MLF Experimental Report	提出日 Date of Report 2012/11/21
課題番号 Project No. 2012A0032 実験課題名 Title of experiment The determination of the hydrogen-bonding structure of methanol in hydrophobic space 実験責任者名 Name of principal investigator Taku Iiyama 所属 Affiliation Faculty of Science, Shinshu University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/(BL No.) BL21 実施日 Date of Experiment 2012/06/23-2012/06/25

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

A new designed measurement cell which keeps a hermetically closed condition was used for BL21 measurement. The ground activated carbon fiber A20 (Ad'all Co.; pore width is 1.13 nm) was used as adsorbent. The 4 types of methanol CH_3OH, CH_3OD, CD_3OH, and CD_3OD were used as adsorbate. We measured neutron diffractions of these samples at the bulk conditions and adsorbed conditions. Adsorbed amounts were controlled at near of saturated adsorbed amount (ϕ = 0.9). The liquid D_2O and A20 itself was measure for the reference. The measurement times were 5 h for adsorbed conditions, and 3 h for bulk liquids with 200 kW pulsed neutron beam. The number of experiments is 11.

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The carbon sample introduced in the cell, and preheated for 4 h at 393 K and 1 mPa before the measurements. Then each adsorbate was introduced via vapor with the adsorbed amount controlling. The sample cells were hermetically closed, and keep over 3 days for the equilibrium.

In this experiment, we planned to investigate the hydrogen-bonding structure of methanol in the hydrophobic nanospace. It is needed to distinguish the hydrogen atoms between on a hydroxyl group (OH) and hydrocarbon (CH_3). We tried to distinguish these by the isotope substitution samples. However, the incoherent scattering from light hydrogen atom (H) is so strong; we could not obtain the correctionable data of H including samples (CH_3OH, CH_3OD, CD_3OH). We report here the 4 data which does not including H samples (liquid CD_3OD, CD_3OD – A20 adsorbed condition, liquid D_2O, A20 in vacuum).

Fig 1 show the ND profiles of A20 in vacuum by 20°, 45°, 90°, and BS bank. All data show the broad peaks due to the amorphous carbon structure. However, the raw data do not agree each other. We must correct these. The method of data correction on 45° bank of A20 in vacuum is explained for example.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

We assumed the existence of two terms for correction. First one (blue line in Fig 1) is the error of neutron absorbing correction. It would be produced by the difference of sample density between the expected and real one. The determination of sample density of porous carbons includes some ambiguity. This first term is negligible in the liquid samples.

Second one is the incoherent (inelastic) scattering from samples (green line in Fig 2). It is expected that this incoherent term increase with the scattering angle increasing. We assumed these term as

$$S_{\mathrm{corr}}(Q) = n \cdot \{S_{\mathrm{obs}}(Q) - A_1 \exp(-B_1 Q) - A_2 \exp(-B_2 Q) - C\}$$

We estimated 6 unknown parameters by the comparison of 4 bank data using GRG routine. Fig 3 shows the corrected data. Although the data different by the Q resolution, the all data well agree. The strength of incoherent scattering A_2 is systematically change with data correction bank (A_2 = 0.47, 1.15, 1.76, 2.08 for 20°, 45°, 90°, and BS bank, respectively), and sensitivity of each bank n is within 5 % (n = 0.95, 1(fix), 0.96, 1.02 for each bank).

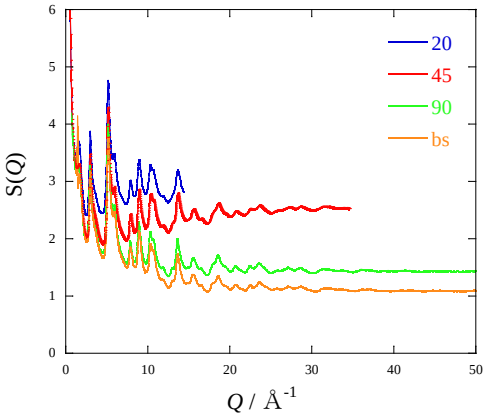

Fig.1 ND profiles of A20 in vacuum

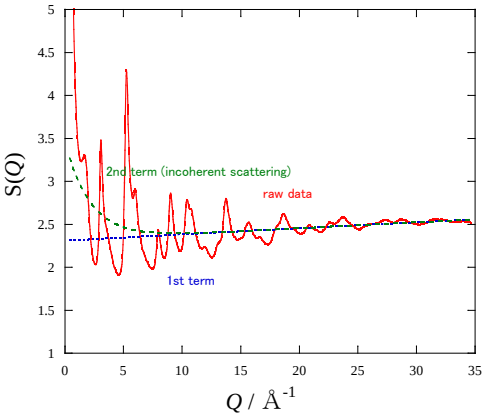

Fig.2 Data correction on 45° bank of

By these corrections, we obtained the ND profiles of liquid CD_3OD, A20, and CD_3OD adsorbed A20 (Fig 4). Adsorbed sample (green) include the both of A20 and adsorbed CD_3OD. Although the first peak at Q = 1.7 is overlapped carbon (002) peak, the intensity is noticeably strong compared with 2nd and 3rd peaks of CD_3OD (Q = 4.0, 7.2). It indicated that CD_3OD form 2−dimentional ordered structure, which corresponded with previous XRD results.

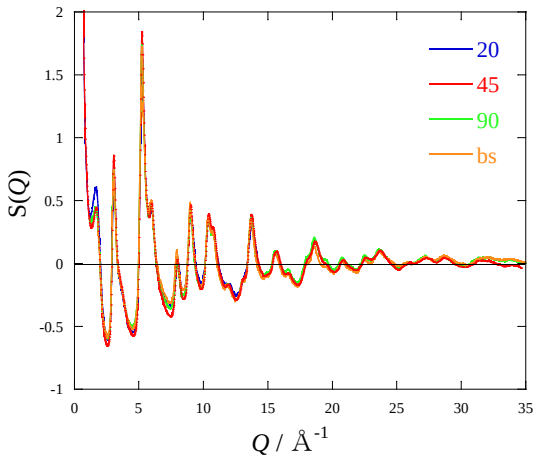

Fig.3 Corrected ND profiles of A20

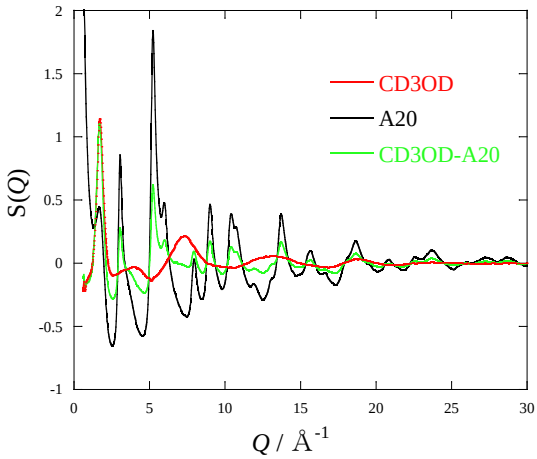

Fig.4 ND profiles of liquid CD3OD, A20 and CD3OD adsorbed A20