

# Magnetic Excitation in Oxygen Molecule Adsorbed in Nanoporous Metal Complex $\text{Cu}_2(4\text{-F-bza})_4(2\text{-mpyz})$

Takatsugu Masuda, Minoru Soda, Shinichiro Asai  
*Institute for Solid State Physics, the University of Tokyo*

In some types of nanoporous metal organic complex, gas molecules are adsorbed in the porous, leading to realization of supercrystal of the molecules. One of the most interesting examples is a Cu complex, CPL-1, that adsorbs O<sub>2</sub> molecule,  $S = 1$  magnetic entity, in its one dimensional cylindrical porous [1]. The O<sub>2</sub> molecules form ladder like structure and  $S = 1$  spin gap system was expected. The neutron spectrum at low temperature was explained by the singlet-triplet excitation of  $S = 1$  dimer [2]. Meanwhile the temperature dependence deviates from the dimer model. Combination of calculation on spin-dependent molecular potential [3] and neutron scattering results indicated that the origin of the unconventional dynamics was the soft framework of oxygen supercrystal. In this studies, unfortunately, protonated samples were used, and the signal to noise ratio was not good, leading to difficulty in the precise measurement on weak intensities, particularly at higher temperatures.

A Cu complex,  $\text{Cu}_2(4\text{-F-bza})_4(2\text{-mpyz})$ , is a new nanoporous material. The adsorbed O<sub>2</sub> molecules form trimer structure in its nanopore [4]. M-H curve at 2 K is reasonably explained by antiferromagnetic  $S=1$  trimer model with intratrimer interaction  $J = -20$  K and single-ion anisotropy  $D = 2.1$  K. In contrast to the magnetization, the temperature dependence of the susceptibility is not reproduced by the trimer model indicated by solid curve. This suggests that the higher energy scheme is not explained by conventional spin system. We performed a neutron scattering experiment using chopper spectrometer to obtain overall spectrum of the supercrystal of O<sub>2</sub> molecules. Neutron scattering experiment was performed on cold-neutron TOF spectrometer PELICAN at ANSTO. We used cryogen-

free cryostat for achieving low temperature. We used 1.2 g of deuterated sample. We chose the incident neutron energy of 2.2, 3.7, 14.9 meV.

Figure 1(a) shows the inelastic neutron scattering spectra for O<sub>2</sub>-adsorbed  $\text{Cu}_2(4\text{-F-bza})_4(2\text{-mpyz})$  at 4.6 K. We observed non-dispersive excitation at 0.4 meV, which cannot be observed in the spectra for the sample after O<sub>2</sub> gas evacuation shown in Fig. 1(b). It indicates that the excitation is the magnetic excitation for the adsorbed O<sub>2</sub> molecules. In order to obtain the spectra of the adsorbed O<sub>2</sub> molecules, we regards the spectra for the O<sub>2</sub>-removed sample as the background and subtract it from the spectra for O<sub>2</sub>-adsorbed sample. Figure 2 shows the temperature dependence of one-dimensional Q cuts of the spectra of the adsorbed O<sub>2</sub> molecules. The intensity at 0.4 meV decreases with increasing temperature, and is well suppressed at 40 K.

[1] R. Kitaura et al., *Science* 298, 2358 (2002). [2] T. Masuda et al., *J. Phys. Soc. Jpn.* 77, 083703 (2008). [3] B. Bussery and P.E.S. Wormer, *J. Chem. Phys.* 99, 1230 (1993). [4] Y. Takasaki and S. Takamizawa, *JACS* 136, 6806 (2014).

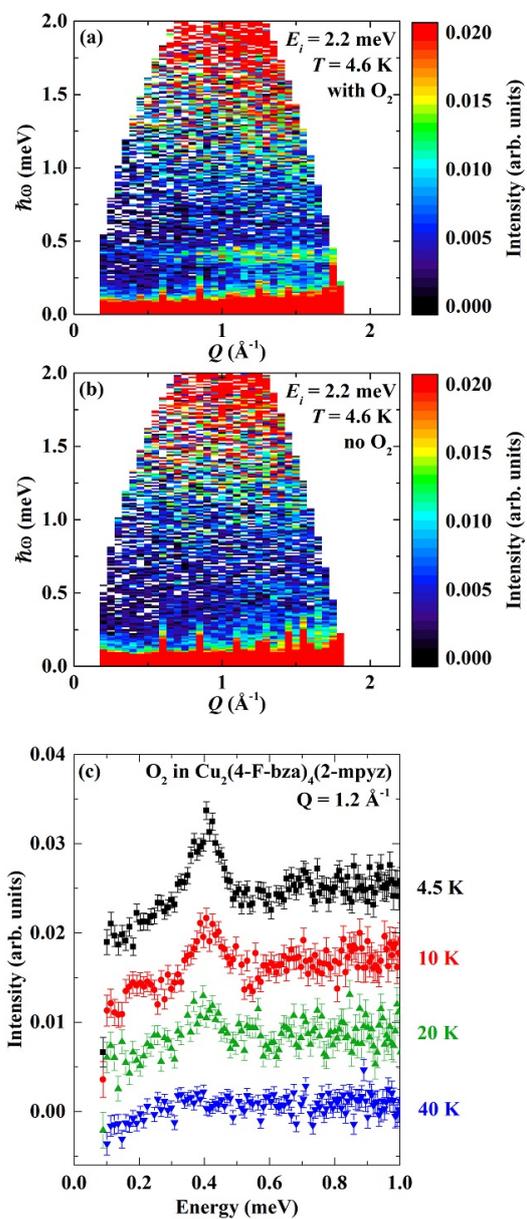


Fig. 1. Inelastic neutron scattering spectra for (a) O<sub>2</sub>-adsorbed and (b) O<sub>2</sub>-removed Cu<sub>2</sub>(4-F-bza)<sub>4</sub>(2-mpyz) at  $T = 4.6$  K. (c) Temperature dependence of one-dimensional  $Q$  cuts for the spectra of the adsorbed O<sub>2</sub>.