

Charge and lattice fluctuations in molecule-based spin liquids

Electron spin is one of the fundamental properties of electrons. A magnetic moment is caused by electron spins. Electron spins tend to align in a crystal, affecting the magnetic behavior. On the other hand, there is no consensus on the magnetic behavior induced by three electron spins accommodated into the corners of an isosceles triangle (Fig. 1(a)). One reason for this is because there is no stable alignment condition even at zero Kelvin. Such situation is called the “spin liquid” [1]. The spin liquid has been attracting attention because of its potential properties arising from quantum fluctuations. To obtain evidence for the spin liquid, physicists and chemists have focused on crystalline materials having triangular, kagome and pyrochlore lattices.

A metal-dithiolene complex salt, $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$, whose 2D layer belongs to the triangular lattice, is one of the candidate compounds exhibiting spin liquid behavior (Figs. 1(b) and 1(c)). Magnetic and transport property measurements revealed the absence of any ordering near absolute zero Kelvin [2-4]. Nevertheless, anomalous behaviors that suggest

the release of a small amount of entropy near liquid-helium temperature were observed in the transport and magnetic measurements [2-4]. Furthermore, a slight deviation from the isosceles triangular lattice was revealed, whereas the 2D layers in two nonmagnetic insulators ($\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ and $\text{EtMe}_3\text{P}[\text{Pd}(\text{dmit})_2]_2$) were close to the isosceles triangular lattice. These contradictory properties were elucidated by vibrational spectroscopy focusing on the C=C stretching modes denoted as A–D modes (Fig. 2(a)).

Some vibrational modes of molecule-based conducting materials are sensitive to a slight change in intermolecular interactions and molecular charges, which is useful for analyzing the fluctuation of a hidden ordered state. To capture all C=C stretching modes as much as possible, the polarization dependence of the infrared spectra and the dependence of the excitation energy in Raman spectra were examined [5]. The thickness of a platelike crystal is smaller than 50 μm . When the polarization direction is parallel to the thickness direction, the narrow infrared beam at SPRing-8 BL431R is suitable for such a material. We also observed the C=C stretching modes in three related compounds that are in the antiferromagnetic state at low temperatures.

Figures 2(b) and 2(c) show the conductivity spectra and Raman spectra, respectively. The conductivity spectrum corresponds to the infrared spectrum. When dimers are regularly arranged in the 2D layer, the number of C=C stretching modes should be four (= $A_D - D_D$ modes, which are identical to A–D modes, respectively (Fig. 2(a)). A_D in the Raman spectra corresponds to regularly arranged dimers (Fig. 3(a)), whereas A_T and D_O do not. A_T is assigned to one of the C=C stretching modes of a tetramer (Fig. 3(a)), where the A_D modes of two neighboring dimers in the tetramer are combined. A_T is observed as a weak and non-negligible shoulder of the B mode (Fig. 2(b)). This phenomenon is ascribed to fluctuating tetramers rather than static tetramers. The D_O mode corresponds to the C=C stretching modes of an octamer, where the D_D modes of four contiguous dimers are combined. Because the static octamer consists of two shrunk and two expanded dimers (Fig. 3(a)), D_O should exhibit separate peaks, which is inconsistent with the broad linewidth in Fig. 2(c). The broad linewidth is ascribed to the dynamical repetition of the expansion and contraction of dimers due to the fluctuating octamer. Our experimental result reveals the dynamical

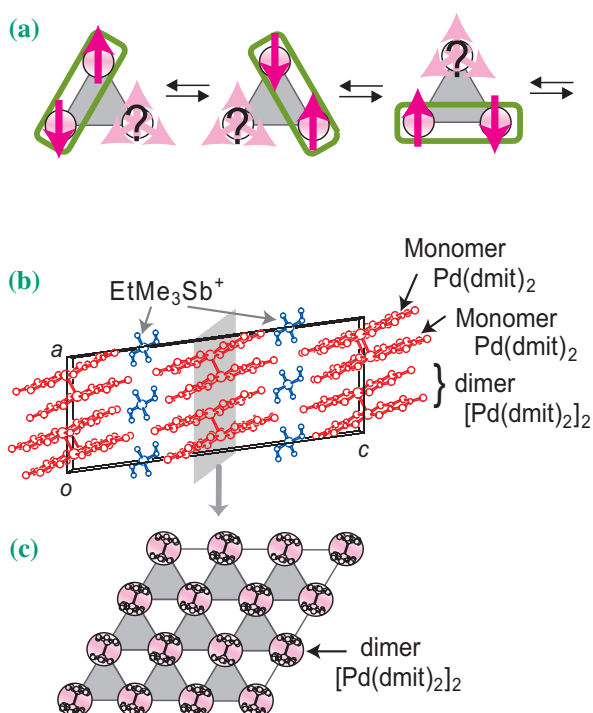


Fig. 1. (a) Frustration of electron spins in isosceles triangle. (b) Crystal structure of $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ viewed along the *b* axis. (c) Schematic views of molecular arrangement in the 2D layer, which is parallel to the *ab*-plane. A triangular lattice is formed by dimers consisting of two monomers.

alternation among dimers, tetramers and octamers (Fig. 3(a)). The dynamical alternation induces the charge fluctuation in the 2D layer. The broad linewidth in the B mode (Fig. 2(b)), whose frequency is sensitive to the monomer charge, is ascribed to the charge fluctuation.

The dynamical alternation is ascribed to the competition among dimers, tetramers and octamers due to the degeneracy among these three ordered states (Fig. 3(b)). As shown in the energy diagram of molecular orbitals (Fig. 3(b)), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a normal dimer become the LUMO (H-H) and HOMO (L+L) in a tight dimer, respectively. The singly occupied orbital of [Tight dimer]⁻ (H-H) is antibonding, whose energy should be decreased by the formation of any ordering. One of the ordered states is the antiferromagnetic ordering by the regular arrangement of tight dimers. Another ordered state is a tetramer. The highest occupied orbital of [Tetramer]²⁻ consists of H-H orbitals, which form the valence bond order in a crystal. L+L orbitals form the next highest occupied orbital of [Tetramer]²⁻, which induces the charge separation. The valence bond order and charge separation are cooperative with each other. The other ordered state is the octamer. A similar cooperative mechanism is applied to the formation of

an octamer. When the energy levels among the three ordered states are identical, the system becomes stable owing to the dynamical exchange between them. This mechanism resolves the contradictory phenomena previously observed in the transport and magnetic measurements [2-4]. This mechanism is also consistent with the slight deviation from the isosceles triangular lattice.

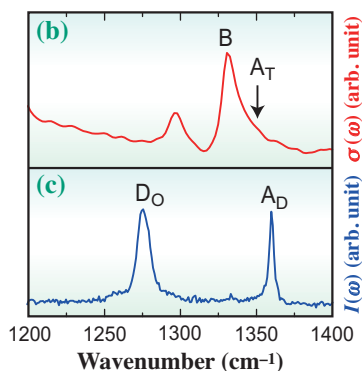
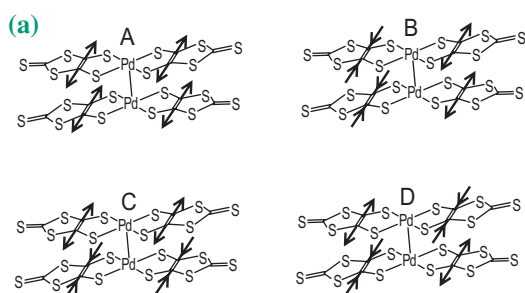


Fig. 2. (a) Four C=C stretching modes (A–D modes) in a tight dimer ([Pd(dmit)₂]₂). (b) Conductivity spectra ($\sigma(\omega)$) calculated from the infrared reflectance spectra obtained at BL43IR. The incident light was polarized along the interlayer direction of a single crystal. (c) Raman spectra ($I(\omega)$) obtained using spectrometer in the Institute for Molecular Science.

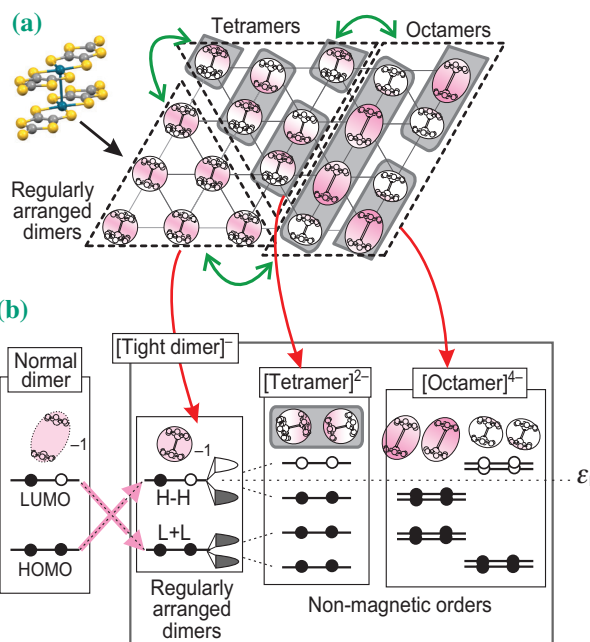


Fig. 3. (a) Coexistence between regularly arranged dimers, tetramers and octamers in triangular lattice, which can be interchanged at approximately the liquid helium temperature. (b) Energy diagrams of normal dimer, tight dimer, tetramer and octamer. Interchange of energy levels occurs between normal and tight dimers. Magenta contours in (a) and (b) denote the electron density of the singly occupied orbital of [Tight dimer]⁻¹ and the highest occupied orbitals of [Tetramer]²⁻ and [Octamer]⁴⁻.

Takashi Yamamoto^{a,b,c}

^a Graduate School of Science and Engineering, Ehime University

^b Geodynamics Research Center, Ehime University

^c RIKEN/Wako

Email: yamataka@ehime-u.ac.jp

References

[1] L. Balents: Nature **464** (2010) 199.
 [2] S. Yamashita *et al.*: Nat. Comm. **2** (2911) 275.
 [3] M. Yamashita *et al.*: Science **328** (2010) 1246.
 [4] T. Itou *et al.*: Nat. Phys. **6** (2010) 673.
 [5] T. Yamamoto, T. Fujimoto, T. Naito, Y. Nakazawa, M. Tamura, K. Yakushi, Y. Ikemoto, T. Moriwaki and R. Kato: Sci. Rep. **7** (2017) 12930.