High-Field Magnetization Process of O$_2$ Adsorbed in a Microporous Coordination Polymer CPL-1 at Various Temperatures

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Abstract. High-field magnetization measurements have been performed at various temperatures on the molecular oxygen adsorbed in a microporous coordination polymer CPL-1. Molecular oxygen with $S = 1$ forms O$_2$-O$_2$ dimer in the nanochannels of CPL-1. The magnetic properties can be explained by not the $S = 1$ Heisenberg antiferromagnetic dimer model but the O$_2$-O$_2$ dimer model taking into account the spin-dependent intermolecular potential. This feature is attributed to the fact that the magnetic interaction between O$_2$ is comparable to the van der Waals force.

The alterable physical properties of adsorbed molecules, especially in the case of O$_2$ with $S = 1$, which are confined into one-dimensional (1D) nanochannels of coordination polymers, offer the possibility of realizing the nature of intermolecular interaction. In the low-dimensional magnetic spin system, the quantum effect dominates the magnetic properties. In a microporous coordination polymer Cu$_2$(pzdc)$_2$(pyz) (CPL-1), it is known that the adsorbed O$_2$ forms O$_2$-O$_2$ dimer with H-geometry (Fig. 1).[1],[2] The adsorption and desorption isotherms for O$_2$ are reversible and show the physisorption which is not specific adsorption without any specific bonding site but is dominated by the van der Waals interaction. In this system, the magnetic interaction between Cu-ions and O$_2$ is not expected. Thus the magnetic properties of adsorbed O$_2$ in CPL-1 can be explained by the O$_2$-O$_2$ dimer. The temperature dependence of magnetic susceptibility and the high-field magnetization process indicates the singlet ground state ($S_{total} = 0$) at low temperatures but cannot be fully interpreted by the $S = 1$ Heisenberg antiferromagnetic (HAF) dimer model.[3] Unfortunately, the critical field of metamagnetic-like transition is too high to obtain the complete magnetization process up to the saturation. Similar magnetic behavior has been observed in Cu-cyclohexanedicarboxylic acid (Cu-CHD).[4] Recently the arrangement of O$_2$ adsorbed in Cu-CHD can be determined successfully to form the alternating chain based on O$_2$-O$_2$ dimer. In this compound, the absence of the half plateau characteristic to the $S = 1$ HAF dimer model reveals clearly in the magnetization process. From these results, we suggested the possible explanation by taking into account the spin-dependent intermolecular potential. The intermolecular interaction of O$_2$ consists of not only van der
Waals force but the magnetic interaction with comparable energy scale. In other words, the magnetic interaction depends strongly on the molecular arrangement. As a result, the field-induced rearrangement is expected at low temperature, as shown in Fig. 1, since the stable molecular arrangement with $S_{\text{total}} = 2$ in sufficiently high field differs from that in zero field.

In this paper, we report the high-field magnetization process of O$_2$ adsorbed in CPL-1 at various temperatures. Since it is difficult to obtain the complete magnetization process up to the saturation, the measurements at higher temperatures are required for the investigation of higher excited states. These experimental results and the temperature dependence of susceptibility can be successfully interpreted by the O$_2$-O$_2$ dimer model described later.

The high-field magnetization process was measured by using a pulsed magnet. We prepared the adsorption cell where the powder of a degassed host compound CPL-1 was sealed with the appropriate amount of O$_2$ gas in the quartz tube. At first, we heated CPL-1 up to 373 K under reduced pressure to remove the water molecules from the channels and measured the O$_2$ adsorption isotherm at 77 K to estimate the appropriate amount and then sealed the quartz tube.

![H-geometry S-geometry](image)

**Figure 1.** Field-induced rearrangement predicted in O$_2$-O$_2$ dimer. The most stable arrangement at zero field is H-geometry in the singlet state ($S_{\text{total}} = 0$). The stable arrangement in the quintet state ($S_{\text{total}} = 2$) is S-geometry.

The magnetization process of O$_2$ adsorbed in CPL-1 at various temperatures are shown in Fig. 2. These data are obtained by subtracting the magnetization process of CPL-1 without O$_2$ from that for CPL-1 with O$_2$. The Cu$^{2+}$ ions in CPL-1 have the nearly isolated moment with Weiss temperature of $-2.2$ K. In the magnetization process at 4.2 K, the contribution from adsorbed O$_2$ shows the small paramagnetic-like behavior in the low-field region and increases steeply above 50 T. The metamagnetic-like transition is ascribed to O$_2$-O$_2$ dimer in the nanochannels while the small paramagnetic-like behavior is considered to come mainly from the nearly isolated O$_2$ adsorbed in the surface of powdered sample. The magnetization at maximum field (57 T) increases with increasing temperature and reaches $0.64 \mu_B/O_2$ at 40 K.

In the $S = 1$ HAF dimer model, the energy gap between the ground state singlet ($S_{\text{total}} = 0$) and the excited triplet ($S_{\text{total}} = 1$) is $\Delta_{S-T} = 2J$ and that between the triplet and quintet states ($S_{\text{total}} = 2$) is $\Delta_{T-Q} = 4 J$. Therefore, the plateau exists at a half of the saturated magnetization in the magnetization process. The present results cannot be reproduced by the $S = 1$ HAF dimer model. In the case of O$_2$-O$_2$ dimer, the magnetic interaction in different molecular arrangement causes the variation of these gaps. For instance, the numerical study of spin-dependent intermolecular potential predicted that the ground state of O$_2$-O$_2$ dimer was the H-geometry with $S_{\text{total}} = 0$ and the most stable arrangement of the quintet state $S_{\text{total}} = 2$ was the silted parallel S-geometry (Fig. 1). Similarly the stable arrangement of the triplet state ($S_{\text{total}} = 1$) is predicted to be the H-geometry with an intermolecular distance different from the case of singlet. Here, the relation of two gap parameter does not follow $\Delta_{T-Q} = 2\Delta_{S-T}$ in the $S = 1$ HAF dimer model. Therefore, the data fitting is carried out by the singlet-triplet-quintet model with the independent gap parameters $\Delta_{T-Q}$ and $\Delta_{S-T}$. Though the density of states originated from all O$_2$-O$_2$ configurations should be considered, this model would be strictly correct assuming the same DOS for three spin states. The experimental data can be successfully reproduced by this O$_2$-O$_2$ dimer model with $\Delta_{S-T}/k_B = \Delta_{T-Q}/k_B = 101$. 

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Figure 2. High-field magnetization process of O$_2$ adsorbed in CPL-1 at various temperatures. The solid curves are the magnetization process calculated by the O$_2$-O$_2$ dimer model. Each magnetization process can be reproduced by the same gap parameters: $\Delta_{S-T}/k_B = \Delta_{T-Q}/k_B = 101$ K.

K, as shown in Fig. 2. Here, the temperature is also treated as the fitting parameter since the sample is put into adiabatic atmosphere after adsorption. In the magnetization process of CPL-1 without O$_2$, the effect of magnetization heating is observed particularly at low temperatures. The fitting temperatures are $T = 13, 15, 21$ and $40$ K for the magnetization process at the initial temperatures of $4.2, 10, 20$ and $40$ K, respectively. The small paramagnetic-like contribution (5% of adsorbed O$_2$) is estimated by the Brillouin function in the isolated spin system.

The temperature dependence of magnetic susceptibility of O$_2$ adsorbed in CPL-1 is shown in Fig. 3. This is obtained by subtracting the magnetic susceptibility for CPL-1 without O$_2$ from that for CPL-1 with O$_2$. The increase of $\chi(T)$ from $170$ K to $90$ K is due to the adsorption of O$_2$. The reduction with decreasing temperature at low temperatures indicates a nonmagnetic ground state. In the lowest temperature region, the increment of $\chi(T)$ is caused by the nearly isolated O$_2$ (6% of adsorbed O$_2$), corresponding to the small paramagnetic behavior in the magnetization process. The experimental data below $110$ K where O$_2$ has adsorbed completely can be successfully fitted by the O$_2$-O$_2$ dimer model with the gap parameters $\Delta_{T-Q}$ and $\Delta_{S-T}$ same as the fitting of the magnetization process.

From these results, the gap parameter can be determined in the O$_2$-O$_2$ dimer adsorbed in CPL-1. Recently, an inelastic neutron scattering experiment suggests that the excited triplet exists in 7.8 meV ($= 91$ K)[7], which is consistent with our result. It is noted that the obtained gap parameters are larger than those of O$_2$ adsorbed in Cu-CHD, as can be realized by the higher critical field. The interaction between the host compound and the guest O$_2$ is considered
Figure 3. Temperature dependence of susceptibility of O\textsubscript{2} adsorbed in CPL-1. The solid curve is the susceptibility calculated by the O\textsubscript{2}-O\textsubscript{2} dimer model (Δ\textsubscript{S−T}/k\textsubscript{B} = ΔT−Q/k\textsubscript{B} = 101 K).

to affect the intermolecular potential.

In conclusion, the high-field magnetization process at various temperatures and the temperature dependence of susceptibility in O\textsubscript{2} adsorbed in CPL-1 can be successfully interpreted by the O\textsubscript{2}-O\textsubscript{2} dimer model with the independent gap parameters. These results demonstrate that the spin-dependent intermolecular potential dominates the magnetic properties of O\textsubscript{2}. In other words, the magnetic interaction plays important role in the nature of interaction between O\textsubscript{2}.

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