Experimental report

12/02/2019

Proposal: 5-12-335 **Council:** 4/2018

Title: Anharmonic thermal motion of hydrogen atoms

Research area: Chemistry

This proposal is a new proposal

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Samples: Glycine C2 H5 NO2

Instrument	Requested days	Allocated days	From	To
D9	7	7	27/09/2018	04/10/2018
D19	7	6	06/06/2018	12/06/2018

Abstract:

This is a feasibility study of a possible influence of anharmonic thermal motion of hydrogen atom(s) on quantitative electron density distributions in single crystals of model compounds i.e. perchlorophenol and chloranilic acid. The direct aim of this project is to model the anharmonic motion of hydrogen atoms for compounds containing only one or two H-atoms by using high resolution variable temperature single crystal elastic neutron scattering data. The critical information obtained from the model of motion will then be used in the complementary high resolution X-ray charge density studies performed at the same temperatures. Thus, we will verify the influence of anharmonic thermal motion of H-atoms on other structural and electronic parameters such as, for example, the electron density distributions at the X-H covalent bonds and X-H...Acceptor hydrogen bonding. We propose to collect data at 90K and 200K. We request D19 with very large solid angle detector for the compound (perchlorophenol)with longer unit cell parameters and D9 for the chloranilic acid with shorter unit cell parameters. All measurements should be done with the maximal resolution of data.

Report on neutron data collection

Project 5-12-335: Anharmonic thermal motion of hydrogen atoms

The aims of the project: This is a feasibility study aiming at detection of anharmonic behavior of hydrogen atoms in organic molecule glycine. The long range aim is to detect and describe possible influence of anharmonic thermal motion of hydrogen atom(s) on quantitative electron density distributions in single crystals of model compounds (in this case glycine). The other aim is to detect and verify a possible dependence of different parameters of glycine on resolution of measured neutron data.

Experimental part: A large (0.17 cm x 0.30 cm x 0.41 cm), high-quality single crystals of glycine ($C_2O_2NH_5$) were studied in the proposal 5-12-335 on two neutron lines. The first experiment was conducted on the D19 beamline at 90 K during the period since the 6th up to the 12th of June 2018 with the beamline scientist Dr Laura Canadillas Delgado. The second experiment on single crystal (0.15 cm x 0.25 cm x 0.30 cm) was conducted at 200 K on the D9 beamline within the period 27/09-4/10/2018 with the beamline scientist Dr Oscar Ramon Fabelo Rosa. Data were collected at different temperatures in order to study the motion of the hydrogen atoms in the crystal lattice as the hydrogen atoms do differ much from the heavier atoms which they are attach to. This significant mass difference should lead to imposing anharmonic motion for hydrogen atoms. As X-ray data are always strongly dependent on resolution, in the case of single crystal neutron diffraction data, we also wanted to examine a possible dependences of different structural and thermal parameters of the refined model of crystal structure on the diffraction resolution.

For the first experiment, the reflections were measured up to the resolution of 0.92 Å^{-1} and then cut into series down to the resolutions of 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.60 and 0.51 Å^{-1} creating individual hkl files. For all those different resolutions, the effective measured cell parameters were obtained and then an already prepared model of glycine structure was refined in Jana 2006 with the anharmonic treatment of hydrogen atoms against the neutron hkl data file obtained separately for each resolution. The same procedure was carried out for the second experiment and the final input hkl files were obtained for the resolutions of: 1.02, 0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55 0.50 and 0.45 Å^{-1}. All those data were also independently refined with the harmonic anisotropic treatment of hydrogen atoms using the ShelxL program for comparison of the final parameters.

The main crystal structure parameters for full datasets are shown in Table 1. After the refinement, the structure was then analysed in the PLATON program.

Table 1. Parameters of structure of glycine refined against neutron data collected at 90 K and 200 K.

Temperature /K	90	200
Space group	$P2_1/n$	$P2_1/n$
a/Å	5.4692(2)	5.4655(3)
b/Å	11.8063(2)	11.8937(8)
c/Å	5.0906(1)	5.0980(3)
β/°	111.983(1)	111.807(6)
Volume/Å^3	304.81(1)	307.68(3)
Z	4	4
ρ_{calc}g/cm^3	1.636	1.621
μ/mm^{-1}	0.002	0.002
F(000)	62.3	62.3
Radiation	neutron (λ = 0.9449)	neutron (λ = 0.8377)
2Θ range for data collection/°	9.18 to 121.818	8.08 to 116.68
Index ranges	$-8 \le h \le 10$, $-21 \le k \le 21$, $-9 \le l \le 9$	$-7 \le h \le 10$, $-21 \le k \le 21$, $-9 \le l \le 5$
Reflections collected	6550	3625
Independent reflections	1886 [R_{int} = 0.0376, R_{sigma} = 0.0200]	2351 [R_{int} = 0.0490, R_{sigma} = 0.0517]
Data/restraints/parameters	1886/0/91	2351/0/91
Goodness-of-fit on F^2	1.066	1.179
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0791	R_1 = 0.0529, wR_2 = 0.1115
Final R indexes [all data]	R_1 = 0.0321, wR_2 = 0.0792	R_1 = 0.0651, wR_2 = 0.1170
Largest diff. peak/hole / e Å^{-3}	0.82/-1.169	1.66/-1.86

The asymmetric unit of the crystal lattice contains 1 molecule of glycine which occupies a general position in the crystal lattice. The shape of the molecule with atom labelling scheme and thermal ellipsoids at the level of 50% probablity is shown in Fig. 1. The same labelling scheme of atoms was used during all refinements.

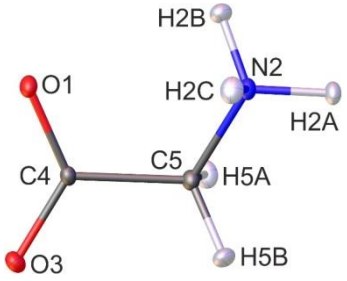


Fig. 1. Single molecule of glycine refined against all neutron data collected at 90.

Results: Parameters that we have analyzed as a function of resolution were the following: the unit cell parameters, bond lengths, ADPs of all atoms and anharmonic motion tensors for the hydrogen atoms.

Cell parameters show monotonic change during the process of changing the resolution of the neutron data. In the first experiment (D19 at 90K), we observed very slow lowering of the cell parameters with decreasing resolution of the data in the direct space. However, in the second experiment, the direction of the change was opposite and much steeper, as all cell parameters clearly expand while decreasing resolution in the direct space. The difference of the behaviour in those trend lines is probably due to the fact, that those two datasets were collected with different detectors and, apparently, they have different properties. It would be interesting to see if this is a systematic effect. This needs further investigations with focus on row data processing and scaling. Interestingly, these contradictory relations for the unit cell parameters were not transmitted on dependences of other structural and thermal parameters on resolution. The dependence of the unit cell volume and exemplary unit cell parameters b on the resolution of the hkl datasets for both temperatures is shown in Fig. 2.

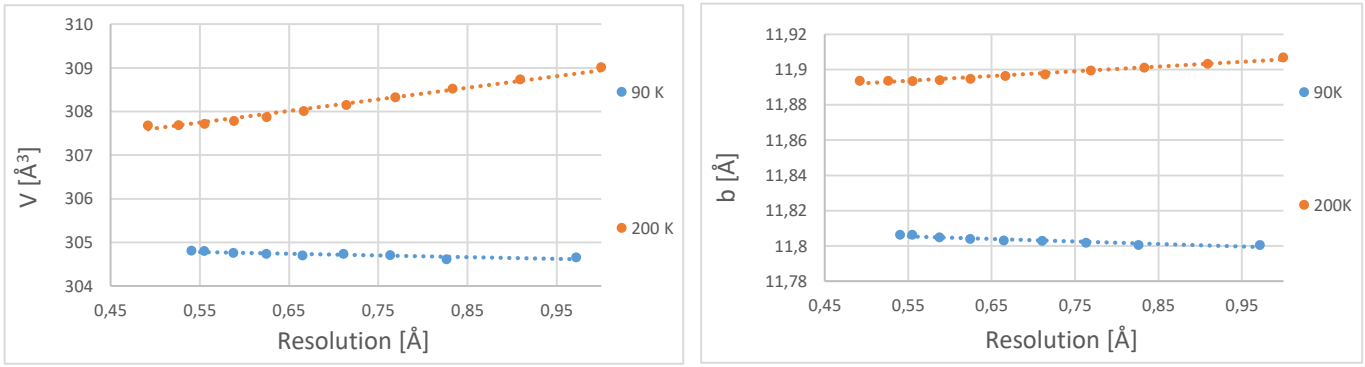


Fig. 2. Dependence of volume and b parameter of unit cell on the resolution for 90 K and 200 K.

As far as **the bond lengths** are concerned, one can see, as expected, that the bond lengths are not much affected by resolution. The fact that there is no dependence of structural results on resolution ensures us on the quality of the other results. Lengths of all 9 bonds present in the glycine molecule and their change during the process of cutting down the resolution are presented in Fig. 3.

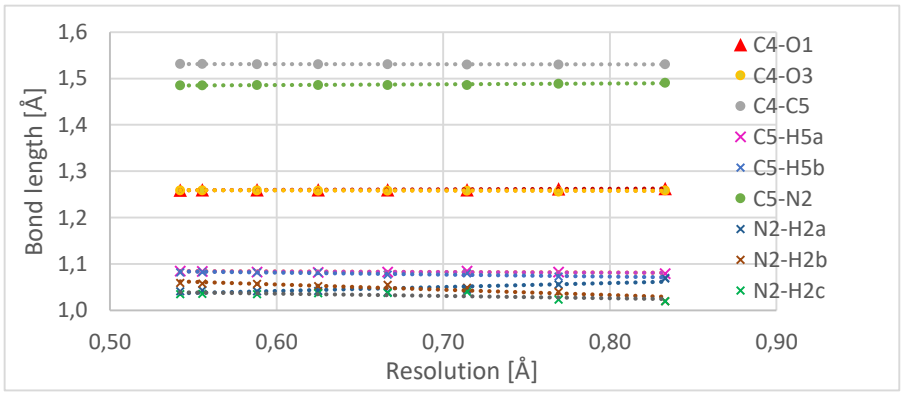
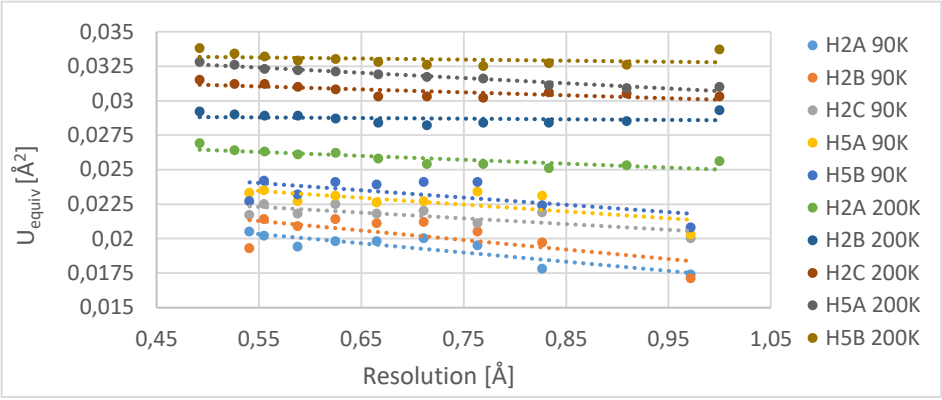


Fig. 3. Dependence of glycine bond lengths on resolution for experiment conducted at 90 K.

ADPs of all atoms depend both on the resolution of the data and the treatment of the hydrogen atoms (harmonic vs anharmonic). If structure is refined with H-atoms able to move only harmonically anisotropically, all atoms for



both experiments show the tendency to have smaller U_{eqiv} value when the resolution is cut down. This tendency is shown in Fig. 4. When H-atoms are allowed to move anharmonically this tendency is broken and some atoms exhibit small rise of the values of U_{eqiv} while excluding the high-angle reflections.

Fig. 4. Dependence of ADPs for hydrogen atoms treated harmonically on the resolution of the data.

The values of the tensors of anharmonic movement of hydrogen atoms do not show any clear tendency while the data are cut off. The anharmonic motion parameters for the hydrogen atoms for both temperatures refined with the full sets of reflections are summarized in Tables 2.

Table 2. The anharmonic tensors for hydrogen atoms in the structure of glycine refined against all neutron data collected at 90 K and 200 K, respectively.

90K	C_{111}	C_{112}	C_{113}	C_{122}	C_{123}	C_{133}	C_{222}	C_{223}	C_{233}	C_{333}
H5a	**-0.013(4)**	**0.0009(7)**	**-0.013(3)**	**0.0006(2)**	**0.0015(6)**	**-0.010(3)**	**0.0008(2)**	**0.0001(2)**	**0.0024(8)**	**-0.012(5)**
H5b	**0.002(3)**	**-0.0027(8)**	**-0.001(2)**	**0.0002(3)**	**0.0001(6)**	**-0.003(2)**	**-0.0005(3)**	**-0.0008(4)**	**-0.0015(9)**	**-0.005(3)**
H2a	**-0.007(3)**	**-0.0014(6)**	**-0.002(2)**	**-0.0004(2)**	**-0.0011(5)**	**-0.001(2)**	**0.0001(2)**	**-0.0001(3)**	**-0.0007(7)**	**0.002(4)**
H2b	**0.005(3)**	**-0.0006(7)**	**0.001(2)**	**-0.0003(3)**	**-0.0008(5)**	**-0.001(2)**	**-0.0001(2)**	**0.0003(3)**	**-0.0008(7)**	**-0.004(3)**
H2c	**0.004(3)**	**-0.0010(6)**	**0.004(2)**	**-0.0002(2)**	**-0.0011(5)**	**0.005(2)**	**0.0002(2)**	**0.0002(2)**	**-0.0010(8)**	**0.000(4)**
200K	C_{111}	C_{112}	C_{113}	C_{122}	C_{123}	C_{133}	C_{222}	C_{223}	C_{233}	C_{333}
H5a	**0.004(5)**	**0.001(1)**	**-0.001(4)**	**0.0006(4)**	**0.001(1)**	**-0.004(5)**	**0.0008(2)**	**0.0007(4)**	**0.004(1)**	**-0.012(7)**
H5b	**-0.004(3)**	**0.001(1)**	**-0.003(2)**	**-0.0011(6)**	**0.0011(8)**	**0.003(2)**	**0.0005(5)**	**-0.0017(6)**	**0.001(1)**	**0.004(3)**
H2a	**-0.004(3)**	**0.0005(8)**	**-0.004(2)**	**0.0004(4)**	**-0.0002(7)**	**-0.002(2)**	**-0.0003(3)**	**-0.0003(4)**	**-0.000(1)**	**-0.002(4)**
H2b	**0.002(3)**	**-0.0024(9)**	**0.001(2)**	**0.0004(5)**	**-0.0022(7)**	**-0.001(2)**	**-0.0007(4)**	**-0.0001(4)**	**-0.0021(9)**	**-0.001(3)**
H2c	**0.001(4)**	**0.0005(9)**	**0.005(3)**	**-0.0007(4)**	**-0.0008(9)**	**0.005(4)**	**-0.0004(3)**	**-0.0004(4)**	**-0.002(1)**	**-0.005(6)**

Most of the anharmonic motion tensor elements show no significance as their ratio of value over the uncerteinty does not exceed 2. However, some of the anharmonic tensor parameters show significance and, therefore, improvement of the model while refining against the collected neutron data. This implies that the anharmonicity can to some small degree be observed in the structure of glycine examined with the neutron radiation. However, this effect is only seen when single wavelength data are used. We can see same examples of linear relations between U_{equiv} of the hydrogen atoms, components of the harmonic motion tensor and anharmonic parameters vs resolution on Fig 5. So an interesting conclusions can be drawn, that although structural parameters do not depend on resolution, the thermal parameters do seem to be dependent, which raises the questions of what is the right resolution which is giving us the most accurate harmonic and anharmonic thermal parameters of atoms for single wavelength neutron experiments.

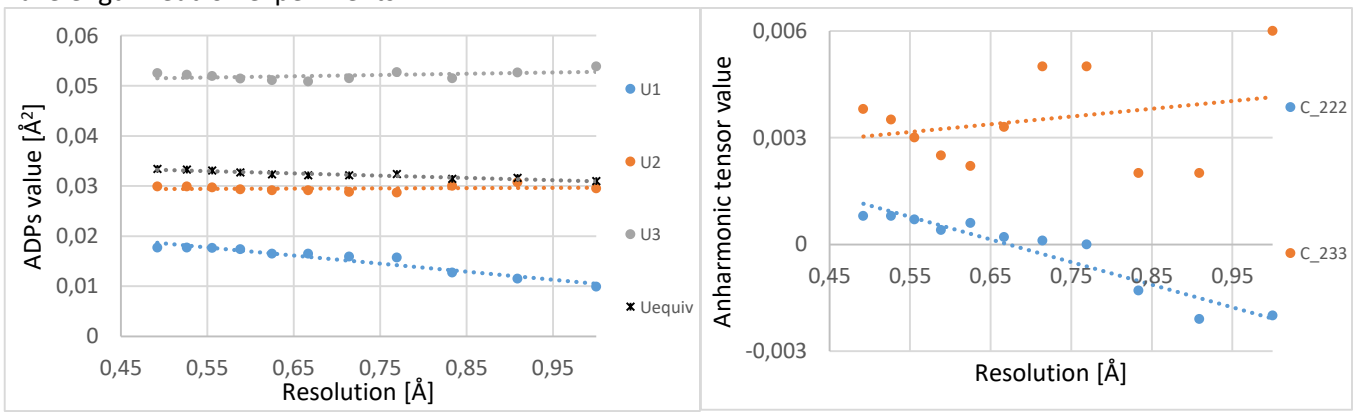


Fig. 5. Dependence of significant anharmonic tensor parameters (right) and ADPs (left) on resolution for H5A with hydrogen atoms treated anharmonically (at 200 K).