Ab initio Calculation Approach to the Intramolecular Charge Ordering in (TTM-TTP) I_3

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Charge-ordering phenomena have been one of the main research subjects in molecular solids. In (TTM-TTP)I_3 crystal [1], a new type of charge-ordered (CO) state has been claimed by the Raman-scattering [2] and the X-ray [3] measurements. We call this state the "intra-molecule CO" state, where the inversion center on the middle point of the TTM-TTP molecule is lost and the charge is disproportionated within the molecule. This state cannot be described by the conventional theoretical treatment based on the single-site approximation of the molecule, i.e., based on the single molecular-orbital (MO) approximation.

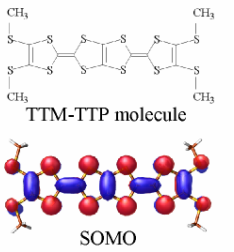

Fig.1: The TTM-TTP molecule and SOMO

We examine characteristics of the frontier molecular orbitals of the TTM-TTP (Fig.1.) molecule based on the multi-configuration *ab initio* calculation. It is shown that the energy levels of the singly-occupied molecular orbital (SOMO) and of the second highest-occupied molecular orbital (HOMO-1) are close to each other, i.e., this system can be regarded as an effectively two-orbital system. We find that the SOMO and HOMO-1 have common wave function with respect to the left and right parts of the TTM-TTP molecule and the SOMO has a bonding character of them while the HOMO-1 has an anti-bonding character. In order to clarify this nontrivial feature of these MOs, we divide virtually the TTM-TTP molecule into the three fragments; namely, left, right, and center fragments. Based on this three-fragment model, we clarify the relevant interactions between the fragments which can reproduce the MOs obtained from *ab initio* calculations. Furthermore, in order to analyze the symmetry breaking observed experimentally at low temperature, we take into account neighboring two TTM-TTP molecules and analyze the intra-molecular CO state explicitly. The MOs are reconstructed due to the mixing of each fragment, yielding the redistribution of the Mulliken charge, i.e., the electron disproportionation within the TTM-TTP molecule.

[1] T. Mori, et al., Phys. Rev. Lett. 79, 1702 (1997).
[2] K. Yakushi, et al., Synth. Met. 135-136, 583 (2003).
[3] Y. Nogami, et al., Synth. Met. 135-136, 637 (2003).