

Structure analysis on small molecular crystal by high resolution neutron powder diffraction

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Abstract. Deuterated α -glycine was studied by high resolution neutron powder diffraction (NPD). We performed a careful data analysis by Rietveld refinement and compared the result with those of the previous neutron single crystal (NSD) studies. The comparison demonstrates that the deviation of NPD study is generally within 1.2% from the NSD studies, indicating high resolution NPD is by no means inferior to NSD in studying small organic molecular crystals.

1. Introduction

For structure analysis of a crystal, single crystal diffraction has been proved to be the most powerful approach due to its high precision and accuracy. However, the requirement of large size of single crystal imposes tremendous difficulties on the application of this technique to the compound which is hard to grow into adequate size. Under the increasing demand of material science with complicated structures such as inorganic-organic composite materials, super molecules, pharmaceuticals, biomaterials *etc.*, giant effort has been made to develop the capability of neutron powder diffraction (NPD) on studying small molecular crystals. As molecular crystals usually possess large unit cells and low symmetries, many overlapped peaks appear in the powder diffraction pattern, making it more challenging to analyze the structure. High resolution powder diffraction seems to be the only way to overcome the overlap problem. Thus, using the high resolution powder diffractometer, we attempted to push the limit of neutron powder diffraction (NPD) forward by performing a careful data analysis on small molecular crystals of amino acids and peptides such as α -glycine ($C_2NO_2H_5$), L-alanine ($C_3NO_2H_5$), L-serine ($C_3NO_3H_7$) and glycyl-glycine-hydrochloride ($C_4N_2O_4H_{11}Cl$) *etc.*. Here, we are mainly reporting the result of α -glycine.

2. Experiment

The powder α -glycine specimen, D_2NCD_2COOD , was purchased from Cambridge Isotope Laboratories, with deuteration higher than 98%. Neutron powder diffraction for α -glycine was carried out at room temperature, using SuperHRPD, the high resolution neutron power diffractometer installed at the pulsed spallation neutron source of Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan. The data were collected by detectors of the back scattering bank in order to achieve a high resolution. The back scattering bank covers a 2θ range of $150 - 175^\circ$, corresponding to d -spacing range of $0.3 - 4.0 \text{ \AA}$. The best resolution ($\Delta d/d$) of 0.035% can be achieved at 2θ of 175° . In this study all the signals of the bank are focused to 172° by the time focusing method. We repeated the



experiment twice in order to check the reproducibility. The two data are referred to as SuperHRPD1 and SuperHRPD2 hereafter. The diffraction data were analyzed by Rietveld refinement with the Z-Rietveld program in a software suit, Z-Code. A new type of peak shape function optimized for the diffractometer, so called Type 0 profile function, was adopted in the refinement.

3. Result and Discussion

The refinement on SuperHRPD1 was performed at the time-of-flight range of 40 – 190 ms, corresponding to d -spacing range of 0.8 – 4 Å, and the initial structural model was taken from the NSD study [1]. It was found that some weak second-phase peaks appear in the diffraction pattern, the typical intensity of which is approximately 3% of the strongest main-phase peak, and they were all excluded from the refinement. Hydrogen as an impurity of deuterium was taken into account by assigning hydrogen to the corresponding deuterium position and constraining the sum of the occupancy of the two atoms to 1. The occupancies of deuterium atoms are demonstrated in Table 1, the average value of which agrees well with total 98% deuteration of the specimen. As shown in Figure 1, the fitting itself looks good, with R_{wp} value achieving 5.21%. The final atomic coordinates and anisotropic displacement parameters are listed in Table 2.

Table 1. Occupancies of deuterium at different atomic positions

D(1)	D(2)	D(3)	D(4)	D(5)
0.975(2)	0.985(2)	1.000(2)	0.996(2)	0.972(2)

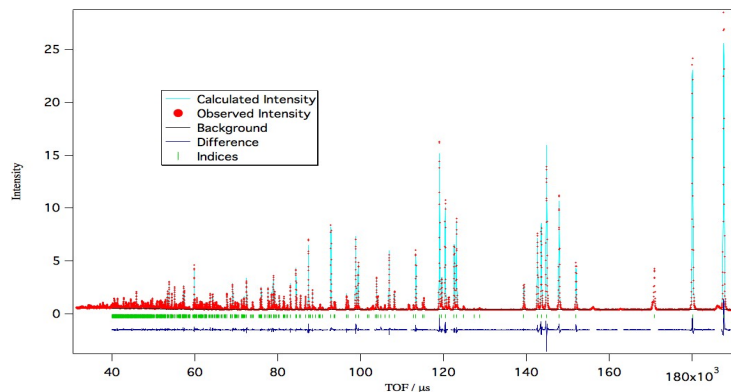


Figure 1. The observed (solid circle) and calculated (light blue line) profiles of α -glycine. Black line indicates the background intensity and dark blue line indicates the difference between observed and calculated intensities.

Table 2. Atomic coordinates and anisotropic displacement parameters with space group $P2_1/n$ [$a = 5.103494(5)$ Å, $b = 11.948140(11)$ Å, $c = 5.466384(5)$ Å, $\beta = 111.73497(5)^\circ$]

	x	y	z	B11	B22	B33	B12	B13	B23
C(1)	0.07463(10)	0.12552(4)	0.06636(8)	1.29(2)	1.68(2)	0.94(2)	-0.07(2)	0.59(2)	0.04(2)
C(2)	0.06512(11)	0.14505(5)	-0.21214(4)	1.36(3)	1.85(3)	0.99(2)	0.57(2)	0.72(2)	0.32(2)
O(1)	0.30675(11)	0.09358(4)	0.23592(10)	1.60(2)	3.16(3)	0.85(2)	0.46(2)	0.86(2)	0.35(2)
O(2)	-0.14769(11)	0.14193(5)	0.10768(9)	1.78(3)	3.85(4)	1.78(3)	0.29(2)	1.49(3)	-0.20(2)
N	0.30056(9)	0.08989(4)	-0.25836(8)	1.49(2)	2.41(2)	0.86(2)	0.59(2)	0.55(2)	0.16(2)
D(1)	0.29119(10)	0.10129(4)	-0.45054(10)	2.17(3)	3.70(3)	1.16(2)	0.20(2)	0.83(2)	0.42(2)
D(2)	0.49414(12)	0.11978(5)	-0.13061(11)	1.82(3)	4.79(4)	1.54(3)	-0.23(3)	0.72(2)	-0.29(2)
D(3)	0.29909(12)	0.00638(6)	-0.22645(11)	4.88(4)	2.43(3)	2.39(3)	1.72(3)	1.55(3)	0.02(2)
D(4)	0.07932(11)	0.23362(5)	-0.24202(11)	4.30(3)	2.33(3)	3.61(3)	1.28(2)	2.08(3)	1.32(2)
D(5)	-0.13255(11)	0.11458(5)	-0.35675(10)	1.66(3)	5.31(4)	1.68(3)	-0.02(3)	0.56(2)	-0.75(2)

Table 3. Intramolecular bond lengths (Å) and angles (degree) of α -glycine from SuperHRPD1, SuperHRPD2, Ref. [1] and Ref. [2]. Discrepancies between them are calculated by “IP-J/I”, “IS1-J/I” and “IS2-J/I”, where J is short for Jönsson and K vick [1], P for Power *et al.* [2], S1 for SuperHRPD1 and S2 for SuperHRPD2.

	SuperHRPD1	SuperHRPD2	Jönsson	Power	IP-J/I	IS1-J/I	IS2-J/I
C(1)-O(1)	1.263(1)	1.261(1)	1.250(1)	1.251(1)	0.08%	1.04%	0.88%
C(1)-O(2)	1.251(1)	1.253(1)	1.251(1)	1.252(1)	0.08%	0.00%	0.16%
C(2)-N	1.472(1)	1.473(1)	1.476(1)	1.475(1)	0.07%	0.27%	0.20%
C(1)-C(2)	1.523(1)	1.522(1)	1.526(1)	1.525(1)	0.07%	0.20%	0.26%
N-H(1)	1.043(0)	1.044(1)	1.054(2)	1.053(2)	0.09%	1.04%	0.95%
N-H(2)	1.039(1)	1.038(1)	1.037(2)	1.036(2)	0.10%	0.19%	0.10%
N-H(3)	1.014(1)	1.015(1)	1.025(2)	1.029(2)	0.39%	1.07%	0.98%
C(2)-H(4)	1.077(1)	1.079(1)	1.090(2)	1.094(2)	0.37%	1.19%	1.01%
C(2)-H(5)	1.088(1)	1.088(1)	1.089(2)	1.087(2)	0.18%	0.09%	0.09%
C(2)-C(1)-O(1)	116.99(3)	117.21(3)	117.46(6)	117.38(7)	0.07%	0.40%	0.21%
C(2)-C(1)-O(2)	117.46(3)	117.39(3)	117.09(7)	117.08(7)	0.01%	0.32%	0.26%
O(1)-C(1)-O(2)	125.55(3)	125.4(3)	125.45(8)	125.53(8)	0.06%	0.08%	0.04%
C(1)-C(2)-N	112.17(5)	112.05(4)	111.85(5)	111.79(6)	0.05%	0.29%	0.18%
C(2)-N-H(1)	112.27(5)	112.07(5)	112.09(10)	112.08(11)	0.01%	0.16%	0.02%
C(2)-N-H(2)	111.36(13)	111.1(12)	111.73(12)	112.00(12)	0.24%	0.33%	0.56%
C(2)-N-H(3)	110.65(7)	110.79(8)	110.37(12)	110.22(14)	0.14%	0.25%	0.38%
H(1)-N-H(2)	108.03(8)	107.89(8)	108.71(15)	109.05(16)	0.31%	0.63%	0.75%
H(1)-N-H(3)	107.54(15)	107.9(14)	107.13(16)	107.02(17)	0.10%	0.38%	0.72%
H(2)-N-H(3)	106.75(6)	106.88(6)	106.56(17)	106.20(19)	0.34%	0.18%	0.30%
C(1)-C(2)-H(4)	108.84(13)	108.78(13)	108.81(12)	108.55(13)	0.24%	0.03%	0.03%
C(1)-C(2)-H(5)	110.65(8)	110.55(7)	110.50(11)	110.38(13)	0.11%	0.14%	0.05%
N-C(2)-H(4)	107.97(7)	108.07(8)	108.51(12)	108.41(13)	0.09%	0.50%	0.41%
N-C(2)-H(5)	108.77(13)	108.75(12)	109.05(12)	109.47(13)	0.38%	0.26%	0.28%
H(4)-C(2)-H(5)	108.32(7)	108.55(7)	108.03(18)	108.14(21)	0.10%	0.27%	0.48%

To evaluate the accuracy of our result, two neutron single crystal diffraction studies were referred [1, 2]. Since α -glycine is a molecular crystal, we look straight into the molecular structure. Table 3 illustrates the intramolecular bond lengths and angles of α -glycine from SuperHRPD1, SuperHRPD2, Jönsson and Kvik [1] and Power *et al.* [2], respectively. It should be noted that the specimens studied in both references [1, 2] were not deuterated. As we know, geometric isotope effect often takes place in hydrogen bonds [3]. If this also exists in α -glycine crystal, which is bound by the hydrogen bonds as well, the two results from NSD cannot be taken as references. So before comparison, it is necessary to check whether or not geometric isotope effect occurs in this α -glycine crystal. Actually, isotope effect in O-H...O hydrogen bond has been widely studied in the past 30 years. Ikeda *et al.* [4] proposed a model which successfully explains both geometric and dynamic isotope effects. According to their model, geometric isotope effect was predicted to occur in the limited range of $2.43 < R < 2.6$ Å, where R is hydrogen bond distance (O...O distance). And the accumulated experimental data on geometric isotope effect of various hydrogen bonds [3] agree well with the Ikeda's prediction. As for the α -glycine crystal, molecules are connected by two roughly linear N-H...O hydrogen bonds forming individual layers parallel to the *ac* plane. Two neighboring layers are first linked by bifurcated N-H...O hydrogen bonds to become anti-parallel layers and then connected by bifurcated C-H...O hydrogen bonds along the *b* axis, becoming the three dimensional crystal structure. We found that all the hydrogen bond distances are over 2.7 Å, thus no geometric isotope effect is anticipated in α -glycine. As a result, the two NSD results can be adopted to check the accuracy of the NPD result, even though the NSD specimen is not deuterated as in our NPD experiment.

We evaluated the discrepancy by calculating the percentage that one deviates from the other. First, the discrepancy between the two single crystal studies [1, 2] is demonstrated in the "IP-JI/J" column of Table 3. It is found that the differences are within 0.4%, so either is qualified to be set as the criterion for comparison. The discrepancies between the result from SuperHRPD1 and that from Jönsson and Kvik [2] were calculated and listed in the "IS1-JI/J" column of Table 3. And the deviations are all within 1.2%. Compared with the 0.4% discrepancy of two single crystal studies, we can draw the conclusion that the molecular structure obtained from SuperHRPD maintains a high accuracy.

To make sure that the high resolution NPD can be applied to the small molecular crystal, reproducibility is also a very crucial criterion to check. By comparison between "IS1-JI/J" column and "IS2-JI/J" column of Table 3, It is unambiguous that the results from both SuperHRPD1 and SuperHRPD2 achieve the same level of accuracy, around 1%, indicating a good reproducibility.

4. Conclusion

It is proved that the application of high resolution neutron powder diffraction can be extended into small molecular crystals. This would be quite helpful for the modern materials science when coming across the problem of growing large single crystal.

5. Acknowledgement

The authors are grateful to Prof. S. Ikeda for useful discussions.

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