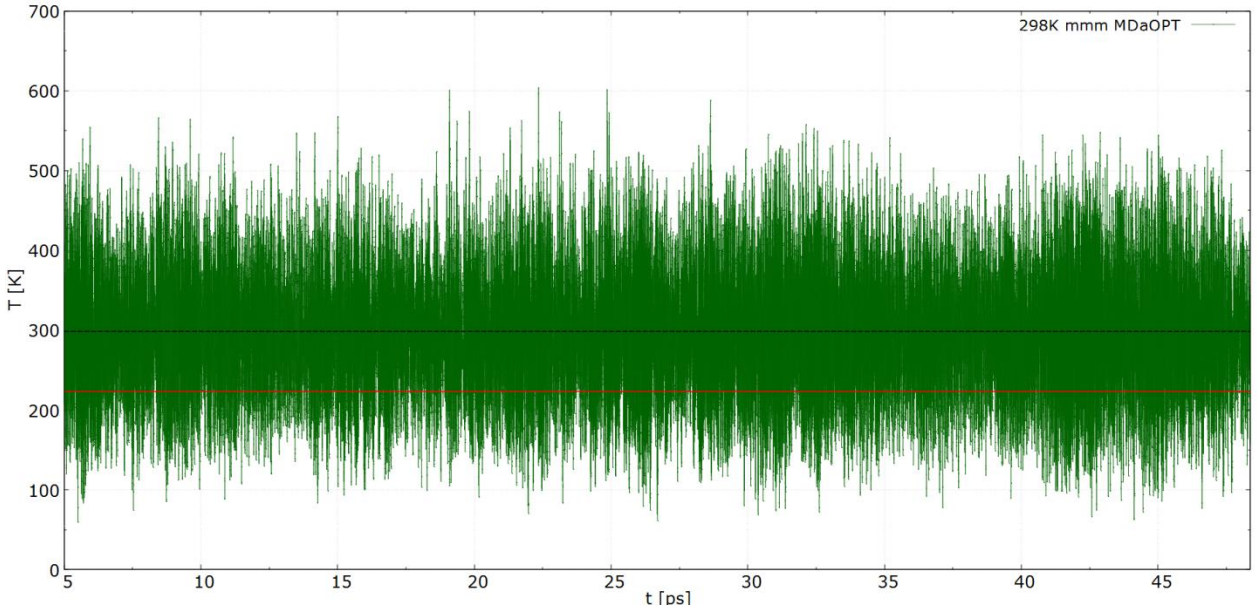
Problem near Tc





Temperature control

mmm
symmetry



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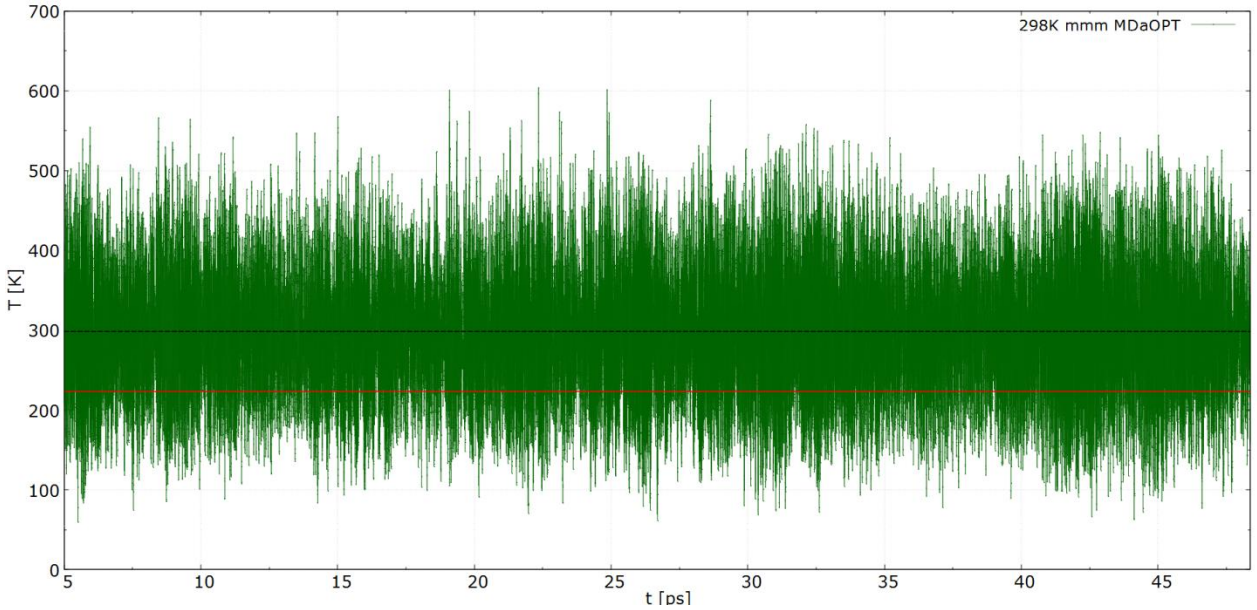

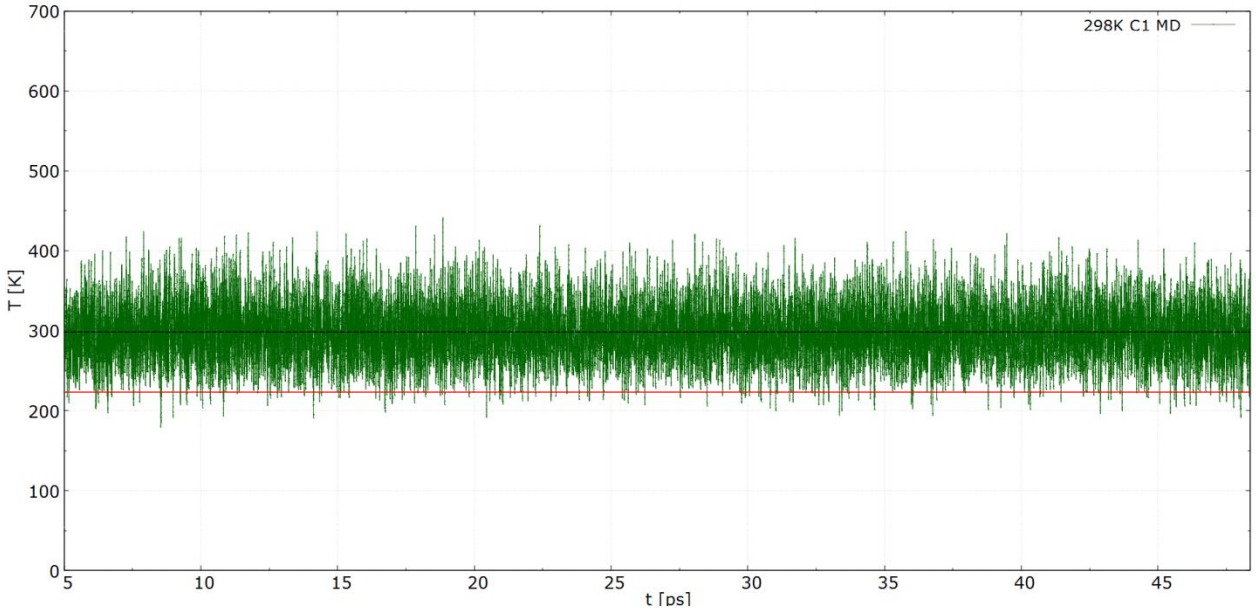

1
symmetry

Analysis of geometrical parameters - PE

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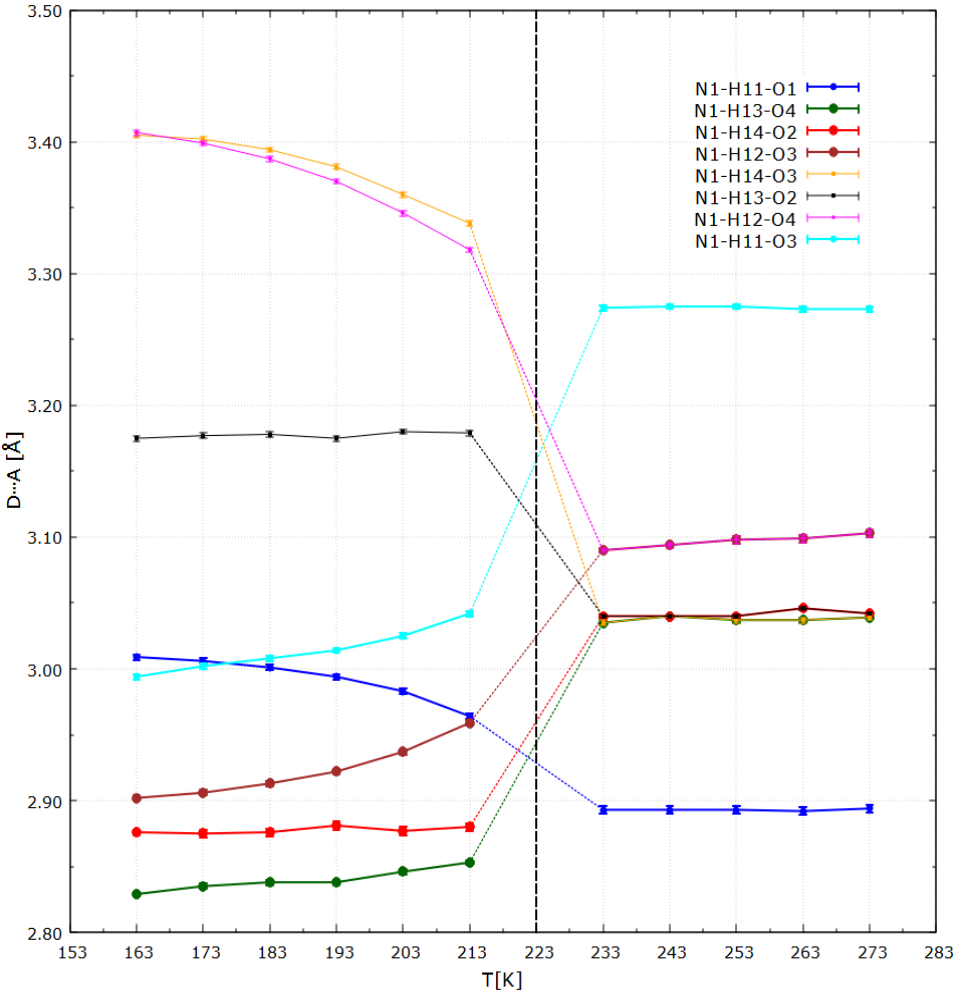
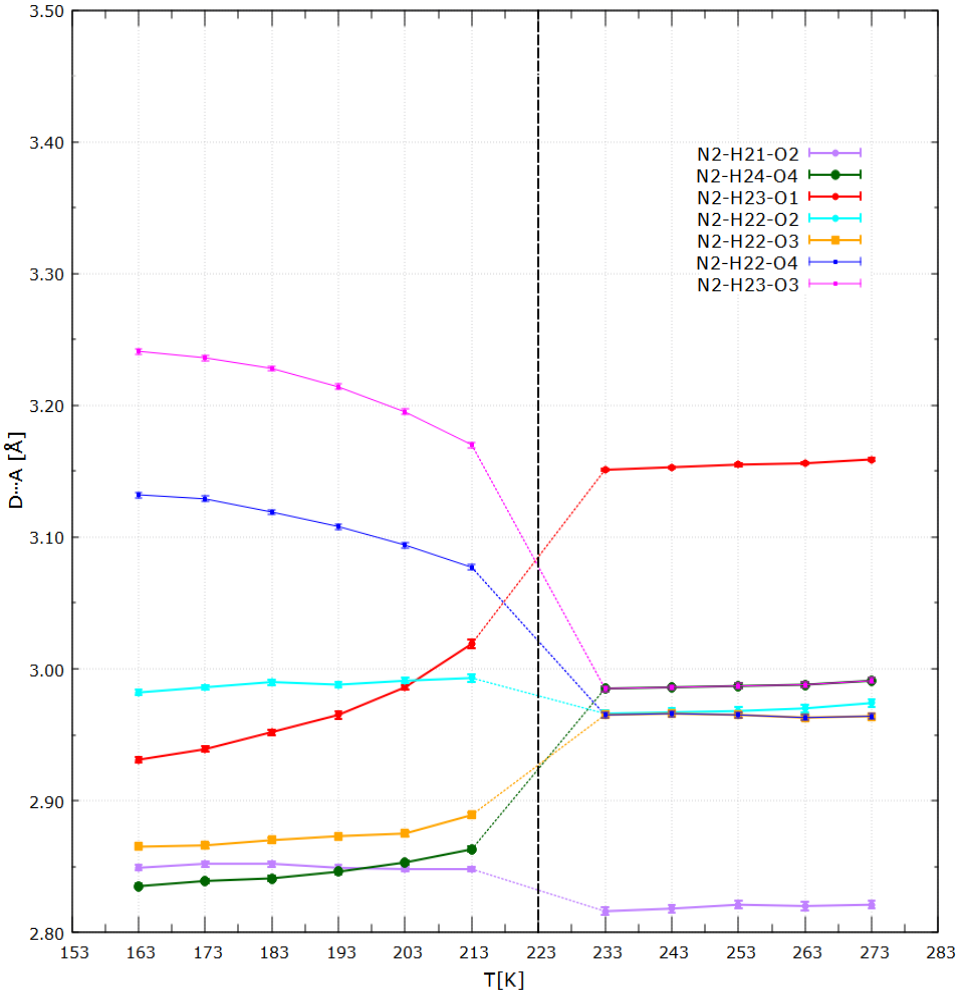
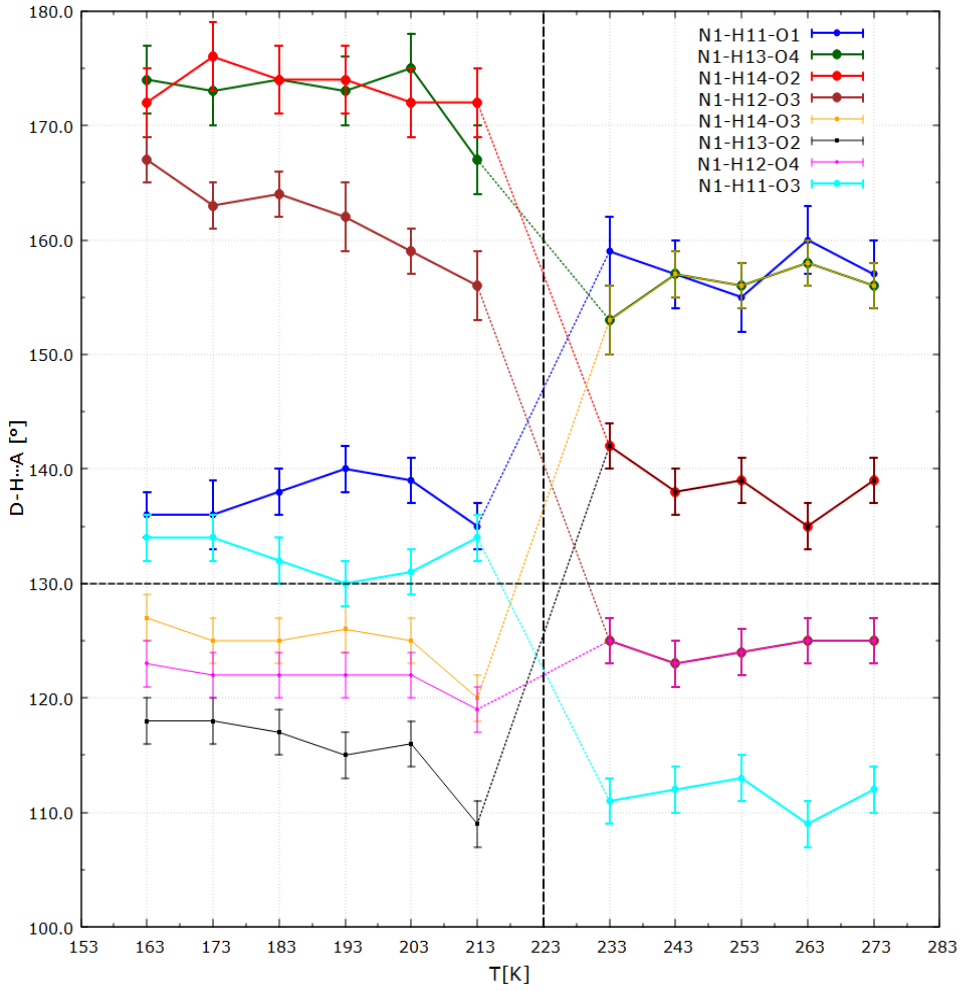
H12-O1	-	1.90	2.68	**H13-O1**	-	-	2.65
H13-O2	2.33	2.48	3.16	**H14-O1**	-	-	2.24
H13-O4	2.22	1.77	-	**H24-O1**	-	2.27	-
H12-O4	2.51	2.80	2.85	**H22-O2**	2.49	1.84	2.63
H14-O4	-	2.93	-	**H24-O4**	2.16	2.30	3.25
H12-O3	2.51	2.80	2.70	**H21-O4**	-	2.45	-
H13-O3	-	2.93	2.98	**H22-O4**	2.41	3.25	2.19
H14-O2	2.33	2.48	2.59	**H23-O1**	2.46	2.27	2.5
H14-O3	2.22	1.77	1.79	**H23-O3**	2.16	2.30	2.69
H11-O1	2.06	1.83	2.52	**H21-O3**	-	2.45	2.31
H11-O2	-	-	2.84	**H22-O3**	2.41	3.25	3.42
H11-O3	2.84	-	2.85	**H21-O2**	1.94	-	-
H11-O4	2.84	-	2.93	**H23-O2**	-	-	2.70
H12-O2	-	-	2.9	**H24-O2**	-	-	2.60

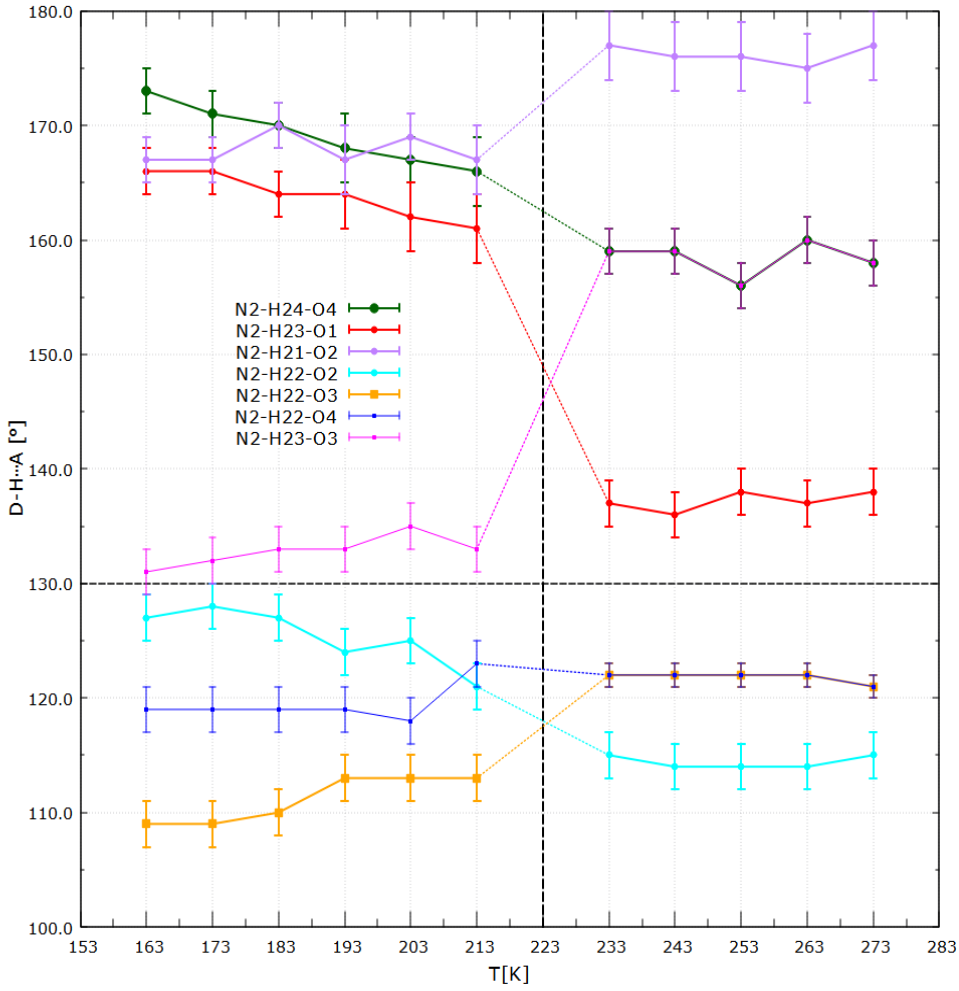
D···A distances in H-bonds formed by N1 (left) and N2 (right) cations



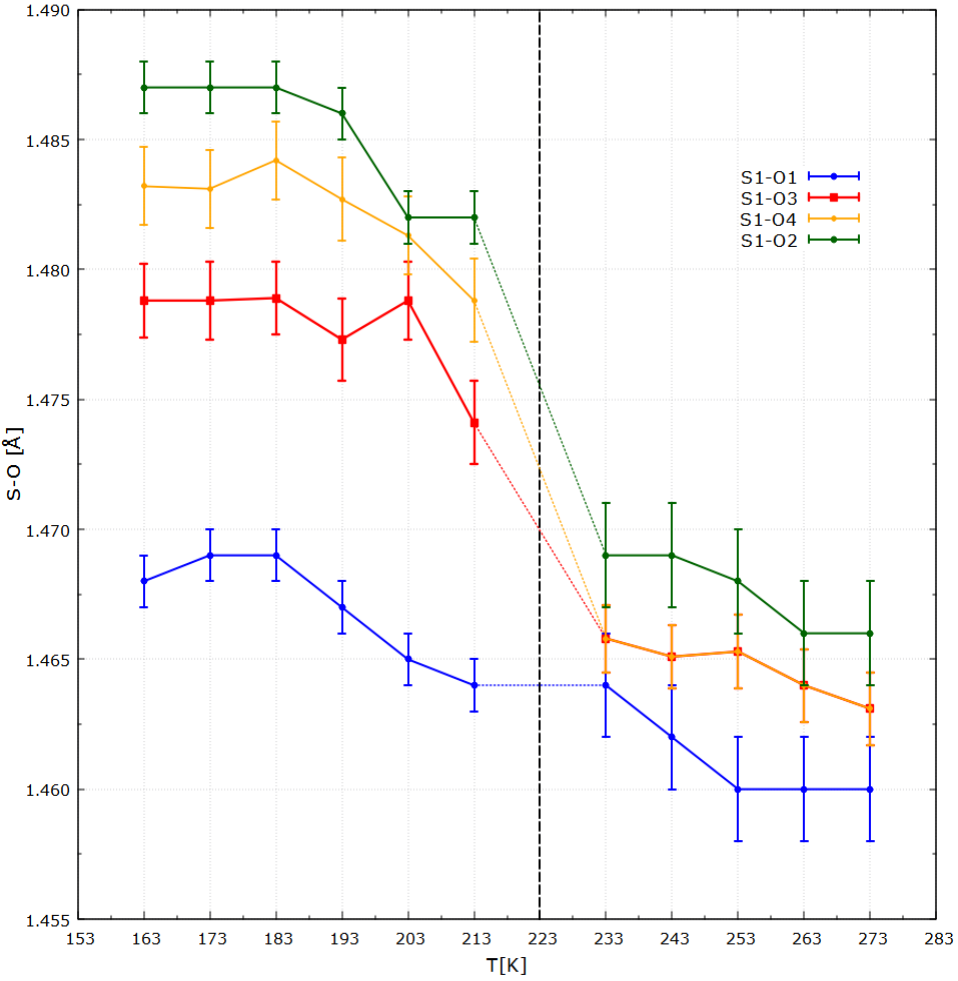


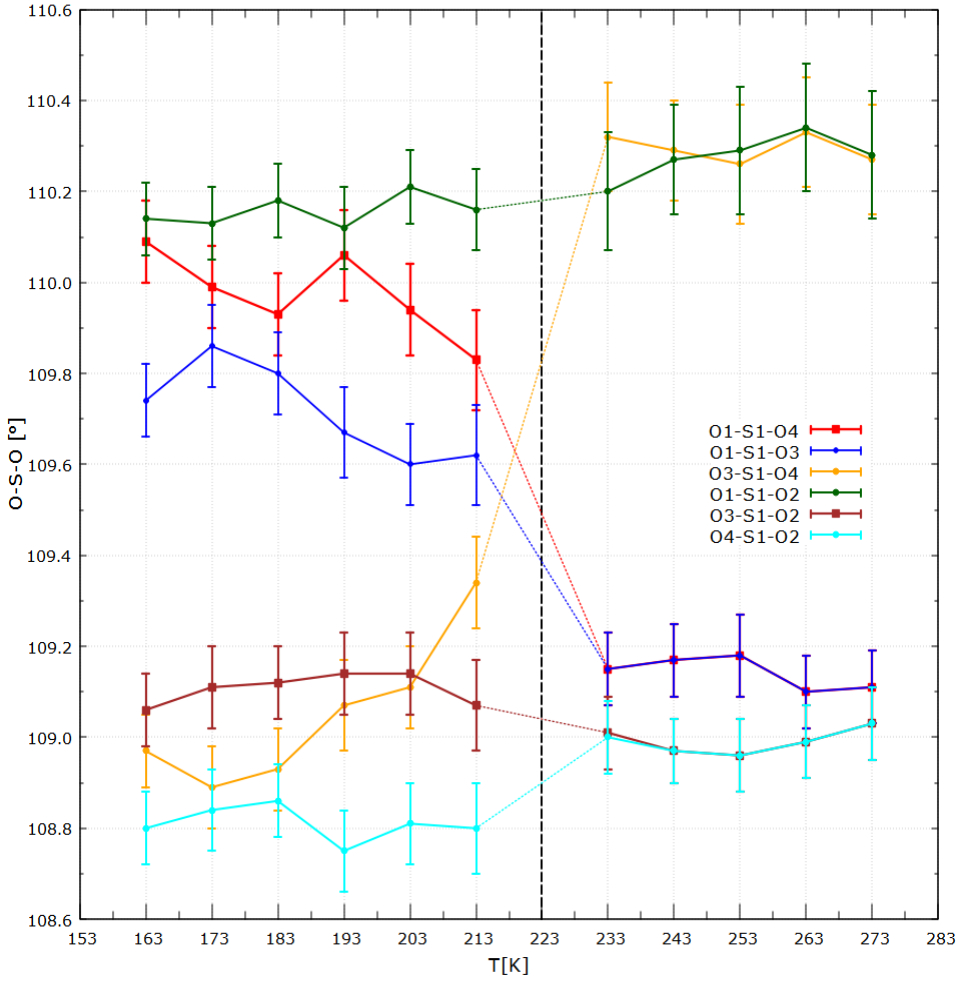
D-H···A angles in H-bonds formed by N1 (left) and N2 (right) cations



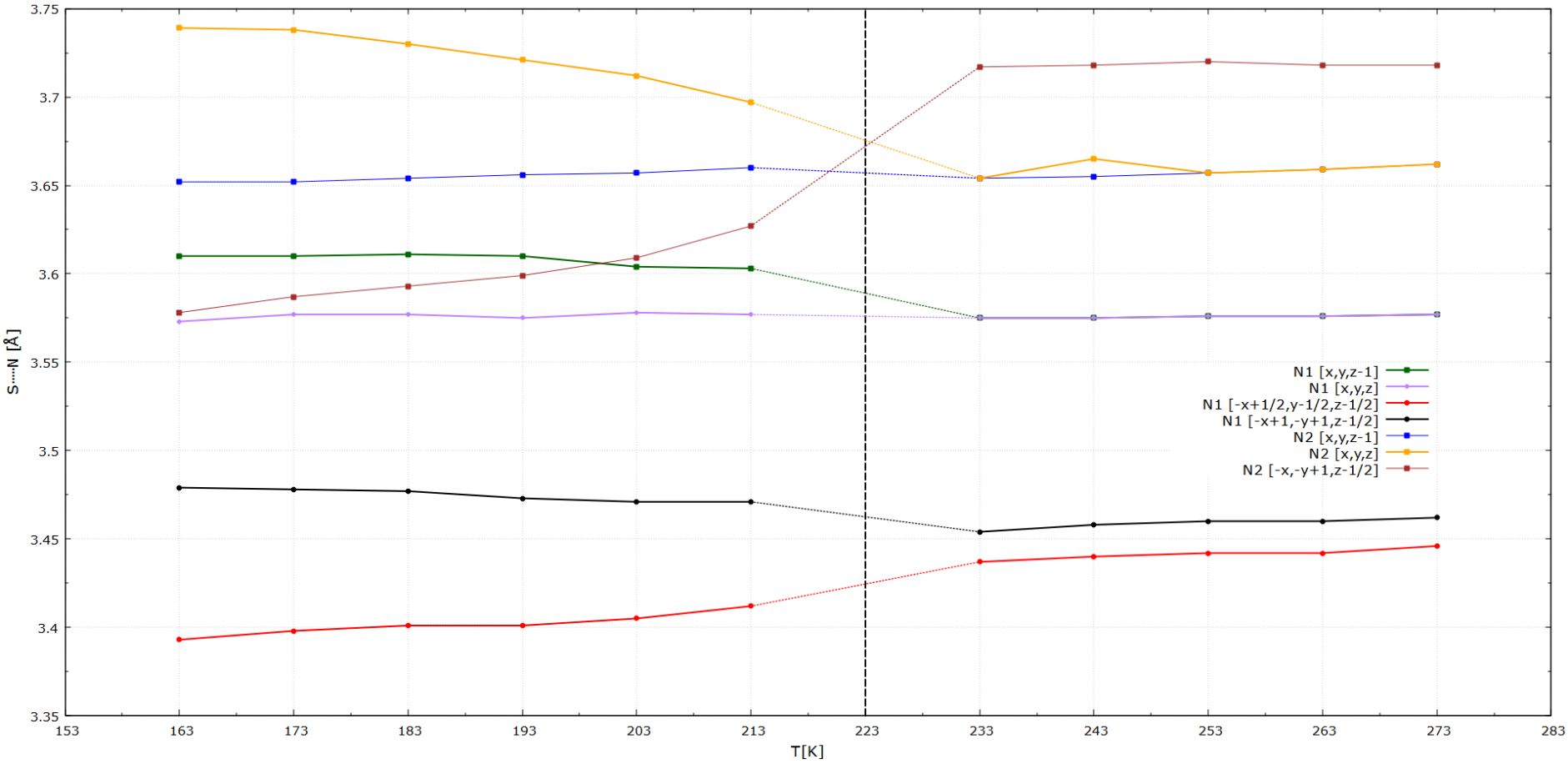


Variation of bond lengths (left) and valence angles (right) of sulfate anion



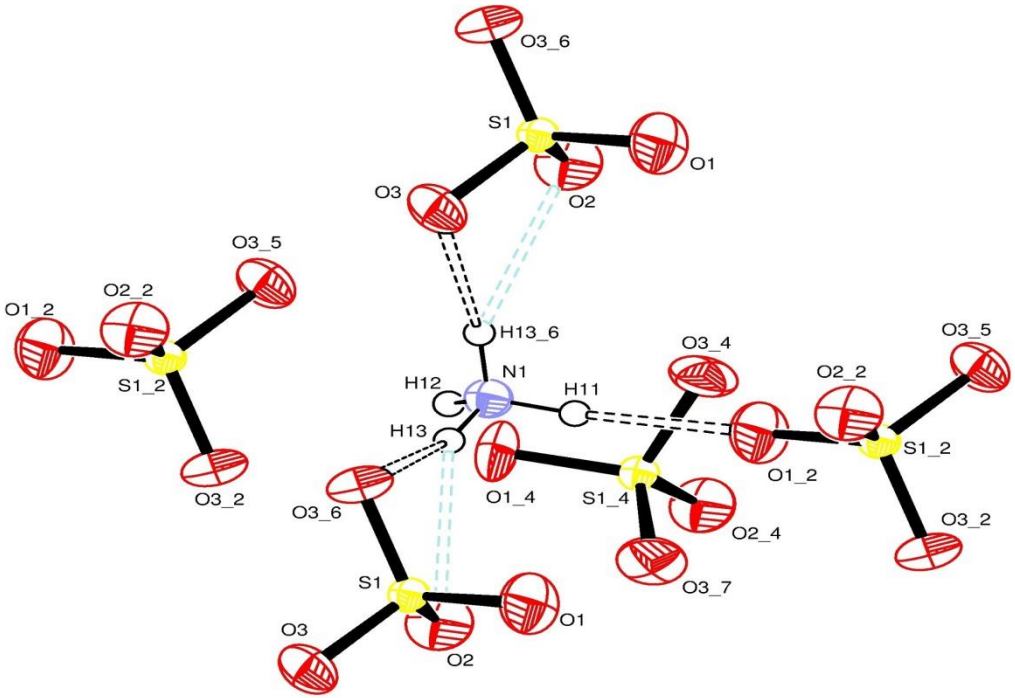


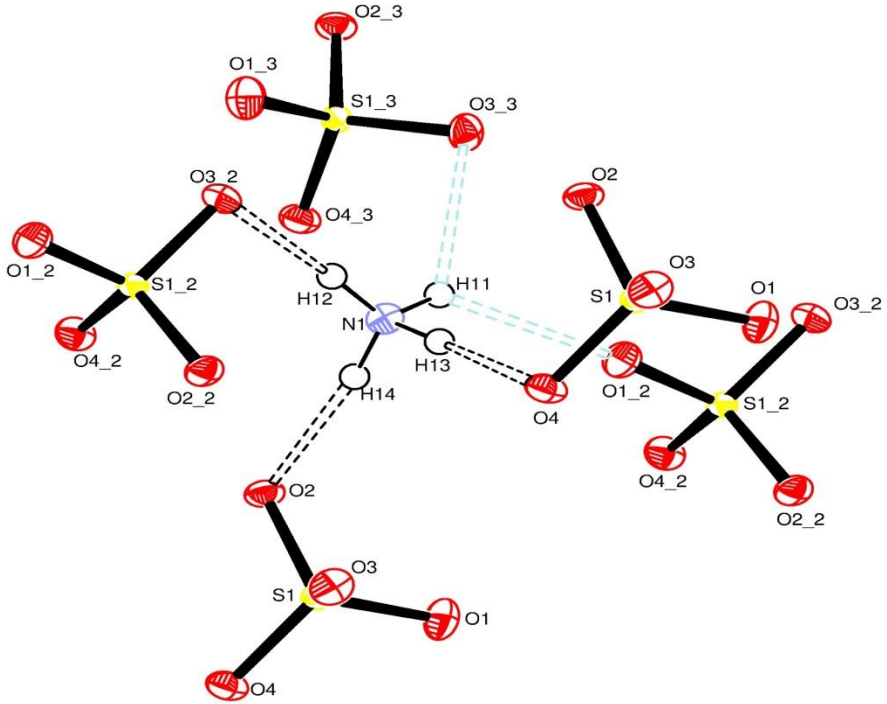
S···N distances in H-bonds formed by N1 (left) and N2 (right) cations



Right
NH_4^+(1) cation as the donor of H-bonds in PE-phase (273 K)

Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones



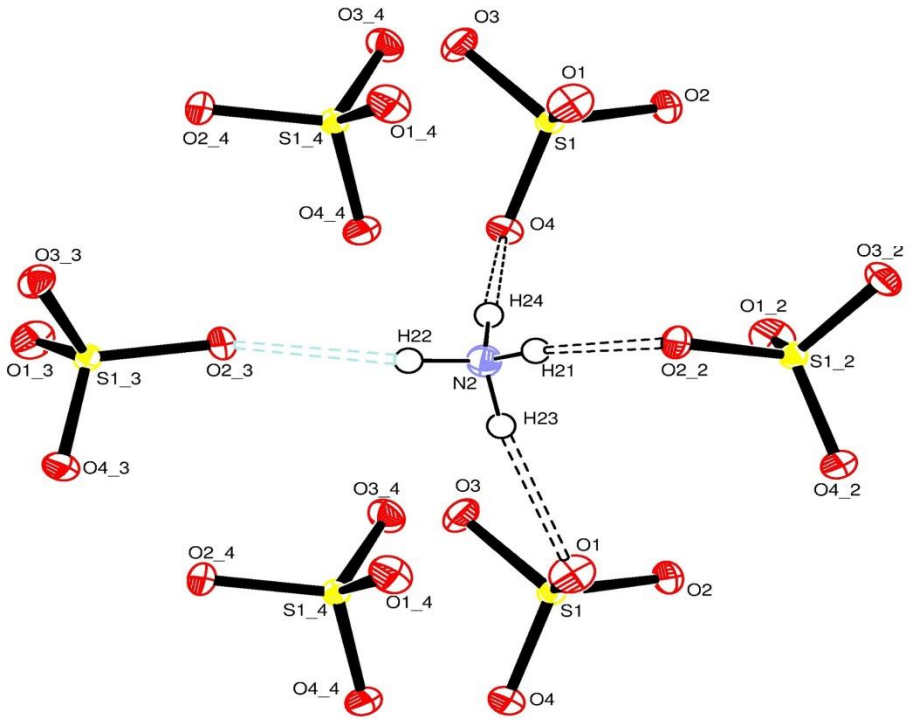


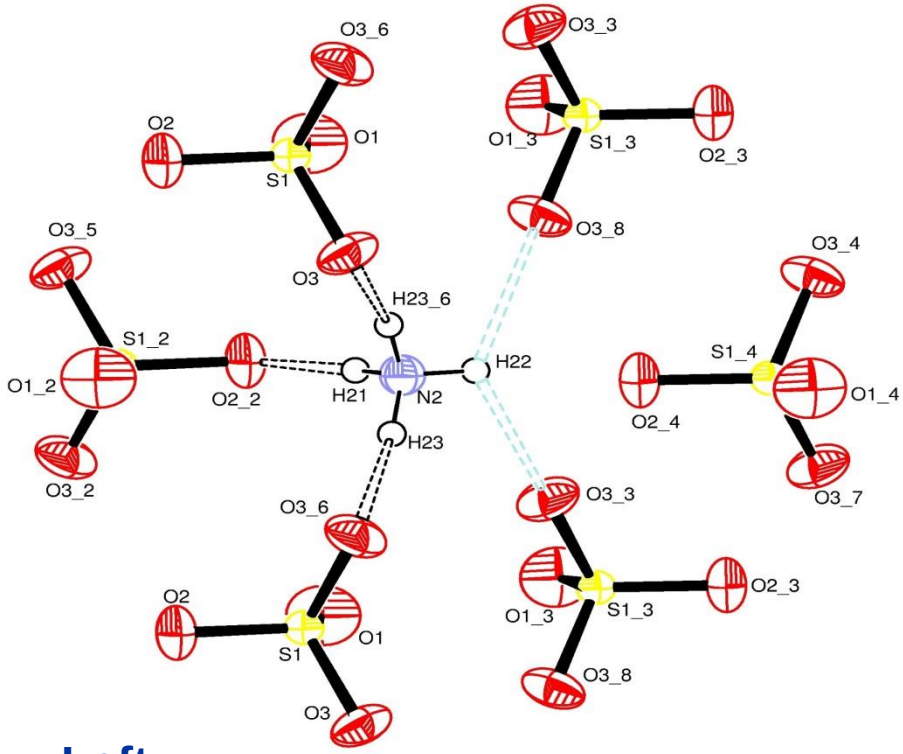
Left
NH_4^+(1) cation as the donor of H-bonds in FE-phase (163 K)

Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones

Right
NH_4^+(2) cation as the donor of H-bonds in PE-phase (273 K)

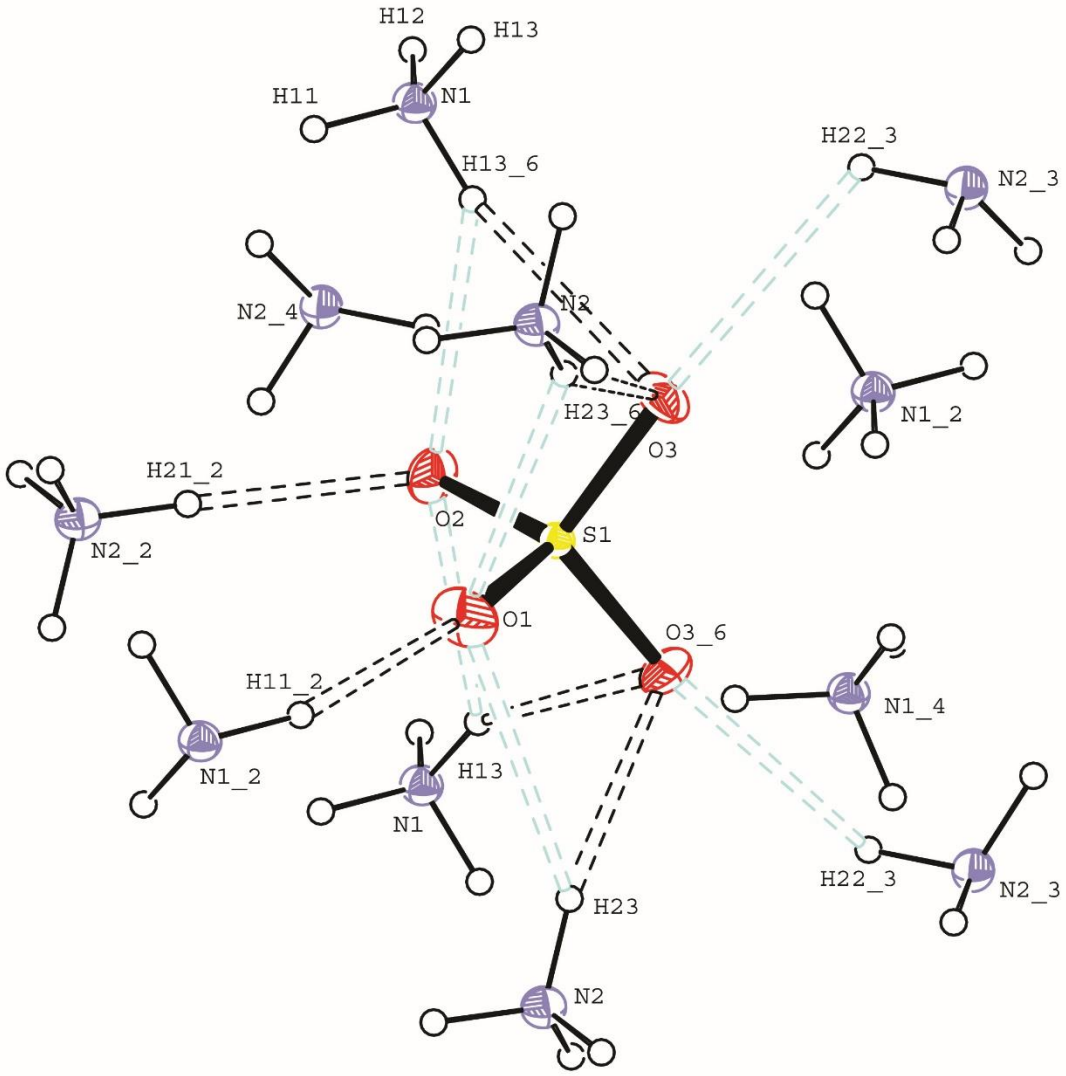
Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones





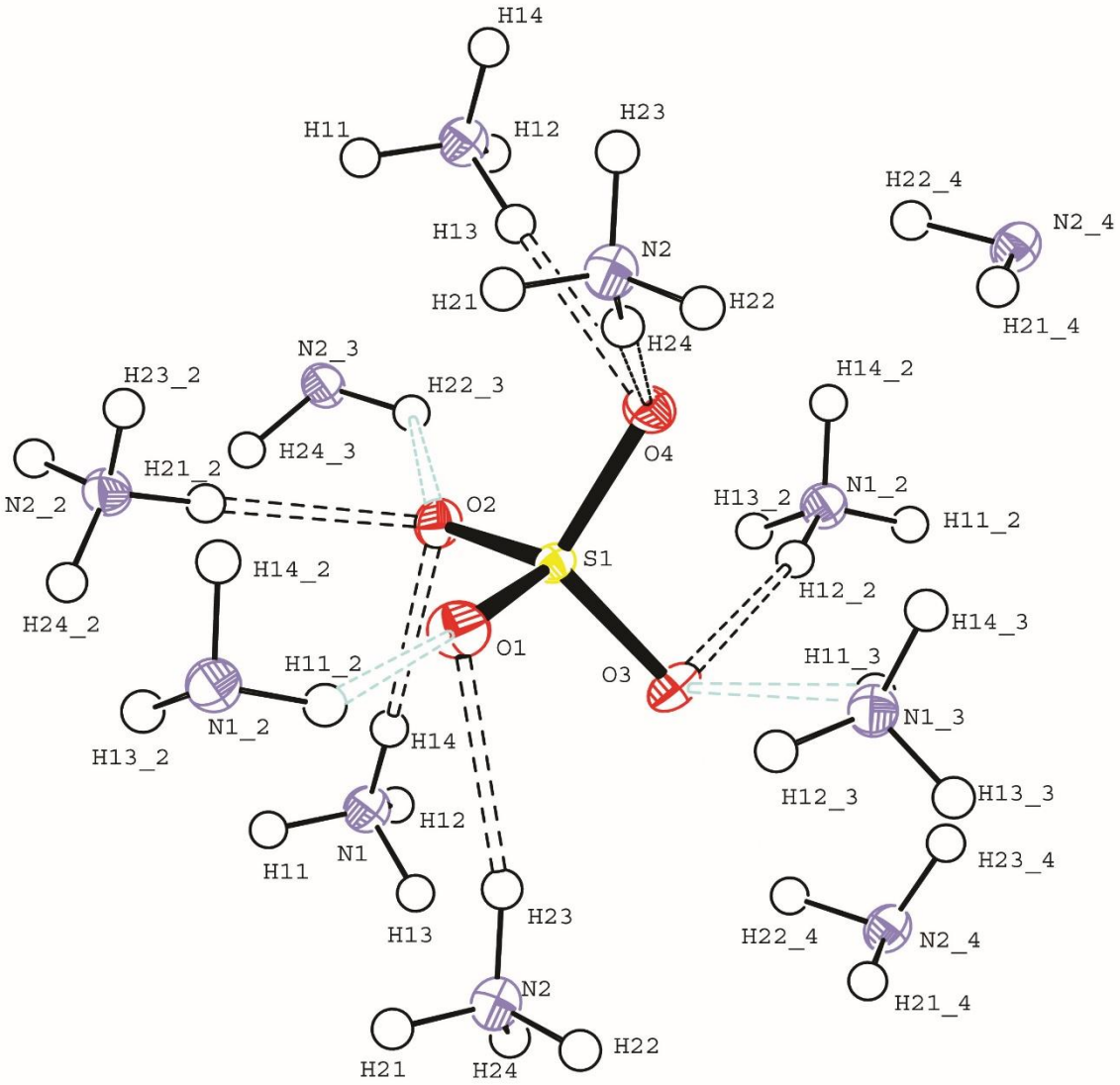
Left
NH_4^+(2) cation as the donor of H-bonds in FE-phase (163 K)

Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones



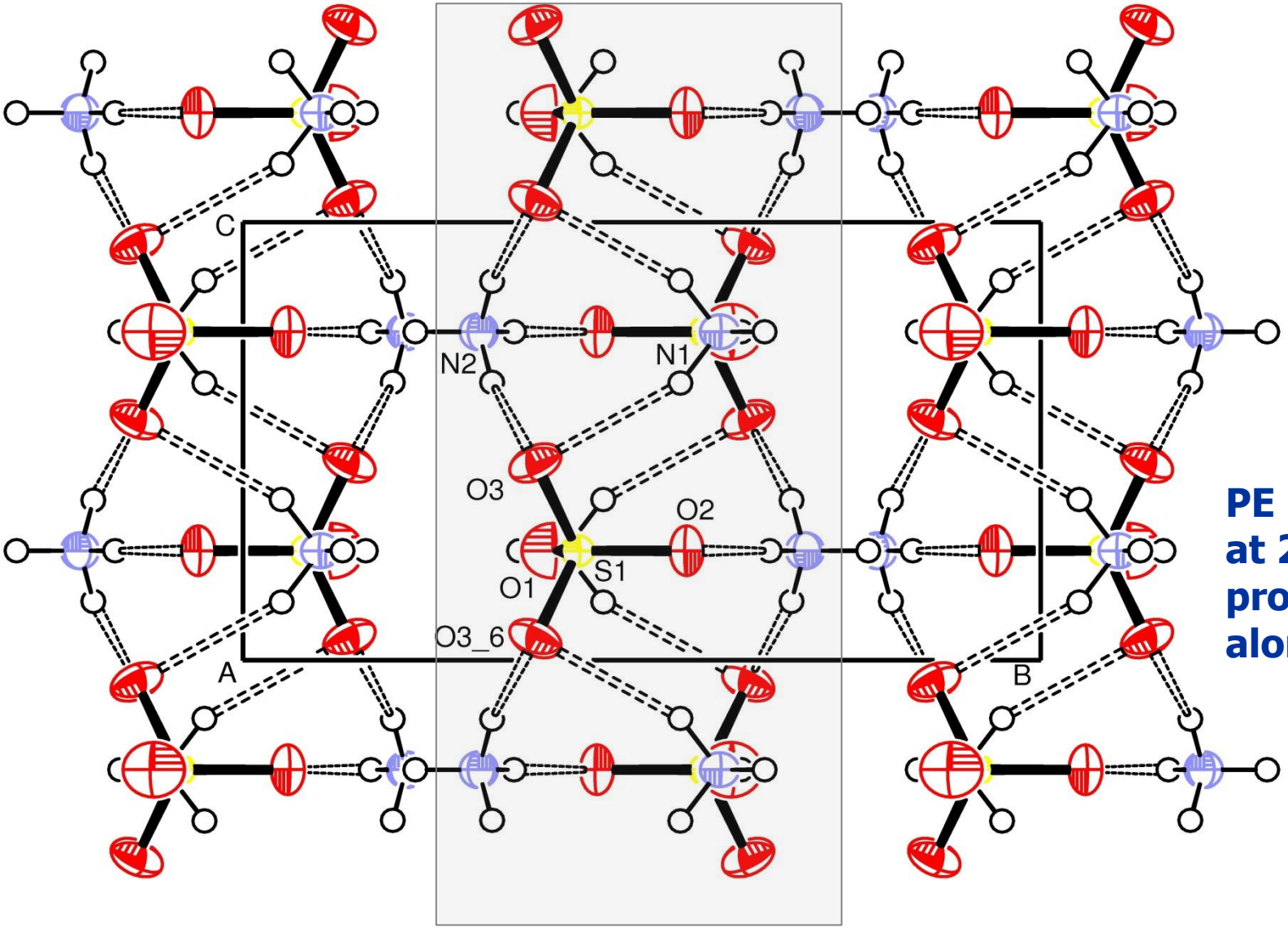
Oxygen atoms of SO_4^{2-} as the acceptors of H-bonds in PE phase (273 K)

Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones

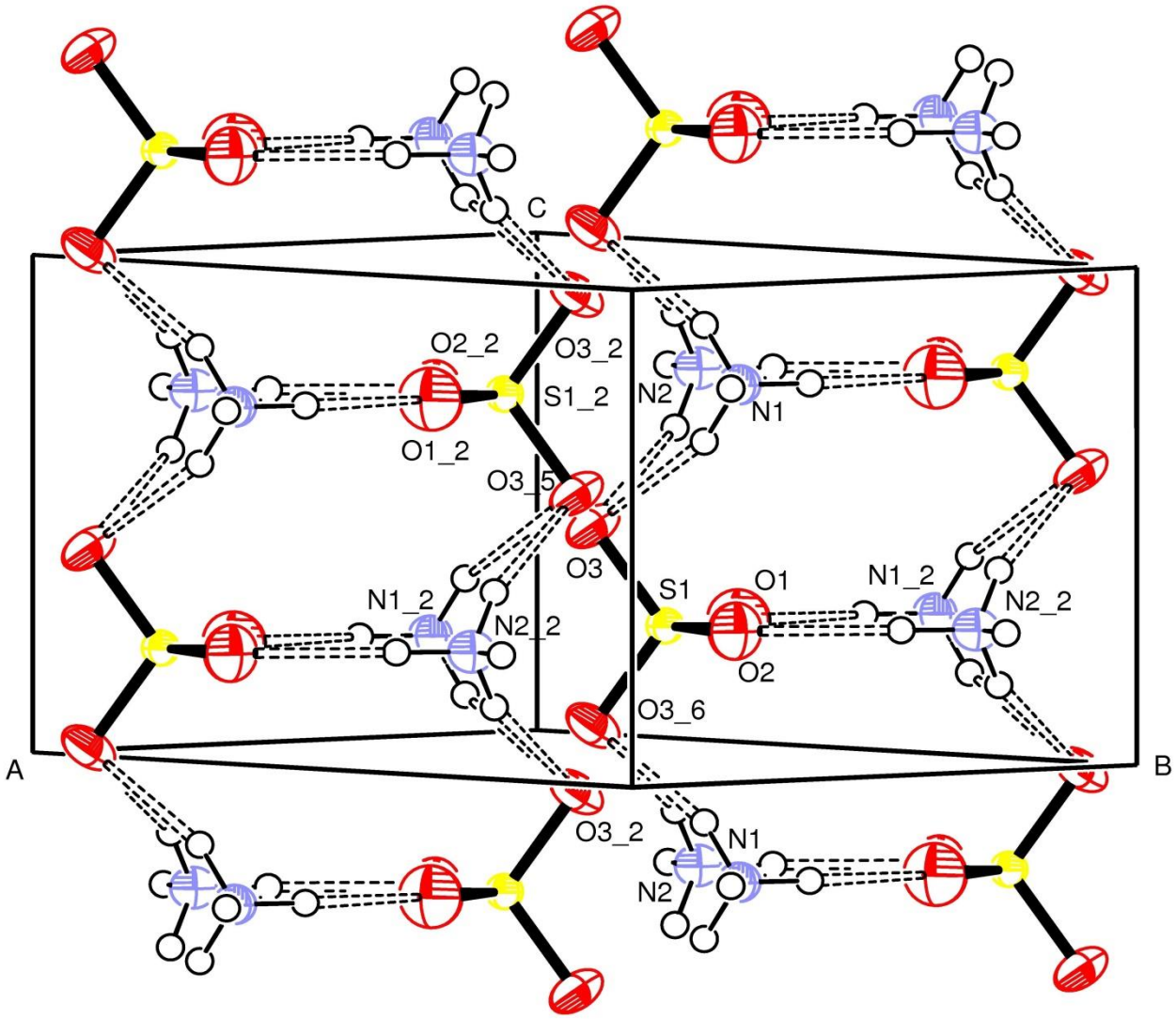


Oxygen atoms of SO_4^{2-} as the acceptors of H-bonds in FE phase (163 K)

Weak H-bonds: turquoise dashed lines
Strong / medium H-bonds: black ones

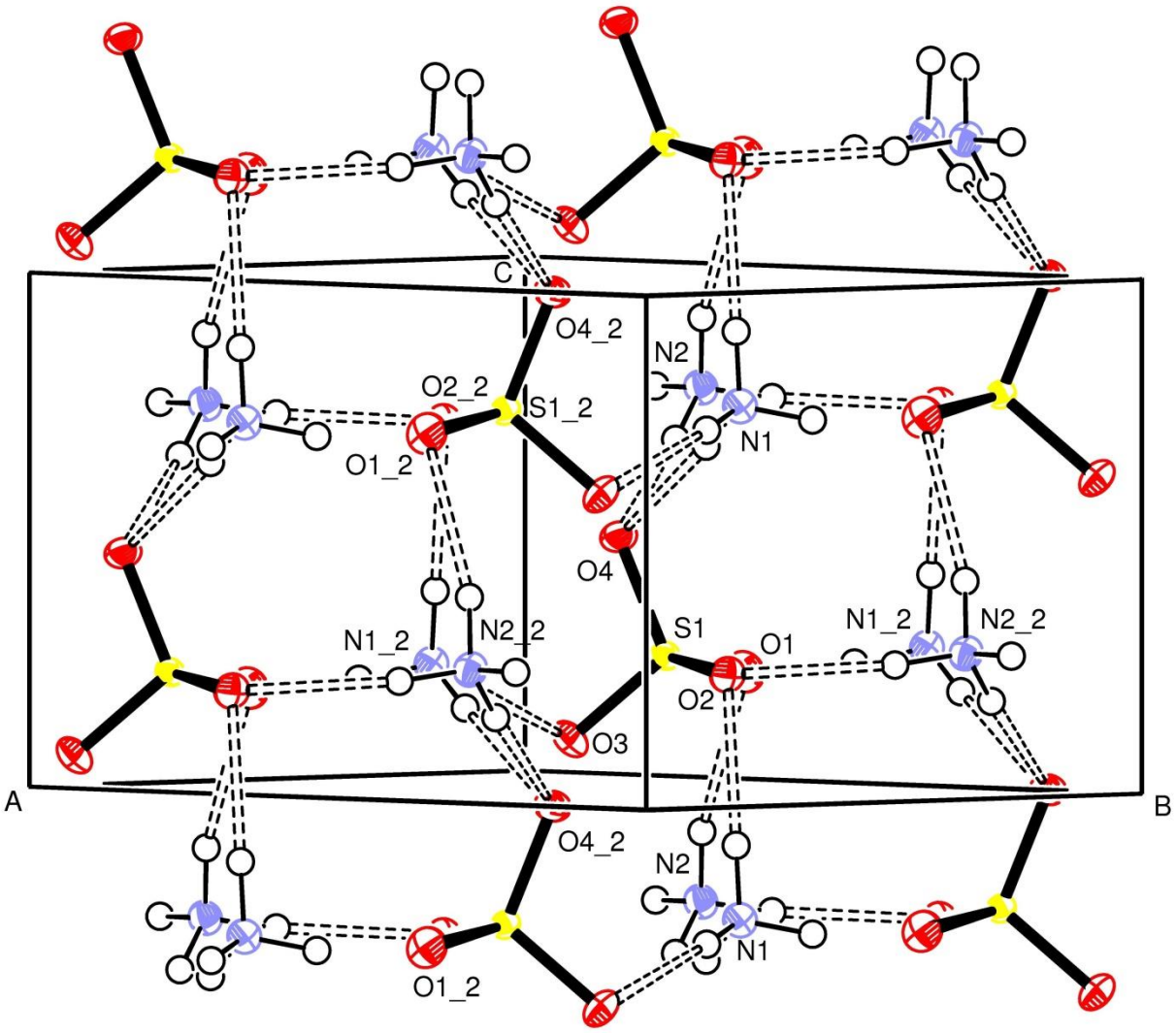


PE phase at 273 K projected along [100]



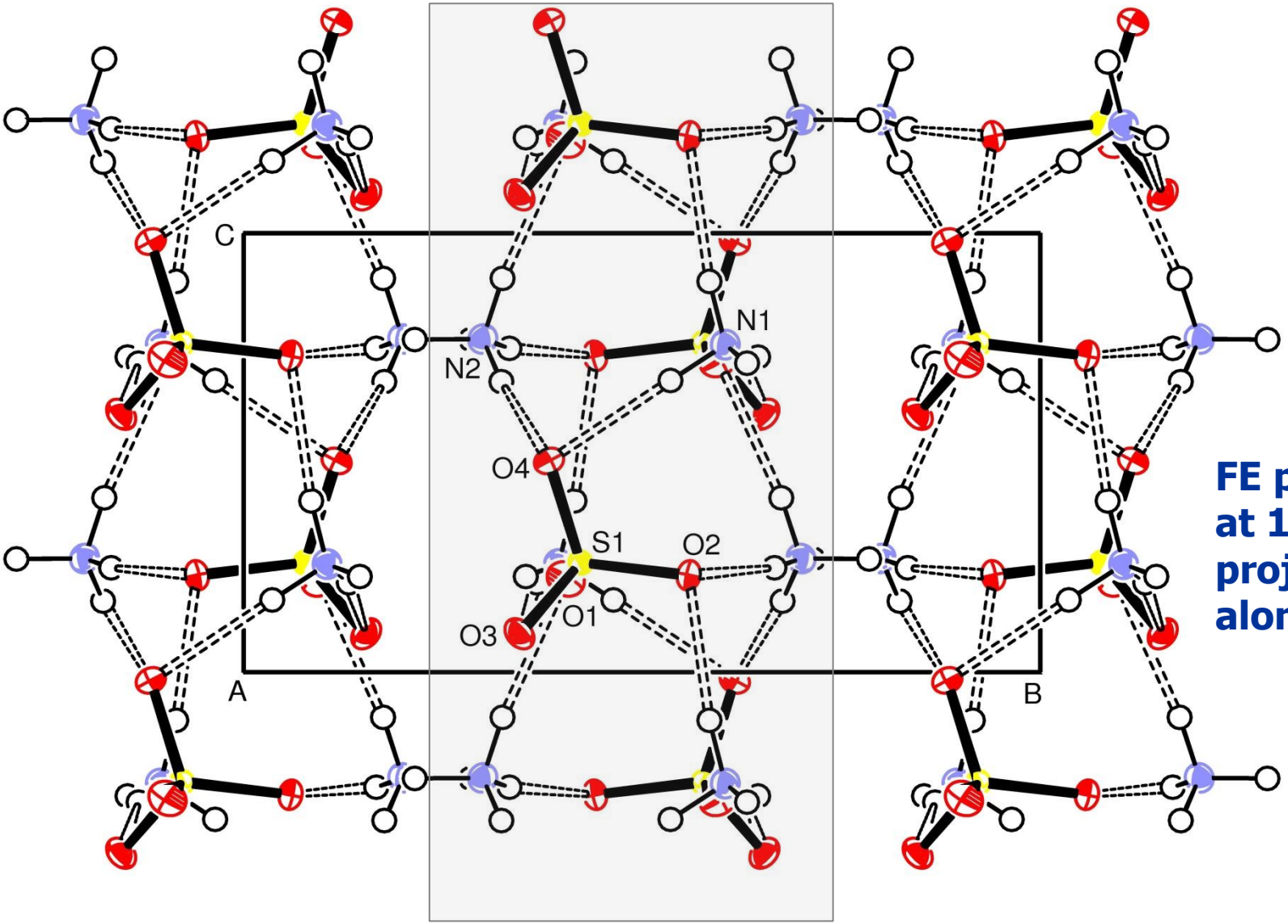
PE phase at 273 K

H-bond system in the marked column



FE phase at 163 K

H-bond system in the marked column



FE phase at 163 K projected along [100]

Theory of ferroic phase transitions

Symmetry approach

$$F \subset S \subset P$$

$$P \cap S \neq F$$

Thermodynamics of ferroelectric phase transitions

$$g = g_0 + (1/2)aP^2 + (1/4)bP^4 + (1/6)cP^6 + \ldots$$

$$\eta^N \lambda^{n'} \Sigma_k R_k f_k^{(N,n')}(\phi_i, \phi_i')$$

$$g = g_0 + (1/2)(T - T_0)a\eta^2 + (1/4)b\eta^4 + (1/6)c\eta^6 + K_1\eta P + (1/2)\chi_0^{-1}P^2 + \ldots$$