MLF Experimental Report	提出日 Date of Report 2013/03/20
課題番号 Project No. 2012B0201 実験課題名 Title of experiment The determination of structure and rotational motion of CCl_4 in confined spaces 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 Toru Ishigaki 装置名 Name of Instrument/(BL No.) BL20 実施日 Date of Experiment 2013/02/11-2012/02/13

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.

The original designed measurement cell for the measurement with cryostat of BL20 was used. The 1.10 g of ground activated carbon fiber A20 (Ad'all Co.; pore width is 1.13 nm) was introduced in the cell, and preheated for 4h at 393 K and 1 mPa before the measurements. Then CCl_4 vapor was introduced to the cell. The amount adsorbed is 2.52 g which is corresponded to saturated adsorbed amount. We measured the neutron diffractions of this CCl_4 adsorbed A20, and also bulk CCl_4 and A20 (298 K) itself. The measurement time is 100 m with 300 kW pulsed neutron beam, at double-frame mode. ND of CCl_4 adsorbed activated carbon A20 (ϕ = 1) was measured at 255, 238, 221, and 100 K in cooling process, and at 135, 170, 187, 204, 221, 238, 255 ,273, 290 K at warming process. ND of bulk CCl_4 was measured at 221, 238, 255 K.

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.

In this experiment, we tried to determine the structure and its temperature dependency of CCl_4 in hydrophobic small space. CCl_4 is a spherical molecule, and have a long-range ordered structure even in a liquid state at room temperature. The diameter of CCl_4 molecule (0.59 nm) is comparable with pore width of microporous carbons (around 1.0 nm). A molecular packing should be sensitive to the pore width. Furthermore, CCl_4 has a plastic crystal phase between 225 and 250 K. The rotational motion of CCl_4 molecule will be strongly affected by the space restriction.

We measured ND of CCl_4 adsorbed activated carbon (AC) at fractional filling ϕ = 1. The AC sample was preheated in the cell, and then CCl4 vapor was

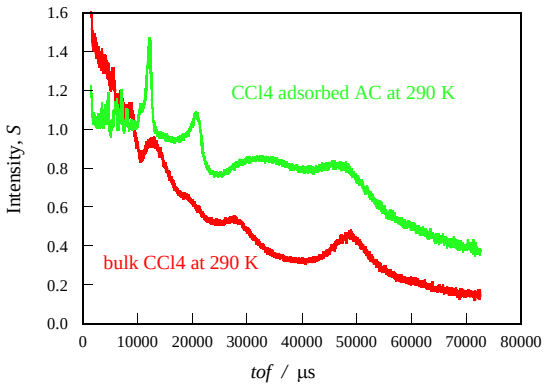

Fig.1 ND profiles of bulk CCl4 and CCl_4 adsorbed AC (SE bank)

introduced. Equilibrium time was 2 day. The ND was measured between 290 and 100 K every 17 K in warming process. The ND of AC itself (at 298 K), and bulk CCl4 (at 290 – 221 K) were also measured. Measurement time was set 100 min with 300 kW pulsed neutron beam at double-frame mode.

Fig.1 shows the ND profiles of bulk CCl_4 and CCl_4 adsorbed AC at 290 K. The all ND profiles of bulk CCl_4 and CCl_4 adsorbed AC show that decreasing intensity with tof increasing. It will become from the absorption of neutron by the sample itself, because the Cl atom has a high thermal absorption cross section σ_{abs} (σ_{abs}(Cl) = 33.5, the other concerning atoms (C, D) are nearly 0). We tried to correct of this effect using follow relation. The cross section of thermal neutron absorption is inverse proportional to the velocity of neutron.

$$I/I_0 = \exp(-N\alpha x/v)$$

Fig 2 shows the plot of log I vs $1/v$. The linear relation in this plot means that the absorption coefficient is proportional to $1/v$. We used this relation for the correction of thermal absorption. $I' = I \cdot \exp(N\alpha x/v)$ We assumed that the coefficient $N\alpha x$ is constant in all temperature; therefore, it was obtained by the line fitting for the averaged profile of all temperature.

Fig 3 is the radial distribution functions (RDF) of bulk CCl_4. The ND profiles of bulk CCl4 at 221, 238, and 255 K show the sharp peaks due to the crystal structure, but we obtained RDF by the same procedure for the liquid profiles in this analysis. The profiles show clearly the periodic peaks at 0.6, 1.1, 1.5, 2.0 nm due to the spherical molecular shape and its ordered structure. The intensity of peak at 0.4 nm show the strong dependency with T, this peak is attributed to Cl-Cl distance of near-side of neighbor molecules. It is indicated that the rotational motion of CCl_4 can be detected by the neutron diffraction. Fig 4 shows the corrected ND profiles (using MAT00XX.SE.bin02Double_0.histogramIgor). The adsorbed samples show the high-Q shifted 1st peak (at Q=1.3 A^{-1}) and low-Q shifted 2nd peak (at 2 A^{-1}). The peak position and shape of these peaks changes with T clearly in wide T-range. These peaks are attributed to the intermolecular structure of adsorbed CCl_4. We will elucidate the detailed structure of that using RDF and RMC analysis.

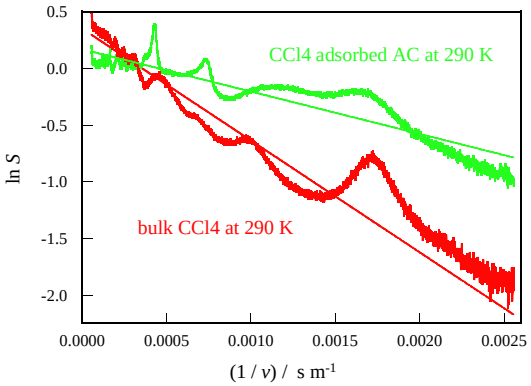

Fig.2 Reciprocal relation between ln I vs v.

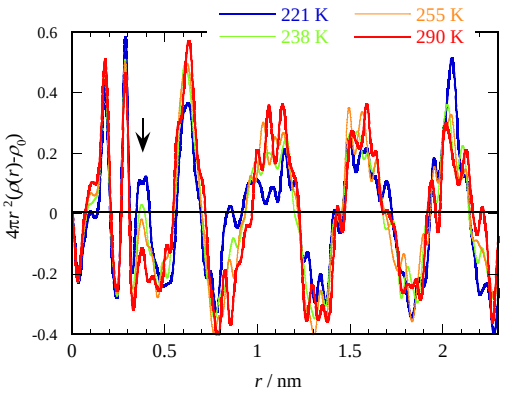

Fig 3 RDF of bulk CCl_4

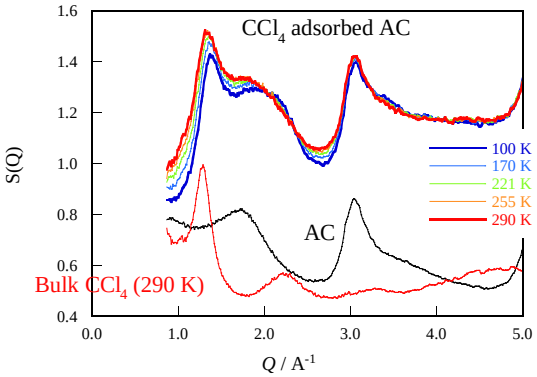

Fig.4 corrected ND profiles of CCl_4 adsorbed AC (SE bank)